Part 2 Structure

In Part 1 we examined the properties of bulk matter from the viewpoint of thermodynamics. In Part 2 we turn to the study of individual atoms and molecules from the viewpoint of quantum mechanics. The two viewpoints merge in Chapter 19.

11

Quantum theory: introduction and principles

This chapter introduces some of the basic principles of quantum mechanics. First, it reviews the experimental results that overthrew the concepts of classical physics. These experiments led to the conclusion that particles may not have an arbitrary energy and that the classical concepts of 'particle' and 'wave' blend together. The overthrow of classical mechanics inspired the formulation of a new set of concepts and the formulation of quantum mechanics. In quantum mechanics, all the properties of a system are expressed in terms of a wavefunction which is obtained by solving the Schrödinger equation. We see how to interpret wavefunctions. Finally, we introduce some of the techniques of quantum mechanics in terms of operators, and see that they lead to the uncertainty principle, one of the most profound departures from classical mechanics.

To understand the structures of individual atoms and molecules, we need to know how subatomic particles move in response to the forces they experience. It was once thought that the motion of atoms and subatomic particles could be expressed using the laws of **classical mechanics** introduced in the seventeenth century by Isaac Newton, for these laws were very successful at explaining the motion of everyday objects and planets. However, towards the end of the nineteenth century, experimental evidence accumulated showing that classical mechanics failed when it was applied to very small particles, and it took until the 1920s to discover the appropriate concepts and equations for describing them. We describe the concepts of this new mechanics, which is called **quantum mechanics**, in this chapter, and apply them throughout the remainder of the text.

The origins of quantum mechanics

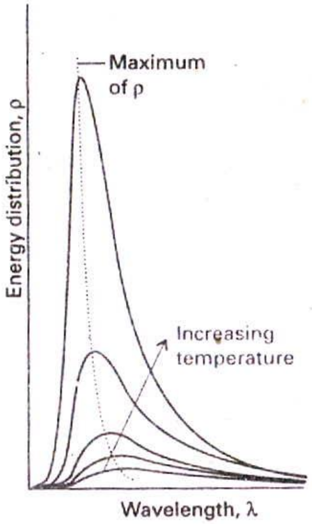
The basic principles of classical mechanics are reviewed in *Further information 4*. In brief, they show that classical physics (1) predicts a precise trajectory for particles, with precisely specified locations and momenta at each instant, and (2) allows the translational, rotational, and vibrational modes of motion to be excited to any energy simply by controlling the forces that are applied. These conclusions agree with everyday experience. Everyday experience, however, does not extend to individual atoms, and careful experiments of the type described below have shown that classical mechanics fails when applied to the transfers of very small quantities of energy and to objects of very small mass.

11.1 The failures of classical physics

In this section we review some of the experimental evidence which showed that several concepts of classical mechanics are untenable. In particular, we shall see that observations of black-body radiation, heat capacities, and atomic and molecular spectra indicate that systems can take up energy only in discrete amounts.

(a) Black-body radiation

A hot object emits electromagnetic radiation. An appreciable proportion of the radiation is in the visible region of the spectrum at high temperatures, and a higher proportion of short-wavelength blue light is generated as the temperature is raised. This behaviour is seen when a heated iron bar glowing red hot becomes white hot when heated further. The dependence is illustrated in Fig. 11.1, which shows how the energy output varies with wavelength at several temperatures. The curves are those of an ideal emitter called a **black body**, which is an object capable of emitting and absorbing all frequencies of radiation uniformly. A good approximation to a black body is a pinhole in an empty container maintained at a constant temperature, because any radiation leaking out of the hole has been absorbed and re-emitted inside so many times that it has come to thermal equilibrium with the walls (Fig. 11.2).



11.1 The energy distribution in a black-body cavity at several temperatures. Note how the energy density increases in the visible region as the temperature is raised, and how the peak shifts to shorter wavelengths. The total energy density (the area under the curve) increases as the temperature is increased (as T^4).

Figure 11.1 shows that the peak in the energy output shifts to shorter wavelengths as the temperature is raised. As a result, the short-wavelength tail of the energy distribution strengthens in the visible region and the perceived colour shifts towards the blue, as already mentioned. An analysis of the data led Wilhelm Wien (in 1893) to formulate the **Wien displacement law**:

$$T\lambda_{\max} = \tfrac{1}{5}c_2 \qquad c_2 = 1.44\ \mathrm{cm\,K} \tag{1}$$

where $\lambda_{\max}$ is the wavelength corresponding to the maximum of the distribution at a temperature T. The constant c_2 is called the **second radiation constant**. Using its value, we can predict that $\lambda_{\max} \approx 2900$ nm at 1000 K.

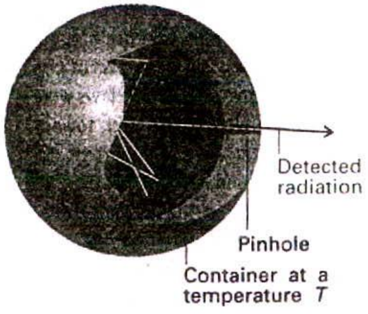
A second feature of black-body radiation had been noticed in 1879 by Josef Stefan, who considered the **total energy density**, $\mathcal{E}$, the total electromagnetic energy in a region divided by the volume of the region ($\mathcal{E} = E/V$). The energy density of the electromagnetic field inside the container in Fig. 11.2 increases as the temperature is increased, and specifically the **Stefan–Boltzmann law** states that

$$\mathcal{E} = aT^4 \tag{2a}$$

Ludwig Boltzmann's name is attached to this law because he explained it theoretically. An alternative form of the law is in terms of the **excitance**, M, the power[1] emitted by a region of surface divided by the area of the surface: the excitance is a measure of the brightness of the emission. Because the excitance is proportional to the energy density in the container, M is also proportional to T^4, and we can write

$$M = \sigma T^4 \qquad \sigma = 5.67\times10^{-8}\ \mathrm{W\,m^{-2}\,K^{-4}} \tag{2b}$$

The constant σ is called the **Stefan–Boltzmann constant**. The Stefan–Boltzmann law implies that 1 cm^2 of the surface of a black body at 1000 K radiates about 6 W when all



11.2 An experimental representation of a black body is a pinhole in an otherwise closed container. The radiation is reflected many times within the container and comes to thermal equilibrium with the walls at a temperature T. Radiation leaking out through the pinhole is characteristic of the radiation within the container.

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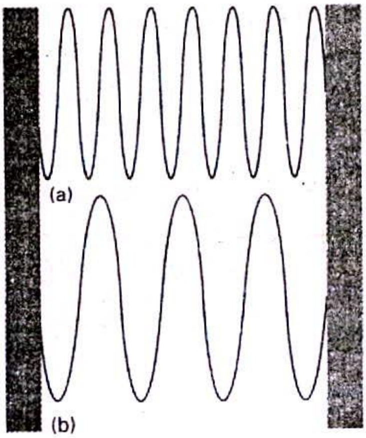
[1] Power is the rate of supply of energy. Its SI units are watts, W: 1 W = 1 J s^{-1}.



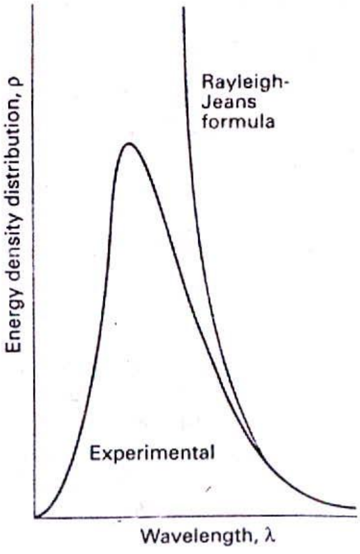
11.3 The electromagnetic vacuum can be regarded as able to support oscillations of the electromagnetic field. When a high-frequency short-wavelength oscillator (a) is excited, that frequency of radiation is present. The presence of low-frequency long-wavelength radiation (b) signifies that an oscillator of the corresponding frequency has been excited.

wavelengths of the emitted radiation are taken into account. The explanation of black-body radiation was a major challenge for nineteenth-century scientists, and in due course it was found to be beyond the capabilities of classical physics. The physicist Lord Rayleigh studied it theoretically from a classical viewpoint, and thought of the electromagnetic field as a collection of oscillators of all possible frequencies. He regarded the presence of radiation of frequency ν (and therefore of wavelength $\lambda = c/\nu$, where c is the speed of light) as signifying that the electromagnetic oscillator of that frequency had been excited (Fig. 11.3). Rayleigh used the equipartition principle (see the *Introduction*) to calculate the average energy of each oscillator as kT. Then, with minor help from James Jeans, he arrived at the **Rayleigh–Jeans law**:

$$d\mathcal{E} = \rho\, d\lambda \qquad \rho = \frac{8\pi kT}{\lambda^4} \tag{3}$$

where ρ is the proportionality constant between $d\lambda$ and the energy density in that range of wavelengths; k is the Boltzmann constant ($k = 1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}$).

Unfortunately (for Rayleigh, Jeans, and classical physics), although the Rayleigh–Jeans law is quite successful at long wavelengths (low frequencies), it fails badly at short wavelengths (high frequencies). Thus, as λ decreases, ρ increases without going through a maximum (Fig. 11.4). The equation therefore predicts that oscillators of very short wavelength (corresponding to ultraviolet light, X-rays, and even γ-rays) are strongly excited even at room temperature. This absurd result, which implies that a large amount of energy is radiated in the high-frequency region of the electromagnetic spectrum, is called the **ultraviolet catastrophe**. According to classical physics, even cool objects should radiate in the visible and ultraviolet regions: according to classical physics, objects should glow in the dark; there should in fact be no darkness.



11.4 The Rayleigh–Jeans law (eqn 3) predicts an infinite energy density at short wavelengths. This prediction is called the ultraviolet catastrophe.

(b) The Planck distribution

The German physicist Max Planck studied black-body radiation from the viewpoint of thermodynamics. In 1900 he found that he could account for the experimental observations by proposing that *the energy of each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily*. This proposal is quite contrary to the viewpoint of classical physics (on which the equipartition principle used by Rayleigh is based), in which all possible energies are allowed. The limitation of energies to discrete values is called the **quantization of energy**. In particular, Planck found that he could account for the observed distribution of energy if he supposed that the permitted energies of an electromagnetic oscillator of frequency ν are integer multiples of $h\nu$:

$$E = nh\nu \qquad n = 0, 1, 2, \ldots \tag{4}$$

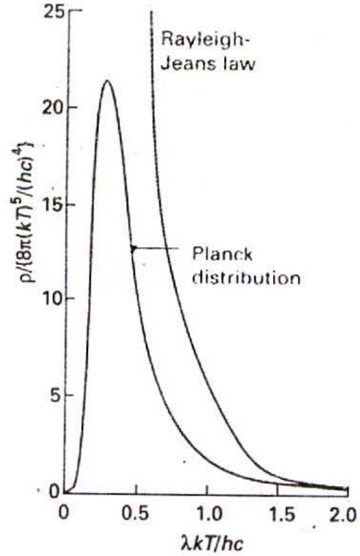
where h is a fundamental constant now known as the **Planck constant**.

On the basis of this assumption, Planck was able to derive the **Planck distribution**:

$$d\mathcal{E} = \rho\, d\lambda \qquad \rho = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT} - 1}\right) \tag{5}$$

This expression fits the experimental curve very well at all wavelengths (Fig. 11.5), and the value of h, which is an undetermined parameter in the theory, may be obtained by varying its value until a best fit is obtained. The currently accepted value for h is $6.62608 \times 10^{-34}\ \mathrm{J\,s}$.

The Planck distribution resembles the Rayleigh–Jeans law (eqn 3) apart from the all-important exponential factor in the denominator. For short wavelengths, $hc/\lambda kT$ is large and $e^{hc/\lambda kT} \to \infty$ faster than $\lambda^5 \to 0$; therefore $\rho \to 0$ as $\lambda \to 0$ or $\nu \to \infty$. Hence, the energy density approaches zero at high frequencies, in agreement with observation. For long



11.5 The Planck distribution (eqn 5) accounts very well for the experimentally determined distribution of radiation. Planck's quantization hypothesis essentially quenches the contributions of high-frequency, short-wavelength oscillators. The distribution coincides with the Rayleigh–Jeans distribution at long wavelengths.

wavelengths, $hc/\lambda kT \ll 1$, and the denominator in the Planck distribution can be replaced by

$$e^{hc/\lambda kT} - 1 = \left(1 + \frac{hc}{\lambda kT} + \cdots\right) - 1 \approx \frac{hc}{\lambda kT}$$

When this approximation is substituted into eqn 5, we find that the Planck distribution reduces to the Rayleigh–Jeans law.

The Planck distribution also accounts for the Stefan–Boltzmann and Wien laws. The former is obtained by integrating the energy density over all wavelengths from $\lambda = 0$ to $\lambda = \infty$, which gives

$$\mathcal{E} = \int_0^\infty \rho \, d\lambda = aT^4 \qquad a = \frac{4\sigma}{c}, \ \sigma = \frac{2\pi^5 k^4}{15c^2h^3} \tag{6}$$

Substitution of the values of the fundamental constants gives $\sigma = 56.704\ \mathrm{nW\,m^{-2}\,K^{-4}}$, in accord with the experimental value. The Wien law is obtained by looking for the wavelength at which $d\rho/d\lambda = 0$, the condition for the maximum in the distribution. When we take the derivative, set it equal to zero, and make the approximation that the wavelength is so short that $hc/\lambda \gg kT$, we obtain

$$T\lambda_{\mathrm{max}} = \frac{hc}{5k} \tag{7}$$

This result lets us identify the second radiation constant as $c_2 = hc/k = 1.439$ cm K, which is also in good agreement with experiment.

It is quite easy to see why Rayleigh's approach was unsuccessful and Planck's hypothesis was successful. The thermal motion of the atoms in the walls of the black body excites the oscillators of the electromagnetic field. According to classical mechanics, all the oscillators of the field share equally in the energy supplied by the walls, so even the highest frequencies are excited. The excitation of very high frequency oscillators results in the ultraviolet catastrophe. According to Planck's hypothesis, however, oscillators are excited only if they can acquire an energy of at least $h\nu$. This energy is too large for the walls to supply in the case of the very high frequency oscillators, so the latter remain unexcited. The effect of quantization is to reduce the contribution from the high frequency oscillators, for they cannot be significantly excited with the energy available.

(c) Heat capacities

In the early nineteenth century, the French scientists Pierre-Louis Dulong and Alexis-Thérèse Petit determined the heat capacities of a number of monatomic solids.[2] On the basis of some somewhat slender experimental evidence, they proposed that the molar heat capacities of all monatomic solids are the same, and close to $25\ \mathrm{J\,K^{-1}\,mol^{-1}}$ (in modern units).

Dulong and Petit's law is easy to justify in terms of classical physics. If classical physics were valid, the equipartition principle could be used to calculate the heat capacity of a solid. According to this principle, the mean energy of an atom as it oscillates about its mean position in a solid is kT for each direction of displacement. As each atom can oscillate in three dimensions, the average energy of each atom is $3kT$; for N atoms the total energy is $3NkT$. The contribution of this motion to the molar internal energy is therefore

$$U_{\mathrm{m}} = 3N_{\mathrm{A}}kT = 3RT$$

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[2] As explained in Section 2.4b, the constant-volume heat capacity, C_V, is defined as $C_V = (\partial U/\partial T)_V$. A small heat capacity indicates that a large rise in temperature results from a given transfer of energy.

because $N_\mathrm{A}k = R$, the gas constant. The molar constant-volume heat capacity (eqn 2.19) is then predicted to be

$$C_{V,\mathrm{m}} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_V = 3R \tag{8}$$

This result, with $3R = 24.9\ \mathrm{J\,K^{-1}\,mol^{-1}}$, is in striking accord with Dulong and Petit's value.

Significant deviations from Dulong and Petit's law were observed when technological advances made it possible to measure heat capacities at low temperatures. It was found that the molar heat capacities of all metals are lower than $3R$ at low temperatures, and that the values approach zero as $T \rightarrow 0$. To account for these observations, Einstein (in 1905) assumed that each atom oscillated about its equilibrium position with a single frequency ν. He then invoked Planck's hypothesis to assert that the energy of oscillation is confined to discrete values, and specifically to $nh\nu$, where n is an integer. Einstein first calculated the contribution of the oscillations of the atoms to the total molar energy of the metal (by a method described in Section 20.4) and obtained

$$U_\mathrm{m} = \frac{3N_\mathrm{A}h\nu}{e^{h\nu/kT} - 1}$$

in place of the classical expression $3RT$. Then he found the heat capacity by differentiating U_m with respect to T. The resulting expression is now known as the **Einstein formula**:

$$C_{V,\mathrm{m}} = 3Rf^2 \cdot \qquad f = \frac{\theta_\mathrm{E}}{T}\left(\frac{e^{\theta_\mathrm{E}/2T}}{e^{\theta_\mathrm{E}/T} - 1}\right) \tag{9}$$

where the **Einstein temperature**, $\theta_\mathrm{E} = h\nu/k$, is a way of expressing the frequency of oscillation of the atoms as a temperature: a high frequency corresponds to a high Einstein temperature.

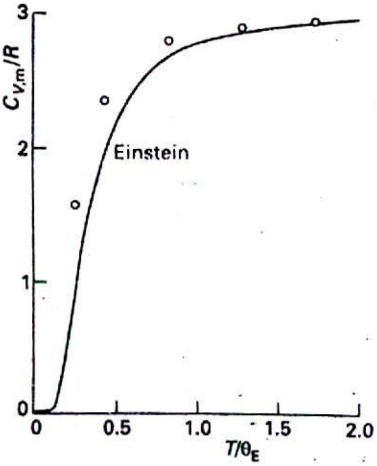
At high temperatures (when $T \gg \theta_\mathrm{E}$) the exponentials in f can be expanded as $1 + \theta_\mathrm{E}/T + \cdots$ and higher terms ignored. The result is

$$f = \frac{\theta_\mathrm{E}}{T}\left\{\frac{1 + \theta_\mathrm{E}/2T + \cdots}{(1 + \theta_\mathrm{E}/T + \cdots) - 1}\right\} \approx 1 \tag{10a}$$

Consequently, the classical result ($C_{V,\mathrm{m}} = 3R$) is obtained at high temperatures. At low temperatures, when $T \ll \theta_\mathrm{E}$,

$$f \approx \frac{\theta_\mathrm{E}}{T}\left(\frac{e^{\theta_\mathrm{E}/2T}}{e^{\theta_\mathrm{E}/T}}\right) = \frac{\theta_\mathrm{E}}{T}e^{-\theta_\mathrm{E}/2T} \tag{10b}$$

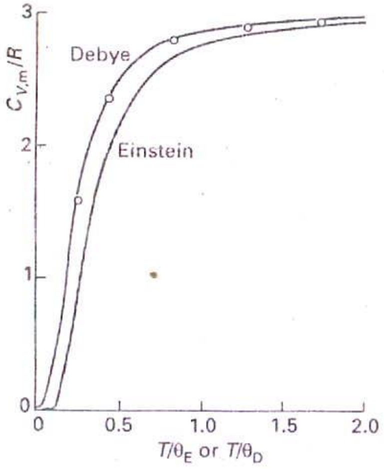
The strongly decaying exponential function goes to zero more rapidly than $1/T$ goes to infinity; so $f \rightarrow 0$ as $T \rightarrow 0$, and the heat capacity therefore approaches zero too. We see that Einstein's formula accounts for the decrease of heat capacity at low temperatures. The physical reason for this success is that at low temperatures only a few oscillators possess enough energy to oscillate significantly. At higher temperatures, there is enough energy available for all the oscillators to become active: all $3N$ oscillators contribute, and the heat capacity approaches its classical value.



11.6 Experimental low-temperature molar heat capacities and the temperature dependence predicted on the basis of Einstein's theory. His equation (eqn 9) accounts for the dependence fairly well, but is everywhere too low.

The temperature dependence of the heat capacity predicted by the Einstein formula is plotted in Fig. 11.6. The general shape of the curve is satisfactory, but the numerical agreement is in fact quite poor. The poor fit arises from Einstein's assumption that all the atoms oscillate with the same frequency, whereas in fact they oscillate over a range of frequencies from zero up to a maximum value, ν_D. This complication is taken into account by averaging over all the frequencies present, the final result being the **Debye formula**:

$$C_{V,\mathrm{m}} = 3Rf \qquad f = 3\left(\frac{T}{\theta_\mathrm{D}}\right)^3 \int_0^{\theta_\mathrm{D}/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx \tag{11}$$



11.7 Debye's modification of Einstein's calculation (eqn 11) gives very good agreement with experiment. For copper, $T/\theta_D = 2$ corresponds to about 670 K.

where $\theta_D = h\nu_D/k$ is the Debye temperature. The integral in eqn 11 has to be evaluated numerically, but that is simple with mathematical software. The details of this modification, which, as Fig. 11.7 shows, gives improved agreement with experiment, need not distract us at this stage from the main conclusion, which is that quantization must be introduced in order to explain the thermal properties of solids.

(d) Atomic and molecular spectra

The most compelling evidence for the quantization of energy comes from the observation of the frequencies of radiation absorbed and emitted by atoms and molecules.

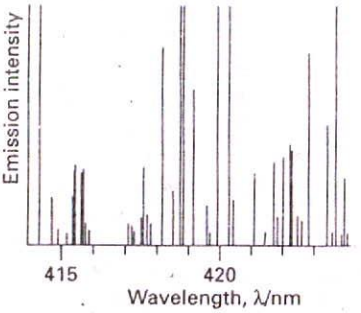
A typical atomic spectrum is shown in Fig. 11.8, and a typical molecular spectrum is shown in Fig. 11.9. The obvious feature of both is that radiation is emitted or absorbed at a series of discrete frequencies. This observation can be understood if the energy of the atoms or molecules is also confined to discrete values, for then energy can be discarded or absorbed only in discrete amounts (Fig. 11.10). Then, if the energy of an atom decreases by ΔE, the energy is carried away as radiation of frequency $\nu = \Delta E/h$, and a line appears in the spectrum.

11.2 Wave–particle duality

At this stage we have established that the energies of the electromagnetic field and of oscillating atoms are quantized. In this section we shall see the experimental evidence that led to the revision of two other basic concepts concerning the nature of the world. One experiment shows that electromagnetic radiation—which classical physics treats as wave-like—actually also displays the characteristics of particles. Another experiment shows that electrons—which classical physics treats as particles—also display the characteristics of waves.

(a) The particle character of electromagnetic radiation

The observation that electromagnetic radiation of frequency ν can possess only the energies $0, h\nu, 2h\nu, \ldots$ suggests that it can be thought of as consisting of $0, 1, 2, \ldots$ particles, each particle having an energy $h\nu$. Then, if one of these particles is present, the energy is $h\nu$, if two are present the energy is $2h\nu$, and so on. These particles of electromagnetic radiation are now called **photons**. The observation of discrete spectra from atoms and molecules can be pictured as the atom or molecule generating a photon of energy $h\nu$ when it discards an energy of magnitude ΔE, with $\Delta E = h\nu$.



11.8 A region of the spectrum of radiation emitted by excited iron atoms consists of radiation at a series of discrete wavelengths (or frequencies).

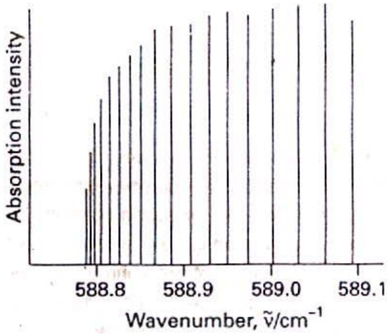
Example 11.1 Calculating the number of photons

Calculate the number of photons emitted by a 100 W yellow lamp in 1.0 s. Take the wavelength of yellow light as 560 nm and assume 100 per cent efficiency.

Method Each photon has an energy $h\nu$, so the total number of photons needed to produce an energy E is $E/h\nu$. To use this equation, we need to know the frequency of the radiation (from $\nu = c/\lambda$) and the total energy emitted by the lamp. The latter is given by the product of the power (P, in watts) and the time ($E = Pt$). In general, to avoid rounding and other numerical errors, it is best to carry out algebraic calculations first, and to substitute numerical values into a single, final formula.

Answer The number of photons is

$$N = \frac{E}{h\nu} = \frac{Pt}{h(c/\lambda)} = \frac{\lambda Pt}{hc}$$



11.9 When a molecule changes its state, it does so by absorbing radiation at definite frequencies. This suggests that it can possess only discrete energies, not an arbitrary energy. This spectrum is part of that due to the vibrations and rotations of dinitrogen oxide (N_2O) molecules.

Substitution of the data gives

$$N = \frac{(5.60\times10^{-7}\ \mathrm{m})\times(100\ \mathrm{J\,s^{-1}})\times(1.0\ \mathrm{s})}{(6.626\times10^{-34}\ \mathrm{J\,s})\times(2.998\times10^{8}\ \mathrm{m\,s^{-1}})} = 2.8\times10^{20}$$

Comment Note that it would take nearly 40 min to produce 1 mol of these photons.

Self-test 11.1 How many photons does a monochromatic (single-frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s?

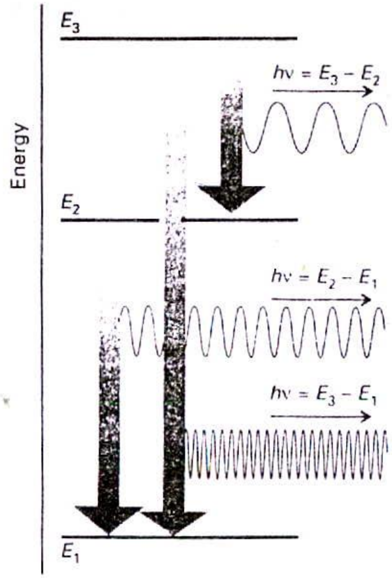
[5×10^{14}]

Further evidence for the particle-like character of radiation comes from the measurement of the energies of electrons produced in the **photoelectric effect**. This effect is the ejection of electrons from metals when they are exposed to ultraviolet radiation. The experimental characteristics of the photoelectric effect are as follows:

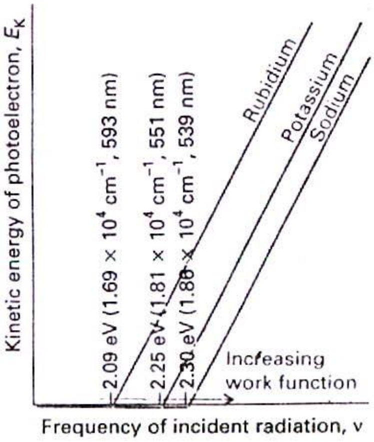
1. No electrons are ejected, regardless of the intensity of the radiation, unless the frequency of the radiation exceeds a threshold value characteristic of the metal.
2. The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
3. Even at low light intensities, electrons are ejected immediately if the frequency is above threshold.

The second characteristic is illustrated by the experimental data in Fig. 11.11.

These observations strongly suggest that the photoelectric effect depends on the ejection of an electron when it is involved in a collision with a particle-like projectile that carries



11.10 Spectral lines can be accounted for if we assume that a molecule emits a photon as it changes between discrete energy levels. Note that high-frequency radiation is emitted when the energy change is large.



11.11 In the photoelectric effect, it is found that no electrons are ejected when the incident radiation has a frequency below a value characteristic of the metal and, above that value, the kinetic energy of the photoelectrons varies linearly with the frequency of the incident radiation.

enough energy to eject the electron from the metal. If we suppose that the projectile is a photon of energy $h\nu$, where ν is the frequency of the radiation, then the conservation of energy requires that the kinetic energy of the ejected electron should obey

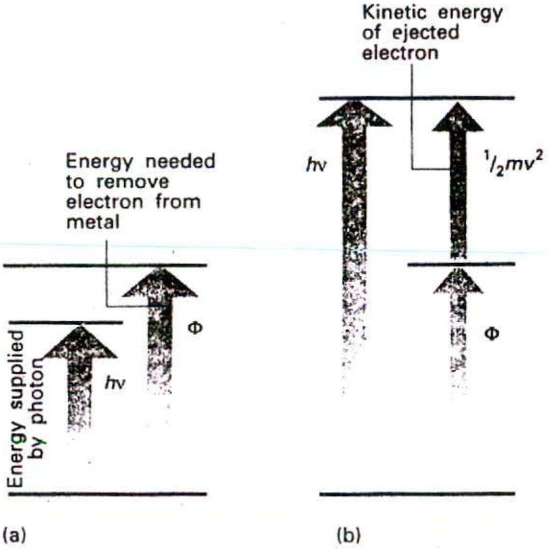
$$\tfrac{1}{2}m_e v^2 = h\nu - \Phi \qquad (12)$$

In this expression Φ is a characteristic of the metal called its **work function**, the energy required to remove an electron from the metal to infinity (Fig. 11.12). Photoejection cannot occur if $h\nu < \Phi$ because the photon brings insufficient energy: this conclusion accounts for observation (1). Equation 12 predicts that the kinetic energy of an ejected electron should increase linearly with frequency, in agreement with observation (2). When a photon collides with an electron, it gives up all its energy, so we should expect electrons to appear as soon as the collisions begin, provided the photons have sufficient energy: this conclusion agrees with observation (3).

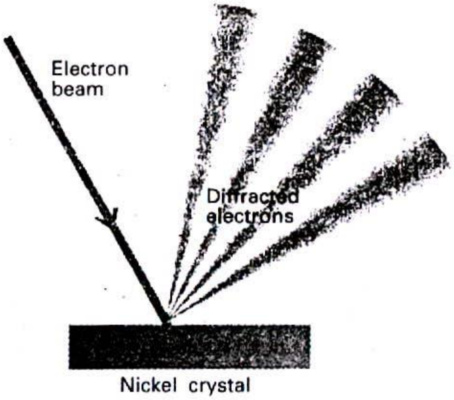
(b) The wave character of particles

Although contrary to the long-established wave theory of light, the view that light consists of particles had been held before, but discarded. No significant scientist, however, had taken the view that matter is wave-like. Nevertheless, experiments carried out in 1925 forced people to even that conclusion. The crucial experiment was performed by the American physicists Clinton Davisson and Lester Germer, who observed the diffraction of electrons by a crystal (Fig. 11.13). Diffraction is a characteristic property of waves because it occurs when there is interference between their peaks and troughs. Depending on whether the interference is constructive or destructive, the result is a region of enhanced or diminished intensity. Davisson and Germer's success was a lucky accident, because a chance rise of temperature caused their polycrystalline sample to anneal, and the ordered planes of atoms then acted as a diffraction grating. At almost the same time, G.P. Thomson, working in Scotland, showed that a beam of electrons was diffracted when passed through a thin gold foil.

The Davisson–Germer experiment, which has since been repeated with other particles (including molecular hydrogen), shows clearly that particles have wave-like properties. We have also seen that waves of electromagnetic radiation have particle-like properties. Thus we



11.12 The photoelectric effect can be explained if it is supposed that the incident radiation is composed of photons that have energy proportional to the frequency of the radiation. (a) The energy of the photon is insufficient to drive an electron out of the metal. (b) The energy of the photon is more than enough to eject an electron, and the excess energy is carried away as the kinetic energy of the photoelectron (the ejected electron).



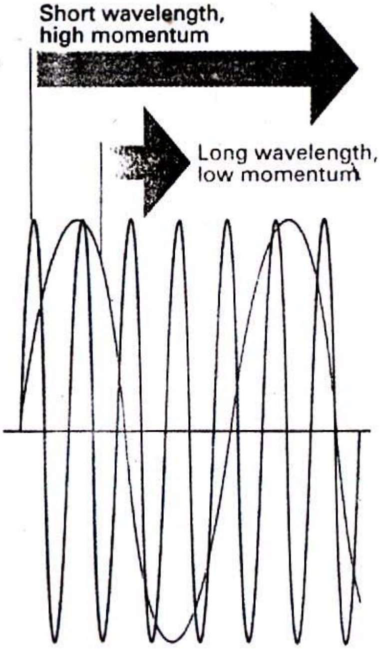
11.13 The Davisson–Germer experiment. The scattering of an electron beam from a nickel crystal shows a variation of intensity characteristic of a diffraction experiment in which waves interfere constructively and destructively in different directions.

are brought to the heart of modern physics. When examined on an atomic scale, the classical concepts of particle and wave melt together, particles taking on the characteristics of waves, and waves the characteristics of particles.

Some progress towards coordinating these properties had already been made by the French physicist Louis de Broglie when, in 1924, he suggested that any particle, not only photons, travelling with a linear momentum p should have (in some sense) a wavelength given by the **de Broglie relation:**

$$\lambda = \frac{h}{p} \tag{13}$$

That is, a particle with a high linear momentum has a short wavelength (Fig. 11.14). Macroscopic bodies have such high momenta (even when they are moving slowly) that their wavelengths are undetectably small, and the wave-like properties cannot be observed.



11.14 An illustration of the de Broglie relation between momentum and wavelength. The wave is associated with a particle (shortly this wave will be seen to be the wavefunction of the particle). A particle with high momentum has a wavefunction with a short wavelength, and vice versa.

Example 11.2 Estimating the de Broglie wavelength

Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of 40 kV.

Method To use the de Broglie relation, we need to know the linear momentum, p, of the electrons. To calculate the linear momentum, we note that the energy acquired by an electron accelerated through a potential difference $\mathcal{V}$ is $e\mathcal{V}$, where e is the magnitude of its charge. At the end of the period of acceleration, all the acquired energy is in the form of kinetic energy, $p^2/2m_e$, so we can determine p by setting $p^2/2m_e$ equal to $e\mathcal{V}$. As before, carry through the calculation algebraically before substituting the data.

Answer The expression

$$\frac{p^2}{2m_e} = e\mathcal{V}$$

solves to

$$p = (2m_e e\mathcal{V})^{1/2}$$

Then, from the de Broglie relation,

$$\lambda = \frac{h}{(2m_e e\mathcal{V})^{1/2}}$$

Substitution of the data and the fundamental constants (from inside the front cover) gives

$$\lambda = \frac{6.626 \times 10^{-34}\ \mathrm{J\,s}}{\{2 \times (9.109 \times 10^{-31}\ \mathrm{kg}) \times (1.609 \times 10^{-19}\ \mathrm{C}) \times (4.0 \times 10^{4}\ \mathrm{V})\}^{1/2}}$$
$$= 6.1 \times 10^{-12}\ \mathrm{m}$$

Comment The wavelength of 6.1 pm is shorter than typical bond lengths in molecules (about 100 pm). Electrons accelerated in this way are used in the technique of electron diffraction (Section 21.10) for the determination of molecular structure.

Self-test 11.2 Calculate the wavelength of a neutron with a translational kinetic energy equal to kT at 300 K.

[178 pm]

We now have to conclude that, not only has electromagnetic radiation the character classically ascribed to particles, but electrons (and all other particles) have the characteristics classically ascribed to waves. This joint particle and wave character of matter and radiation is called **wave–particle duality**. Duality strikes at the heart of classical physics, where particles and waves are treated as entirely separate entities. We have also seen that the energies of electromagnetic radiation and of matter cannot be varied continuously, and that for small objects the discreteness of energy is highly significant. In classical mechanics, in contrast, energies could be varied continuously. Such total failure of classical physics for small objects implied that its basic concepts were false. A new mechanics had to be devised to take its place.

The dynamics of microscopic systems

Quantum mechanics acknowledges the wave–particle duality of matter by supposing that, rather than travelling along a definite path, a particle is distributed through space like a wave. This remark may seem mysterious at this stage: it will be interpreted more fully shortly. The wave that in quantum mechanics replaces the classical concept of trajectory is called a **wavefunction**, ψ (psi).

11.3 The Schrödinger equation

In 1926, the Austrian physicist Erwin Schrödinger proposed an equation for finding the wavefunction of any system. The time-independent **Schrödinger equation** for a particle of mass m moving in one dimension with energy E is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi \qquad (14)$$

The factor $V(x)$ is the potential energy of the particle at the point x; $\hbar$ (which is read h-cross or h-bar) is a convenient modification of the Planck constant:

$$\hbar = \frac{h}{2\pi} = 1.054\,57 \times 10^{-34}\ \mathrm{J\,s} \qquad (15)$$

Various ways of expressing the Schrödinger equation, of incorporating the time dependence of the wavefunction, and of extending it to more dimensions, are collected in Table 11.1. In Chapter 12 we shall solve the equation for a number of important cases; in this chapter we are mainly concerned with its significance, the interpretation of its solutions, and seeing how it implies that energy is quantized.

Table 11.1 The Schrödinger equation

For one-dimensional systems:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi$$

where $V(x)$ is the potential energy of the particle and E is its total energy. For three-dimensional systems

$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi$$

where V may depend on position and ∇^2 ('del squared') is

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

In systems with spherical symmetry:

$$\nabla^2=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\Lambda^2$$

where

$$\Lambda^2=\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

In the general case the Schrödinger equation is written

$$H\psi=E\psi$$

where H is the hamiltonian operator for the system:

$$H=-\frac{\hbar^2}{2m}\nabla^2+V$$

For the evolution of a system with time, it is necessary to solve the time-dependent Schrödinger equation

$$H\Psi=\mathrm{i}\hbar\frac{\partial\Psi}{\partial t}$$

Justification 11.1

Although the Schrödinger equation should be regarded as a postulate, like Newton's equations of motion, it can be seen to be plausible by noting that it implies the de Broglie relation for a freely moving particle. First, eqn 14 can be rearranged into

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=-\frac{2m}{\hbar^2}\{E-V(x)\}\psi$$

If the potential has a constant value V, a solution of this equation is

$$\psi=\mathrm{e}^{\mathrm{i}kx}=\cos kx+\mathrm{i}\sin kx \qquad k=\left\{\frac{2m(E-V)}{\hbar^2}\right\}^{1/2}$$

For this result, we have used the mathematical relation $\mathrm{e}^{\mathrm{i}x}=\cos x+\mathrm{i}\sin x$, where $\mathrm{i}=(-1)^{1/2}$. Now we recognize that $\cos kx$ (or $\sin kx$) is a wave of wavelength $\lambda=2\pi/k$, as can be seen by comparing $\cos kx$ with the standard form of a harmonic wave, $\cos(2\pi x/\lambda)$. The quantity $E-V$ is equal to the kinetic energy of the particle, E_{K}, so $k=(2mE_{\mathrm{K}}/\hbar^2)^{1/2}$, which implies that $E_{\mathrm{K}}=k^2\hbar^2/2m$. Because $E_{\mathrm{K}}=p^2/2m$, it follows that

$$p=kh$$

Therefore, the linear momentum is related to the wavelength of the wavefunction by

$$p=\frac{2\pi}{\lambda}\times\frac{h}{2\pi}=\frac{h}{\lambda}$$

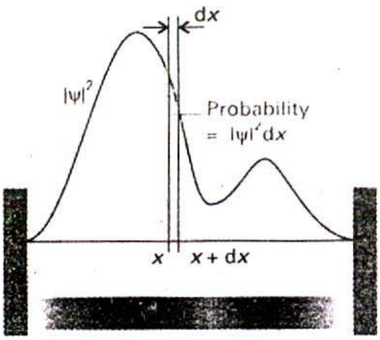
which is the de Broglie relation.

11.4 The Born interpretation of the wavefunction

It is a principal tenet of quantum mechanics that *the wavefunction contains all the dynamical information about the system it describes*. Here we shall concentrate on the information it carries about the location of the particle.

The interpretation of the wavefunction in terms of the location of the particle is based on a suggestion made by Max Born. He made use of an analogy with the wave theory of light, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore (in quantum terms) as a measure of the probability of finding a photon present in the region. The **Born interpretation** of the wavefunction focuses on the square of the wavefunction (or the square modulus, $|\psi|^2 = \psi^*\psi$, if ψ is complex).[3] It states that the value of $|\psi|^2$ at a point is proportional to the probability of finding the particle at that point. Specifically, for a one-dimensional system (Fig. 11.15):

> **If the wavefunction of a particle has the value ψ at some point x, the probability of finding the particle between x and $x+dx$ is proportional to $|\psi|^2 dx$.**



11.15 The wavefunction ψ is a probability amplitude in the sense that its square modulus ($\psi^*\psi$ or $|\psi|^2$) is a probability density. The probability of finding a particle in the region dx located at x is proportional to $|\psi|^2 dx$.

Thus, $|\psi|^2$ is the probability density, and to obtain the probability it must be multiplied by the length of the infinitesimal region dx. The wavefunction ψ itself is called the **probability amplitude**. For a particle free to move in three dimensions (for example, an electron near a nucleus in an atom), the wavefunction depends on the point $\boldsymbol{r}$ with coordinates x, y, and z, and the interpretation of $\psi(\boldsymbol{r})$ is as follows (Fig. 11.16):

> **If the wavefunction of a particle has the value ψ at some point $\boldsymbol{r}$, the probability of finding the particle in an infinitesimal volume $d\tau = dx\,dy\,dz$ at that point is proportional to $|\psi|^2 d\tau$.**

The Born interpretation does away with any worry about the significance of a negative (and, in general, complex) value of ψ because $|\psi|^2$ is real and never negative. There is no *direct* significance in the negative (or complex) value of a wavefunction: only the square modulus, a positive quantity, is directly physically significant, and both negative and positive regions of a wavefunction may correspond to a high probability of finding a particle in a region (Fig. 11.17). However, later we shall see that the presence of positive and negative regions of a wavefunction is of great *indirect* significance, because it gives rise to the possibility of constructive and destructive interference between different wavefunctions.

11.16 The Born interpretation of the wavefunction in three-dimensional space implies that the probability of finding the particle in the volume element $d\tau = dx\,dy\,dz$ at some location $\boldsymbol{r}$ is proportional to the product of $d\tau$ and the value of $|\psi|^2$ at that location.

Example 11.3 Interpreting a wavefunction

We shall see in Chapter 12 that the wavefunction of an electron in the lowest energy state of a hydrogen atom is proportional to e^{-r/a_0}, with a_0 a constant and r the distance from the nucleus. (Notice that this wavefunction depends only on this distance, not the angular position relative to the nucleus.) Calculate the relative probabilities of finding the electron inside a region of volume 1.0 pm^3, which is small even on the scale of the atom, located at (a) the nucleus, (b) a distance a_0 from the nucleus.

Method The region of interest is so small on the scale of the atom that we can ignore the variation of ψ within it and write the probability, P, as proportional to the probability density (ψ^2; note that ψ is real) evaluated at the point of interest multiplied by the volume of interest, δV. That is, $P \propto \psi^2 \delta V$.

---

[3] To form the complex conjugate, ψ^*, of a complex function, replace i wherever it occurs by −i. For instance, the complex conjugate of e^{ikx} is e^{-ikx}. If the wavefunction is real, $|\psi|^2 = \psi^2$.

Answer In each case $\delta V = 1.0\ \text{pm}^3$. (a) At the nucleus, $r = 0$, so

$$P \propto e^0 \times (1.0\ \text{pm}^3) = (1.0) \times (1.0\ \text{pm}^3)$$

(b) At a distance $r = a_0$ in an arbitrary direction,

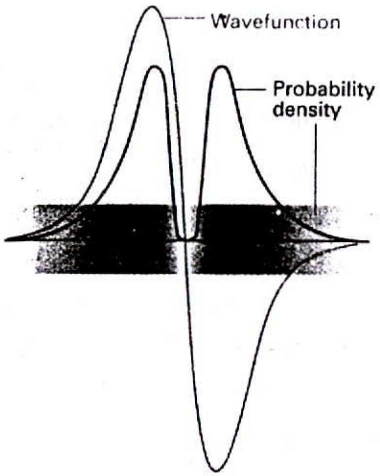
$$P \propto e^{-2} \times (1.0\ \text{pm}^3) = (0.14) \times (1.0\ \text{pm}^3)$$

Therefore, the ratio of probabilities is $1.0/0.14 = 7.1$.

Comment Note that it is more probable (by a factor of 7.1) that the electron will be found at the nucleus than in the same volume element located at a distance a_0 from the nucleus. The negatively charged electron is attracted to the positively charged nucleus, and is likely to be found close to it.

Self-test 11.3 The wavefunction for the lowest energy wavefunction in the ion He^+ is proportional to e^{-2r/a_0}. Repeat the calculation for this ion. Any comment?

[55; more compact wavefunction]



11.17 The sign of a wavefunction has no direct physical significance: the positive and negative regions of this wavefunction both correspond to the same probability distribution (as given by the square modulus of ψ and depicted by the density of shading).

(a) Normalization

A mathematical feature of the Schrödinger equation is that, if ψ is a solution, then so is $N\psi$, where N is any constant. This feature is confirmed by noting that ψ occurs in every term in eqn 14, so any constant factor can be cancelled. This freedom to vary the wavefunction by a constant factor means that it is always possible to find a **normalization constant**, N, such that the proportionality of the Born interpretation becomes an equality.

We find the normalization constant by noting that, for a normalized wavefunction $N\psi$, the probability that a particle is in the region dx is equal to $(N\psi^*)(N\psi)\,dx$ (we are taking N to be real). Furthermore, the sum over all space of these individual probabilities must be 1 (the probability of the particle being somewhere is 1). Expressed mathematically, the latter requirement is

$$N^2 \int \psi^* \psi \, dx = 1 \tag{16}$$

where the integral is over all the space accessible to the particle (for instance, from $-\infty$ to $+\infty$ if the particle can be anywhere in an infinite range). It follows that

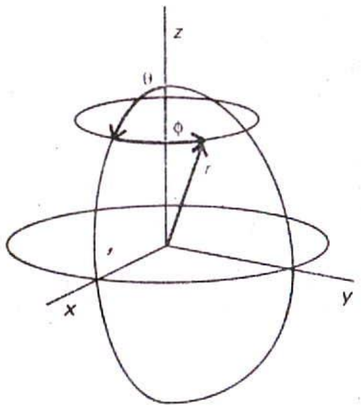
$$N = \frac{1}{\left(\int \psi^* \psi \, dx\right)^{1/2}} \tag{17}$$

Therefore, by evaluating the integral, we can find the value of N and hence 'normalize' the wavefunction. From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1; that is, from now on we assume that ψ already includes a factor which ensures that (in one dimension)

$$\int \psi^* \psi \, dx = 1 \tag{18}$$

In three dimensions, the wavefunction is normalized if

$$\int \psi^* \psi \, dx\, dy\, dz = 1 \tag{19}$$



11.18 The spherical coordinates used for discussing systems with spherical symmetry.

or, more succinctly, if

$$\int \psi^* \psi \, \mathrm{d}\tau = 1 \tag{20}$$

where $d\tau = \mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z$. In all such integrals, the integration is over all the space accessible to the particle. For systems with spherical symmetry, it is best to work in **spherical polar** coordinates r, θ, ϕ (Fig. 11.18):

$$x = r \sin\theta \cos\phi \qquad y = r \sin\theta \sin\phi \qquad z = r \cos\theta \tag{21a}$$

The volume element in spherical polar coordinates is

$$\mathrm{d}\tau = r^2 \sin\theta \, \mathrm{d}r \, \mathrm{d}\theta \, \mathrm{d}\phi \tag{21b}$$

To cover all space, the radius r ranges from 0 to ∞, the colatitude, θ, ranges from 0 to π, and the azimuth, ϕ, ranges from 0 to 2π (Fig. 11.19).

Example 11.4 Normalizing a wavefunction

Normalize the wavefunction used for the hydrogen atom in Example 11.3.

Method We need to find the factor N that guarantees that the integral in eqn 20 is equal to 1. Because the wavefunction is spherically symmetrical, it is sensible to work in spherical polar coordinates.

Answer The integration we require is

$$\begin{aligned}\int \psi^* \psi \, \mathrm{d}\tau &= N^2 \left(\int_0^\infty r^2 \mathrm{e}^{-2r/a_0} \, \mathrm{d}r \right) \left(\int_0^\pi \sin\theta \, \mathrm{d}\theta \right) \left(\int_0^{2\pi} \mathrm{d}\phi \right) \\ &= N^2 \times \tfrac{1}{4} a_0^3 \times 2 \times 2\pi = \pi a_0^3 N^2\end{aligned}$$

Therefore, for this integral to equal 1,

$$N = \left(\frac{1}{\pi a_0^3} \right)^{1/2}$$

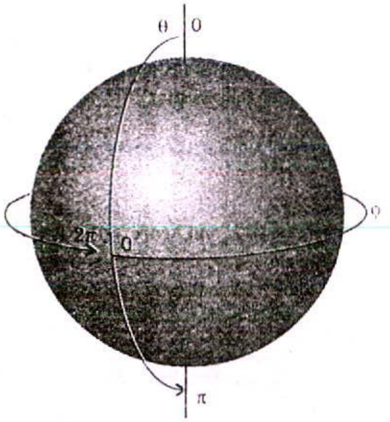
and the normalized wavefunction is

$$\psi = \left(\frac{1}{\pi a_0^3} \right)^{1/2} \mathrm{e}^{-r/a_0}$$

Comment If Example 11.3 is now repeated, we can obtain the actual probabilities of finding the electron in the volume element at each location, not just their relative values. Given (from the end-papers) that $a_0 = 52.9$ pm, the results are (a) 2.2×10^{-6}, corresponding to 1 chance in about 500 000 inspections of finding the electron in the test volume, and (b) 2.9×10^{-7}, corresponding to 1 chance in 3.4 million.

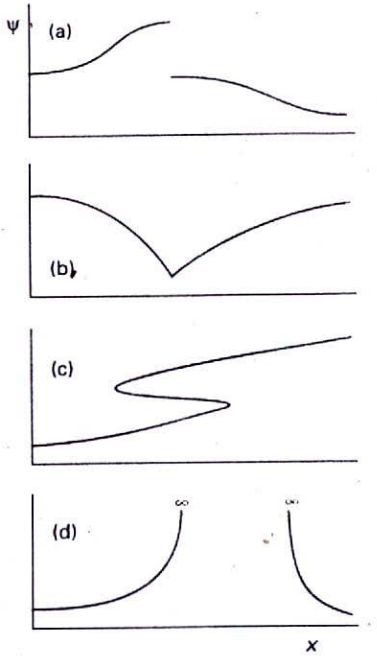
Self-test 11.4 Normalize the wavefunction given in Self-test 11.3.

$[N = (8/\pi a_0^3)^{1/2}]$



11.19 The surface of a sphere is covered by allowing θ to range from 0 to π, and then sweeping that arc around a complete circle by allowing ϕ to range from 0 to 2π.

The quantity $|\psi|^2 \, \mathrm{d}\tau$ is a dimensionless probability and $\mathrm{d}\tau$ has the dimensions of volume, (length)^d, where d is the number of spatial dimensions. Therefore, the dimensions of a normalized wavefunction are 1/(length)$^{d/2}$. Thus, in one spatial dimension, $d = 1$ and a normalized wavefunction has the dimensions of 1/(length)$^{1/2}$. For a three-dimensional system, the wavefunction has the dimensions of 1/(length)$^{3/2}$, as we saw in Example 11.4.



11.20 The wavefunction must satisfy stringent conditions for it to be acceptable. (a) Unacceptable because it is not continuous; (b) unacceptable because its slope is discontinuous; (c) unacceptable because it is not single-valued; (d) unacceptable because it is infinite over a finite region.

(b) Quantization

The Born interpretation puts severe restrictions on the acceptability of wavefunctions. The principal constraint is that ψ must not be infinite anywhere.[4] If it were, the integral in eqn 20 would be infinite and the normalization constant would be zero. The normalized function would then be zero everywhere, except where it is infinite, which would be unacceptable. The requirement that ψ is finite everywhere rules out many possible solutions of the Schrödinger equation, because many mathematically acceptable solutions rise to infinity and are therefore physically unacceptable. We shall meet several examples shortly.

The requirement that ψ is finite everywhere is not the only restriction implied by the Born interpretation. We could imagine (and in Section 12.6a will meet) a solution of the Schrödinger equation that gives rise to more than one value of $|\psi|^2$ at a single point. The Born interpretation implies that such solutions are unacceptable, because it would be absurd to have more than one probability that a particle is at some point. This restriction is expressed by saying that the wavefunction must be *single-valued*, that is, have only one value at each point of space.

The Schrödinger equation itself also implies some mathematical restrictions on the type of functions that will occur. Because it is a second-order differential equation, the second derivative of ψ must be well-defined if the equation is to be applicable everywhere. We can take the second derivative of a function only if it is continuous (so there are no sharp steps in it, Fig. 11.20) and if its first derivative, its slope, is continuous (so there are no kinks).[5]

At this stage we see that ψ must be continuous, have a continuous slope, be single-valued, and be finite everywhere. An acceptable wavefunction cannot be zero everywhere, because the particle it describes must be somewhere. These are such severe restrictions that acceptable solutions of the Schrödinger equation do not in general exist for arbitrary values of the energy E. In other words, *a particle may possess only certain energies, for otherwise its wavefunction would be physically unacceptable*. That is, the energy of a particle is quantized. We can find the acceptable energies by solving the Schrödinger equation for motion of various kinds, and selecting the solutions that conform to the restrictions listed above. That is the task of the next chapter.

Quantum mechanical principles

We have claimed that a wavefunction contains all the information it is possible to obtain about the dynamical properties (for example, its location and momentum) of the particle. We have seen that the Born interpretation tells us as much as we can know about location, but how do we find any additional information?

11.5 The information in a wavefunction

The Schrödinger equation for a particle of mass m free to move parallel to the x-axis with zero potential energy ($V = 0$ everywhere) is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad (22)$$

---

[4] Infinitely sharp spikes are acceptable provided they have zero width. The true constraint is that the wavefunction must not be infinite over any finite region. In elementary quantum mechanics the simpler restriction, to finite ψ, is sufficient.

[5] There are cases, and we shall meet them, where acceptable wavefunctions have kinks. These cases arise when the potential energy has peculiar properties, such as rising abruptly to infinity. When the potential energy is smoothly well-behaved and finite, the slope of the wavefunction must be continuous; if the potential energy becomes infinite, then the slope of the wavefunction need not be continuous. There are only two cases of this behaviour in elementary quantum mechanics, and the peculiarity will be mentioned when we meet them.

The solutions of this equation have the form

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad E = \frac{k^2\hbar^2}{2m} \tag{23}$$

where A and B are constants. To verify that ψ is a solution of eqn 22, we simply substitute it into the left-hand side of the equation and confirm that we obtain $E\psi$.

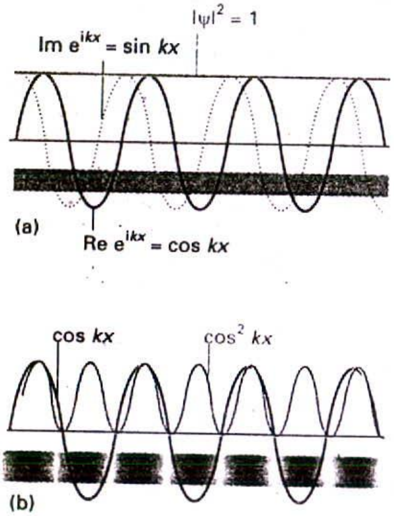
(a) The probability density

Suppose that $B = 0$ in eqn 23;[6] then the wavefunction is simply

$$\psi = Ae^{ikx} \tag{24}$$

Where is the particle? We form the square modulus to find the probability density of the particle:

$$|\psi|^2 = (Ae^{ikx})^*(Ae^{ikx}) = (A^*e^{-ikx})(Ae^{ikx}) = |A|^2 \tag{25}$$



11.21 (a) The square modulus of a wavefunction corresponding to a definite state of linear momentum is a constant, so it corresponds to a uniform probability of finding the particle anywhere. (b) The probability distribution corresponding to the superposition of states of equal magnitude of linear momentum but opposite direction of travel.

This probability is *independent* of x; so, wherever we look along the x-axis, there is an equal probability of finding the particle (Fig. 11.21a). In other words, if the wavefunction of the particle is given by eqn 24, we cannot predict where we will find the particle. The same would be true if the wavefunction in eqn 23 had $A = 0$; then the probability density would be $|B|^2$, a constant.[7]

Now suppose that in the wavefunction $A = B$. Then eqn 23 becomes

$$\psi = A(e^{ikx} + e^{-ikx}) = 2A\cos kx \tag{26}$$

The probability density now has the form

$$|\psi|^2 = (2A\cos kx)^*(2A\cos kx) = 4|A|^2\cos^2 kx \tag{27}$$

This function is illustrated in Fig. 11.21b. As we see, the probability density periodically varies between 0 and $4|A|^2$. The locations where the probability density is zero correspond to nodes in the wavefunction: particles will never be found at the nodes. Specifically, a **node** is a point where a wavefunction passes through zero.

(b) Eigenvalues and eigenfunctions

Because the total energy of the particle is its kinetic energy, $p^2/2m$, it follows from eqn 23 that

$$p = k\hbar \tag{28}$$

This value is independent of the values of A and B.

To find a *systematic* way of extracting information from the wavefunction, we first note that any Schrödinger equation (such as those in eqn 14 and eqn 22) may be written in the succinct form

$$H\psi = E\psi \tag{29}$$

with (in one dimension)

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{30}$$

The quantity H is an **operator**, something that carries out a mathematical operation on the function ψ. In this case, the operation is to take the second derivative of ψ and (after

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[6] We shall see later what determines the values of A and B; for the time being we can treat them as arbitrary constants.

[7] It follows that if x is allowed to range from $-\infty$ to $+\infty$, the normalization constants, A or B, are 0. To avoid this embarrassing problem, x is allowed to range from $-L$ to $+L$, and L is allowed to go to infinity at the end of all calculations. We shall ignore this complication here.

multiplication by $-\hbar^2/2m$) to add the result to the outcome of multiplying ψ by V. The operator H plays a special role in quantum mechanics, and is called the **hamiltonian operator** after the nineteenth century mathematician William Hamilton. Hamilton developed a form of classical mechanics that, it subsequently turned out, is well suited to the formulation of quantum mechanics and which shows very clearly the relation between the two theories. The hamiltonian operator is the operator corresponding to the total energy of the system, the sum of the kinetic and potential energies. Consequently, we can infer that the first term in eqn 30 (the term proportional to the second derivative) must be the operator for the kinetic energy.

When the Schrödinger equation is written as in eqn 29, it is seen to be an **eigenvalue equation**, an equation of the form

(operator)(function) = (constant factor) × (same function)

If we denote a general operator by $\hat{\Omega}$ and a constant factor by ω, this statement is

$$\hat{\Omega}\psi = \omega\psi \tag{31}$$

The factor ω is called the **eigenvalue** of the operator $\hat{\Omega}$. In eqn 29, the eigenvalue is the energy. The function ψ is called an **eigenfunction** and is different for each eigenvalue. In eqn 29, the eigenfunction is the wavefunction corresponding to the energy E. It follows that another way of saying 'solve the Schrödinger equation' is 'find the eigenvalues and eigenfunctions of the hamiltonian operator for the system'. The wavefunctions are the eigenfunctions of the hamiltonian operator, and the corresponding eigenvalues are the allowed energies.

Example 11.5 Identifying an eigenfunction

Show that e^{ax} is an eigenfunction of the operator d/dx, and find the corresponding eigenvalue. Show that e^{ax^2} is not an eigenfunction of d/dx.

Method We need to operate on the function with the operator and check whether the result is a constant factor times the original function.

Answer For $\hat{\Omega} = d/dx$ and $\psi = e^{ax}$:

$$\hat{\Omega}\psi = \frac{d}{dx}e^{ax} = ae^{ax} = a\psi$$

Therefore e^{ax} is indeed an eigenfunction of d/dx, and its eigenvalue is a. For $\psi = e^{ax^2}$

$$\hat{\Omega}\psi = \frac{d}{dx}e^{ax^2} = 2axe^{ax^2} = 2ax \times \psi$$

which is not an eigenvalue equation even though the same function ψ occurs on the right, because ψ is now multiplied by a variable factor ($2ax$), not a constant factor. Alternatively, if the right-hand side is written $2a(xe^{ax^2})$, we see that it is a constant times a *different* function.

Comment Much of quantum mechanics involves looking for functions that are eigenfunctions of a given operator, especially of the hamiltonian operator for the energy.

Self-test 11.5 Is the function $\cos ax$ an eigenfunction of (a) d/dx, (b) d^2/dx^2?

[(a) No, (b) yes]

The importance of eigenvalue equations is that the pattern

$$(\text{energy operator})\psi = (\text{energy})\psi$$

exemplified by the Schrödinger equation is repeated for other **observables**, or measurable properties of a system, such as the momentum or the electric dipole moment. Thus, it is often the case that we can write

$$(\text{operator corresponding to an observable})\psi = (\text{value of observable}) \times \psi$$

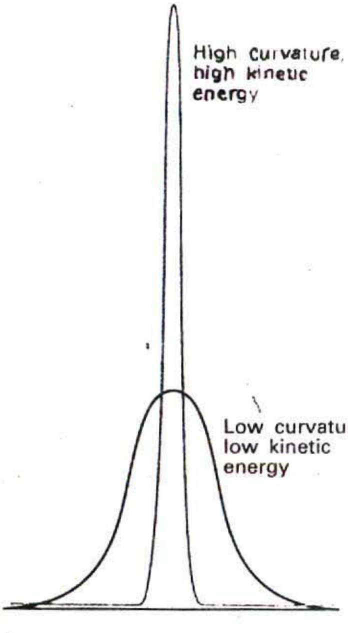
The symbol $\hat{\Omega}$ in eqn 31 is then interpreted as an operator (for example, the hamiltonian, H) corresponding to an observable (for example, the energy), and the eigenvalue ω is the value of that observable (for example, the value of the energy, E). Therefore, if we know both the wavefunction ψ and the operator $\hat{\Omega}$ corresponding to the observable Ω of interest, and the wavefunction is an eigenfunction of the operator $\hat{\Omega}$, we can predict the outcome of an observation of the property Ω (for example, an atom's energy) by picking out the factor ω in the eigenvalue equation, eqn 31.

(c) Operators

To make these abstract procedures concrete, we need to set up and use the operator corresponding to a given observable. The procedure is summarized by the following rule:

Observables, Ω, are represented by operators, $\hat{\Omega}$, built from the following position and momentum operators:

$$\hat{x} = x\times \qquad \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} \tag{32}$$



11.22 Even if a wavefunction does not have the form of a periodic wave, it is still possible to infer from it the average kinetic energy of a particle by noting its average curvature. This illustration shows two wavefunctions: the sharply curved function corresponds to a higher kinetic energy than that of the less sharply curved function.

That is, the operator for location along the x-axis is multiplication (of the wavefunction) by x and the operator for linear momentum parallel to the x-axis is proportional to taking the derivative (of the wavefunction) with respect to x.

For example, to deduce the value of the linear momentum given a specific wavefunction, we set up the eigenvalue equation

$$\hat{p}_x\psi = p_x\psi \tag{33}$$

in the form

$$\frac{\hbar}{i}\frac{d\psi}{dx} = p_x\psi \tag{34}$$

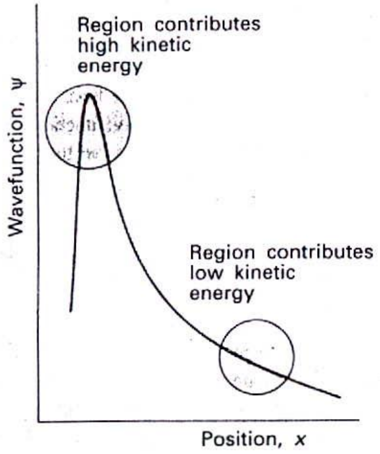
If the wavefunction is the one given in eqn 23 with $B = 0$,

$$\frac{\hbar}{i}\frac{d\psi}{dx} = \frac{\hbar}{i}A\frac{de^{ikx}}{dx} = \frac{\hbar}{i}A \times ike^{ikx} = k\hbar Ae^{ikx} = k\hbar\psi \tag{35}$$

This is an eigenvalue equation, and by comparing it with eqn 33 we find that $p_x = +k\hbar$. The positive value implies that the linear momentum is directed towards positive x. Now suppose instead that the wavefunction is the one in eqn 23 with $A = 0$; then the same kind of calculation gives $p_x = -k\hbar$. It follows that a particle described by the second wavefunction has the same magnitude of momentum (and the same kinetic energy) as before, but its motion is towards $-x$.

The definitions in eqn 32 are used to construct operators for other observables. For example, suppose we wanted the operator for a potential energy of the form

$$V = \tfrac{1}{2}kx^2 \tag{36}$$



11.23 The observed kinetic energy of a particle is an average of contributions from the entire space covered by the wavefunction. Sharply curved regions contribute a high kinetic energy to the average; slightly curved regions contribute only a small kinetic energy.

with k a constant (later, we shall see that this potential describes the vibrations of atoms in molecules). Then it follows from eqn 32 that the operator corresponding to V is multiplication by x^2:

$$\hat{V} = \tfrac{1}{2}kx^2 \times \tag{37}$$

In normal practice, the multiplication sign is omitted. To construct the operator for kinetic energy, we make use of the classical relation between kinetic energy and linear momentum, which in one dimension is

$$E_{\mathrm{K}} = \frac{p_x^2}{2m} \tag{38a}$$

Then, using the operator for p_x in eqn 32 we find:

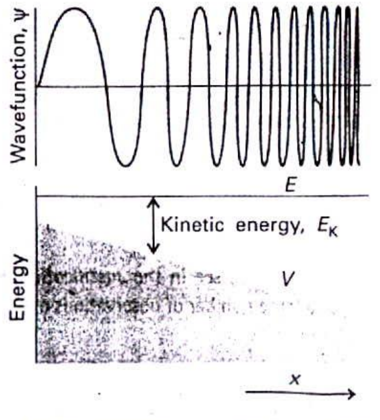
$$\hat{E}_{\mathrm{K}} = \frac{1}{2m}\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{38b}$$

It follows that the operator for the total energy, the hamiltonian operator, is

$$H = \hat{E}_{\mathrm{K}} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \hat{V} \tag{39}$$

The expression for the kinetic energy operator, eqn 38*b*, gives another clue to the qualitative interpretation of a wavefunction. In mathematics, the second derivative of a function is a measure of its curvature: a large second derivative indicates a sharply curved function (Fig. 11.22). It follows that a sharply curved wavefunction is associated with a high kinetic energy, and one with a low curvature is associated with a low kinetic energy. This interpretation is consistent with the de Broglie relation, which predicts a short wavelength (a sharply curved wavefunction) when the linear momentum (and hence the kinetic energy) is high. However, it extends the interpretation to wavefunctions that do not spread through space and resemble those shown in Fig. 11.22. The curvature of a wavefunction in general varies from place to place. Wherever a wavefunction is sharply curved, its contribution to the total kinetic energy is large (Fig. 11.23). Wherever the wavefunction is not sharply curved, its contribution to the overall kinetic energy is low. As we shall shortly see, the observed kinetic energy of the particle is an integral of all the contributions of the kinetic energy from each region. Hence, we can expect a particle to have a high kinetic energy if the average curvature of its wavefunction is high.

The association of high curvature with high kinetic energy will turn out to be a valuable guide to the interpretation of wavefunctions and the prediction of their shapes. For example, suppose we need to know the wavefunction of a particle with a given total energy and a potential energy that decreases with increasing x (Fig. 11.24). Because the difference $E - V = E_{\mathrm{K}}$ increases from left to right, the wavefunction must become more sharply curved as x increases: its wavelength decreases as the local contributions to its kinetic energy increase. We can therefore guess that the wavefunction will look like the function sketched in the illustration, and more detailed calculation confirms this to be so.



11.24 The wavefunction of a particle in a potential decreasing towards the right and hence subjected to a constant force to the right. Only the real part of the wavefunction is shown; the imaginary part is similar, but displaced to the right.

(d) Superpositions and expectation values

Suppose now that the wavefunction is the one given in eqn 26 (with $A = B$). What is the linear momentum of the particle it describes? We quickly run into trouble if we use the operator technique. When we operate with $\hat{p}_x$, we find

$$\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{2\hbar}{\mathrm{i}}A\frac{\mathrm{d}\cos kx}{\mathrm{d}x} = -\frac{2k\hbar}{\mathrm{i}}A\sin kx \tag{40}$$

This expression is not an eigenvalue equation, because the function on the right is different from that on the left.

When the wavefunction of a particle is not an eigenfunction of an operator, the property to which the operator corresponds does not have a definite value. However, in the current example the momentum is not completely indefinite because the cosine wavefunction is a linear combination, or sum, of e^{ikx} and e^{-ikx}, and these two functions, as we have seen, individually correspond to definite momentum states. We say that the total wavefunction is a **superposition** of more than one wavefunction. Symbolically we can write the superposition as

$$\psi = \underset{\substack{\text{Particle with}\\ \text{linear momentum}\\ +k\hbar}}{\psi_{\rightarrow}} + \underset{\substack{\text{Particle with}\\ \text{linear momentum}\\ -k\hbar}}{\psi_{\leftarrow}}$$

The interpretation of this composite wavefunction is that, if the momentum of the particle is repeatedly measured in a long series of observations, then its *magnitude* will found to be $k\hbar$ in all the measurements (because that is the value for each component of the wavefunction). However, because the two component wavefunctions occur equally in the superposition, half the measurements will show that the particle is moving to the right ($p_x = +k\hbar$), and half the measurements will show that it is moving to the left ($p_x = -k\hbar$). According to quantum mechanics, we cannot predict in which direction the particle will in fact be found to be travelling; all we can say is that, in a long series of observations, there are equal probabilities of finding the particle travelling to the right and to the left.

The same interpretation applies to any wavefunction written as a linear combination of eigenfunctions of an operator. Thus, suppose the wavefunction is known to be a superposition of many different linear momentum eigenfunctions and is written as the linear combination

$$\psi = c_1\psi_1 + c_2\psi_2 + \cdots = \sum_k c_k\psi_k \tag{41}$$

where the c_k are numerical coefficients and the ψ_k correspond to different momentum states. Then, according to quantum mechanics,

1. When the momentum is measured, in a single observation *one* of the eigenvalues corresponding to the ψ_k that contribute to the superposition will be found.
2. The probability of measuring a particular eigenvalue in a series of observations is proportional to the square modulus ($|c_k|^2$) of the corresponding coefficient in the linear combination.
3. The average value of a large number of observations is given by the expectation value $\langle\Omega\rangle$ of the operator $\hat{\Omega}$ corresponding to the observable of interest.

The expectation value of an operator $\hat{\Omega}$ is defined as

$$\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi\,\mathrm{d}\tau \qquad [42]$$

This formula is valid only for normalized wavefunctions. As we see in the *Justification* below, an expectation value is the weighted average of a large number of observations of a property.

Justification 11.2

If ψ is an eigenfunction of $\hat{\Omega}$ with eigenvalue ω, the expectation value of Ω is

$$\langle\Omega\rangle = \int \psi^*\hat{\Omega}\psi\,\mathrm{d}\tau = \int \psi^*\omega\psi\,\mathrm{d}\tau = \omega\int \psi^*\psi\,d\tau = \omega$$

because ω is a constant and may be taken outside the integral, and the resulting integral is equal to 1 for a normalized wavefunction. The interpretation of this expression is that, because every observation of the property Ω results in the value ω (because the wavefunction is an eigenfunction of $\hat{\Omega}$), the mean value of all the observations is also ω.

A wavefunction that is not an eigenfunction of the operator of interest can be written as a linear combination of eigenfunctions. For simplicity, suppose the wavefunction is the sum of two eigenfunctions (the general case, eqn 41, can easily be developed). Then

$$\begin{aligned}\langle\Omega\rangle &= \int (c_1\psi_1 + c_2\psi_2)^*\hat{\Omega}(c_1\psi_1 + c_2\psi_2)\,\mathrm{d}\tau \\ &= \int (c_1\psi_1 + c_2\psi_2)^*(c_1\omega_1\psi_1 + c_2\omega_2\psi_2)\,\mathrm{d}\tau \\ &= c_1^*c_1\omega_1\int \psi_1^*\psi_1\,\mathrm{d}\tau + c_2^*c_2\omega_2\int \psi_2^*\psi_2\,\mathrm{d}\tau \\ &\quad + c_1^*c_2\omega_2\int \psi_1^*\psi_2\,\mathrm{d}\tau + c_2^*c_1\omega_1\int \psi_2^*\psi_1\,\mathrm{d}\tau\end{aligned}$$

The first two integrals on the right are both equal to 1 because the wavefunctions are normalized. To deal with the remaining two integrals we need to make use of another property of eigenfunctions, called 'orthogonality': to say that two functions are orthogonal means that

$$\int \psi_i^*\psi_j\,\mathrm{d}\tau = 0 \tag{43}$$

A very general rule in quantum mechanics is that *eigenfunctions corresponding to different eigenvalues of the same operator are orthogonal.*[8] For example, if ψ_1 corresponds to one energy, and ψ_2 corresponds to a different energy, then we know at once that the two functions are orthogonal and that the integral of their product is zero. Because ψ_1 and ψ_2 do correspond to different eigenvalues in the current example, they are orthogonal, so we can conclude that

$$\langle\Omega\rangle = |c_1|^2\omega_1 + |c_2|^2\omega_2 \tag{44}$$

This expression shows that the expectation value is the sum of the two eigenvalues weighted by the probabilities that each one will be found in a series of measurements. Hence, the expectation value is the weighted mean of a series of observations.

Example 11.6 Calculating an expectation value

Calculate the average value of the distance of an electron from the nucleus in the hydrogen atom in its state of lowest energy.

Method The average radius is the expectation value of the operator corresponding to the distance from the nucleus, which is multiplication by r. To evaluate $\langle r\rangle$, we need to know the normalized wavefunction (from Example 11.4) and then evaluate the integral in eqn 42. A useful integral for calculations on atomic wavefunctions is

$$\int_0^\infty x^n e^{-ax}\,\mathrm{d}x = \frac{n!}{a^{n+1}}$$

where $n!$ denotes factorial n: $n! = n(n-1)(n-2)\cdots 1$.

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[8] Strictly speaking, this rule applies only to 'Hermitian operators', which are operators for which $\int \psi_i^*\hat{\Omega}\psi_j\,\mathrm{d}\tau = (\int \psi_j^*\hat{\Omega}\psi_i\,\mathrm{d}\tau)^*$. We shall be dealing only with Hermitian operators.

Answer The average value is given by the expectation value

$$\langle r \rangle = \int \psi^* \hat{r} \psi \, d\tau$$

which we evaluate by using spherical polar coordinates. Using the normalized function in Example 11.4 gives

$$\begin{aligned}\langle r \rangle &= \frac{1}{\pi a_0^3}\left(\int_0^\infty r^3 e^{-2r/a_0}\, dr\right)\left(\int_0^\pi \sin\theta \, d\theta\right)\left(\int_0^{2\pi} d\phi\right)\\ &= \frac{1}{\pi a_0^3} \times \frac{3! a_0^4}{2^4} \times 2 \times 2\pi = \tfrac{3}{2} a_0\end{aligned}$$

Because $a_0 = 52.9$ pm (see end-papers), $\langle r \rangle = 79.4$ pm.

Comment The result means that, if a very large number of measurements of the distance of the electron from the nucleus are made, their mean value will be 79.4 pm. However, each different observation will give a different and unpredictable individual result, because the wavefunction is not an eigenfunction of the operator corresponding to *r*.

Self-test 11.6 Evaluate the root mean square distance, $\langle r^2 \rangle^{1/2}$, of the electron from the nucleus in the hydrogen atom.

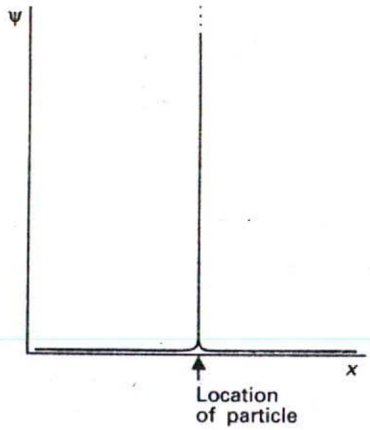
$[3^{1/2} a_0]$

The mean kinetic energy of a particle in one dimension is the expectation value of the operator given in eqn 38*b*. Therefore, we can write

$$\langle E_K \rangle = \int \psi^* \hat{E}_K \psi \, d\tau = -\frac{\hbar^2}{2m} \int \psi^* \frac{d^2\psi}{dx^2} \, d\tau \tag{45}$$

We see that the kinetic energy is a kind of average over the curvature of the wavefunction: we get a large contribution to the observed value from regions where the wavefunction is sharply curved (so $d^2\psi/dx^2$ is large) and the wavefunction itself is large (so that ψ^* is large too).

11.6 The uncertainty principle



11.25 The wavefunction for a particle at a well-defined location is a sharply spiked function which has zero amplitude everywhere except at the particle's position.

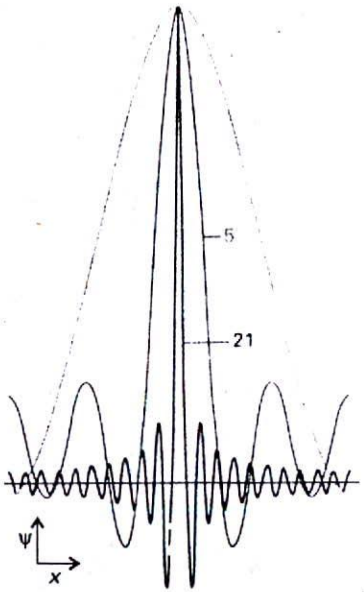
We have seen that, if the wavefunction is Ae^{ikx}, then the particle it describes has a definite state of linear momentum, namely travelling to the right with momentum $p_x = +k\hbar$. However, we have also seen that the position of the particle described by this wavefunction is completely unpredictable. In other words, *if the momentum is specified precisely, it is impossible to predict the location of the particle*. This statement is one-half of a special case of the **Heisenberg uncertainty principle**, one of the most celebrated results of quantum mechanics:

> **It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.**

Before discussing the principle further, we must establish its other half: that if we know the position of a particle exactly, then we can say nothing about its momentum. The argument draws on the idea of regarding a wavefunction as a superposition of eigenfunctions, and runs as follows.

If we know that the particle is at a definite location, its wavefunction must be large there and zero everywhere else (Fig. 11.25). Such a wavefunction can be created by superimposing a large number of harmonic (sine and cosine) functions, or, what is equivalent, a number of

e^{ikx} functions.[9] In other words, we can create a sharply localized wavefunction by forming a linear combination of wavefunctions that correspond to many different linear momenta. The superposition of a few harmonic functions gives a wavefunction that spreads over a range of locations (Fig. 11.26). However, as the number of wavefunctions in the superposition increases, the wavefunction becomes sharper on account of the more complete interference between the positive and negative regions of the individual waves. When an infinite number of components is used, the wavefunction is a sharp, infinitely narrow spike, which corresponds to perfect localization of the particle. Now the particle is perfectly localized. However, we have lost all information about its momentum because, as we saw above, a measurement of the momentum will give a result corresponding to any one of the infinite number of waves in the superposition, and which one it will give is unpredictable. Hence, if we know the location of the particle precisely (implying that its wavefunction is a superposition of an infinite number of momentum eigenfunctions), its momentum is completely unpredictable.



11.26 The wavefunction for a particle with an ill-defined location can be regarded as the superposition of several wavefunctions of definite wavelength which interfere constructively in one place but destructively elsewhere. As more waves are used in the superposition (as given by the numbers attached to the curves), the location becomes more precise at the expense of uncertainty in the particle's momentum. An infinite number of waves is needed to construct the wavefunction of a perfectly localized particle.

A quantitative version of this result is

$$\Delta p \Delta q \geq \tfrac{1}{2}\hbar \tag{46}$$

In this expression Δp is the 'uncertainty' in the linear momentum parallel to the axis q, and Δq is the uncertainty in position along that axis. These 'uncertainties' are precisely defined, for they are the root mean square deviations of the properties from their mean values:

$$\Delta p = \{\langle p^2\rangle - \langle p\rangle^2\}^{1/2} \qquad \Delta q = \{\langle q^2\rangle - \langle q\rangle^2\}^{1/2} \tag*{[47]}$$

If there is complete certainty about the position of the particle ($\Delta q = 0$), the only way that eqn 46 can be satisfied is for $\Delta p = \infty$, which implies complete uncertainty about the momentum. Conversely, if the momentum is known exactly ($\Delta p = 0$), then the position must be completely uncertain ($\Delta q = \infty$).

The p and q that appear in eqn 46 refer to the same direction in space. Therefore, whereas position on the x-axis and momentum parallel to the x-axis are restricted by the uncertainty relation, simultaneous location of position on x and motion parallel to y or z is not restricted.

Example 11.7 Using the uncertainty principle

The speed of a projectile of mass 1.0 g is known to within $1 \times 10^{-6}\ \mathrm{m\,s^{-1}}$. Calculate the minimum uncertainty in its position.

Method Estimate Δp from $m\Delta v$ where Δv is the uncertainty in the speed; then use eqn 46 to estimate the minimum uncertainty in position, Δq.

Answer The minimum uncertainty in position is

$$\begin{aligned}\Delta q &= \frac{\hbar}{2m\Delta v}\\ &= \frac{1.055 \times 10^{-34}\ \mathrm{J\,s}}{2 \times (1.0 \times 10^{-3}\ \mathrm{kg}) \times (1 \times 10^{-6}\ \mathrm{m\,s^{-1}})} = 5 \times 10^{-26}\ \mathrm{m}\end{aligned}$$

Comment The uncertainty is completely negligible for all practical purposes concerning macroscopic objects. However, if the mass is that of an electron, the same uncertainty in speed implies an uncertainty in position far larger than the diameter of an atom, so the

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[9] These sums are equivalent, because $e^{ikx} = \cos kx + i \sin kx$.

concept of a trajectory, the simultaneous possession of a precise position and momentum, is untenable.

Self-test 11.7 Estimate the minimum uncertainty in the speed of an electron in a one-dimensional region of length $2a_0$.

[500 km s^{-1}]

The Heisenberg uncertainty principle is more general than eqn 46 implies. It applies to any pair of observables called **complementary observables**, which are defined in terms of the properties of their operators. Specifically, two observables Ω_1 and Ω_2 are complementary if

$$\hat{\Omega}_1\hat{\Omega}_2 \neq \hat{\Omega}_2\hat{\Omega}_1 \qquad (48)$$

When the effect of two operators depends on their order (as this equation implies), we say that they do not **commute**.

Illustration

To show that the operators for position and momentum do not commute (and hence are complementary observables) we consider the effect of $\hat{x}\hat{p}_x$ on a wavefunction ψ:

$$\hat{x}\hat{p}_x\psi = x \times \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x}$$

Next, we consider the effect of $\hat{p}_x\hat{x}$ on the same function:

$$\hat{p}_x\hat{x}\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}x\psi = \frac{\hbar}{\mathrm{i}}\left(\psi + x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

For this step we have used the standard rule about differentiating a product of functions. The second expression is clearly different from the first, so the two operators do not commute.

With the discovery that some pairs of observables are complementary (we meet more examples in the next chapter), we are at the heart of the difference between classical and quantum mechanics. Classical mechanics supposed, falsely as we now know, that the position and momentum of a particle could be specified simultaneously with arbitrary precision. However, quantum mechanics shows that position and momentum are complementary, and that we have to make a choice: we can specify position at the expense of momentum, or momentum at the expense of position.

The realization that some observables are complementary allows us to make considerable progress with the calculation of atomic and molecular properties, but it does away with some of classical physics' most cherished concepts.

Checklist of key ideas

- ☐ classical mechanics
- ☐ quantum mechanics

The origins of quantum mechanics

11.1 The failures of classical physics

- ☐ black body
- ☐ Wien displacement law (1)
- ☐ second radiation constant
- ☐ total energy density
- ☐ Stefan-Boltzmann law (2a)
- ☐ excitance
- ☐ Stefan-Boltzmann constant
- ☐ Rayleigh-Jeans law (3)
- ☐ ultraviolet catastrophe
- ☐ quantization of energy
- ☐ Planck constant
- ☐ Planck distribution (5)
- ☐ Einstein formula (9)
- ☐ Einstein temperature
- ☐ Debye formula (11)
- ☐ Debye temperature

11.2 Wave-particle duality

- ☐ photon

- ☐ photoelectric effect
- ☐ work function
- ☐ de Broglie relation (13)
- ☐ wave-particle duality

The dynamics of microscopic systems

- ☐ wavefunction

11.3 The Schrödinger equation

- ☐ Schrödinger equation (14, Table 11.1)

11.4 The Born interpretation of the wavefunction

- ☐ Born interpretation
- ☐ probability density
- ☐ probability amplitude
- ☐ normalization constant (17)
- ☐ spherical polar coordinates (21)

Quantum mechanical principles

11.5 The information in a wavefunction

- ☐ node
- ☐ operator
- ☐ hamiltonian operator (30)
- ☐ eigenvalue equation (31)
- ☐ eigenvalue
- ☐ eigenfunction
- ☐ observables
- ☐ linear combination (41)
- ☐ superposition
- ☐ expectation value (42)

11.6 The uncertainty princple

- ☐ Heisenberg uncertainty principle (46)
- ☐ complementary observables
- ☐ commute

Further reading

Texts and sources of data and information

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M. Jammer, *The conceptual development of quantum mechanics.* McGraw-Hill, New York (1966).

D.C. Cassidy, *Uncertainty: the life and science of Werner Heisenberg.* W.H. Freeman & Co., New York (1992).

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Exercises

11.1 (a) Calculate the power radiated by a 2.0 m × 3.0 m section of the surface of a hot body at 1500 K.

11.1 (b) Calculate the power radiated by the surface of a cylindrical wire of length 5.0 cm and radius 0.12 mm that is heated to 3300 K by an electric current.

11.2 (a) Calculate the average power output of a photodetector that collects 8.0×10^7 photons in 3.8 ms from monochromatic light of wavelength 325 nm.

11.2 (b) Calculate the average power output of a photosensitive plate that collects 1.20×10^8 photons in 5.9 ms from monochromatic light of wavelength 297 nm.

11.3 (a) Determine the wavelength of the radiation of the most intense electromagnetic radiation emitted from the surface of the star Sirius, which has a surface temperature of 11 000 K.

11.3 (b) Determine the wavelength of the radiation of the most intense electromagnetic radiation emitted from a furnace at 2500°C.

11.4 (a) Calculate the speed of an electron of wavelength 3.0 cm.

11.4 (b) Calculate the speed of a neutron of wavelength 3.0 cm.

11.5 (a) The fine-structure constant, α, plays a special role in the structure of matter; its approximate value is 1/137. What is the wavelength of an electron travelling at a speed αc, where c is the speed of light? (Note that the circumference of the first Bohr orbit in the hydrogen atom is 331 pm.)

11.5 (b) A certain diffraction experiment requires the use of electrons of wavelength 0.45 nm. Calculate the speed of the electrons.

11.6 (a) Calculate the linear momentum of photons of wavelength 750 nm. What speed does an electron need to travel to have the same linear momentum?

11.6 (b) Calculate the linear momentum of photons of wavelength 350 nm. What speed does a hydrogen molecule need to travel to have the same linear momentum?

11.7 (a) The energy required for the ionization of a certain atom is 3.44×10^{-18} J. The absorption of a photon of unknown wavelength ionizes the atom and ejects an electron with velocity 1.03×10^6 m s^{-1}. Calculate the wavelength of the incident radiation.

11.7 (b) The energy required for the ionization of a certain atom is 5.12 aJ. The absorption of a photon of unknown wavelength ionizes the atom and ejects an electron with velocity 345 km s^{-1}. Calculate the wavelength of the incident radiation.

11.8 (a) The speed of a certain proton is $4.5 \times 10^5\ \mathrm{m\,s^{-1}}$. If the uncertainty in its momentum is to be reduced to 0.0100 per cent, what uncertainty in its location must be tolerated?

11.8 (b) The speed of a certain electron is $995\ \mathrm{km\,s^{-1}}$. If the uncertainty in its momentum is to be reduced to 0.0010 per cent, what uncertainty in its location must be tolerated?

11.9 (a) Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (a) 600 nm (red), (b) 550 nm (yellow), (c) 400 nm (blue).

11.9 (b) Calculate the energy per photon and the energy per mole of photons for radiation of wavelength (a) 200 nm (ultraviolet), (b) 150 pm (X-ray), (c) 1.00 cm (microwave).

11.10 (a) Calculate the speed to which a stationary H atom would be accelerated if it absorbed each of the photons used in Exercise 11.9a.

11.10 (b) Calculate the speed to which a stationary ^{4}He atom (mass 4.0026 u) would be accelerated if it absorbed each of the photons used in Exercise 11.9b.

11.11 (a) A glow-worm of mass 5.0 g emits red light (650 nm) with a power of 0.10 W entirely in the backward direction. To what speed will it have accelerated after 10 y if released into free space and assumed to live?

11.11 (b) A photon-powered spacecraft of mass 10.0 kg emits radiation of wavelength 225 nm with a power of 1.50 kW entirely in the backward direction. To what speed will it have accelerated after 10.0 y if released into free space?

11.12 (a) A sodium lamp emits yellow light (550 nm). How many photons does it emit each second if its power is (a) 1.0 W, (b) 100 W?

11.12 (b) A laser used to read CDs emits red light of wavelength 700 nm. How many photons does it emit each second if its power is (a) 0.10 W, (b) 1.0 W?

11.13 (a) The peak of the Sun's emission occurs at about 480 nm; estimate the temperature of its surface.

11.13 (b) The peak of the emission from the hot iron in a steel furnace occurs at about 1600 nm; estimate the temperature of the steel.

11.14 (a) The work function for metallic caesium is 2.14 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (a) 700 nm, (b) 300 nm.

11.14 (b) The work function for metallic rubidium is 2.09 eV. Calculate the kinetic energy and the speed of the electrons ejected by light of wavelength (a) 650 nm, (b) 195 nm.

11.15 (a) Calculate the size of the quantum involved in the excitation of (a) an electronic oscillation of period 1.0 fs, (b) a molecular vibration of period 10 fs, (c) a pendulum of period 1.0 s. Express the results in joules and kilojoules per mole.

11.15 (b) Calculate the size of the quantum involved in the excitation of (a) an electronic oscillation of period 2.50 fs, (b) a molecular vibration of period 2.21 fs, (c) a balance wheel of period 1.0 ms. Express the results in joules and kilojoules per mole.

11.16 (a) Calculate the de Broglie wavelength of (a) a mass of 1.0 g travelling at $1.0\ \mathrm{cm\,s^{-1}}$, (b) the same, travelling at $100\ \mathrm{km\,s^{-1}}$, (c) an He atom travelling at $1000\ \mathrm{m\,s^{-1}}$ (a typical speed at room temperature).

11.16 (b) Calculate the de Broglie wavelength of an electron accelerated from rest through a potential difference of (a) 100 V, (b) 1.0 kV, (c) 100 kV.

11.17 (a) Calculate the minimum uncertainty in the speed of a ball of mass 500 g that is known to be within 1.0 μm of a certain point on a bat. What is the minimum uncertainty in the position of a bullet of mass 5.0 g that is known to have a speed somewhere between $350.000\,01\ \mathrm{m\,s^{-1}}$ and $350.000\,00\ \mathrm{m\,s^{-1}}$?

11.17 (b) An electron is confined to a linear region with a length of the same order as the diameter of an atom (about 100 pm). Calculate the minimum uncertainties in its position and speed.

11.18 (a) In an X-ray photoelectron experiment, a photon of wavelength 150 pm ejects an electron from the inner shell of an atom and it emerges with a speed of $2.14 \times 10^7\ \mathrm{m\,s^{-1}}$. Calculate the binding energy of the electron.

11.18 (b) In an X-ray photoelectron experiment, a photon of wavelength 121 pm ejects an electron from the inner shell of an atom and it emerges with a speed of $5.69 \times 10^7\ \mathrm{m\,s^{-1}}$. Calculate the binding energy of the electron.

Problems

Numerical problems

11.1 The Planck distribution gives the energy in the wavelength range $d\lambda$ at the wavelength λ. Calculate the energy density in the range 650 nm to 655 nm inside a cavity of volume 100 cm^3 when its temperature is (a) 25°C, (b) 3000°C.

11.2 The wavelength of the emission maximum from a small pinhole in an electrically heated container was determined at a series of temperatures, and the results are given below. Deduce a value for the Planck constant.

$\theta/°\mathrm{C}$	1000	1500	2000	2500	3000	3500
$\lambda_{\max}/\mathrm{nm}$	2181	1600	1240	1035	878	763

11.3 Write a computer program (or use mathematical software) to evaluate the Planck distribution at any temperature and wavelength or frequency, and add to it a routine for evaluating integrals for the energy density of the radiation between any two wavelengths. Use it to calculate the total energy density in the visible region (600 nm to

350 nm) for a black body at (a) 100°C, (b) 500°C, (c) 700 K. What are the classical values at these temperatures?

11.4 The Einstein frequency is often expressed in terms of an equivalent temperature θ_E, where $\theta_E = h\nu/k$. Confirm that θ_E has the dimensions of temperature, and express the criterion for the validity of the high-temperature form of the Einstein equation in terms of it. Evaluate θ_E for (a) diamond, for which $\nu = 4.65 \times 10^{13}$ Hz and (b) for copper, for which $\nu = 7.15 \times 10^{12}$ Hz. What fraction of the Dulong and Petit value of the heat capacity does each substance reach at 25°C?

11.5 The ground-state wavefunction for a particle confined to a one-dimensional box of length L is

$$\psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right)$$

Suppose the box is 10.0 nm long. Calculate the probability that the particle is (a) between $x = 4.95$ nm and 5.05 nm, (b) between $x = 1.95$ nm and 2.05 nm, (c) between $x = 9.90$ nm and 10.00 nm, (d) in the right half of the box, (e) in the central third of the box.

11.6 The ground-state wavefunction of a hydrogen atom is

$$\psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

where $a_0 = 53$ pm (the Bohr radius). (a) Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centred on the nucleus. (b) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it?

Theoretical problems

11.7 Derive Wien's law, that $\lambda_{max}T$ is a constant, from the Planck distribution, and deduce an expression for the constant.

11.8 Normalize the following wavefunctions: (a) $\sin(n\pi x/L)$ in the range $0 \le x \le L$, (b) a constant in the range $-L \le x \le L$, (c) $e^{-r/a}$ in three-dimensional space, (d) $xe^{-r/2a}$ in three-dimensional space. *Hint:* The volume element in three dimensions is $d\tau = r^2\, dr \sin\theta\, d\theta\, d\phi$, with $0 \le r < \infty, 0 \le \theta \le \pi, 0 \le \phi \le 2\pi$. A useful integral was given in Example 11.6.

11.9 Two (unnormalized) excited state wavefunctions of the H atom are (a) $\psi = (2 - r/a_0)e^{-r/2a_0}$, (b) $\psi = r \sin\theta \cos\phi\, e^{-r/2a_0}$. Normalize both functions to 1.

11.10 Identify which of the following functions are eigenfunctions of the operator d/dx: (a) e^{ikx}, (b) $\cos kx$, (c) k, (d) kx, (e) $e^{-\alpha x^2}$. Give the corresponding eigenvalue where appropriate.

11.11 Determine which of the following functions are eigenfunctions of the inversion operator i (which has the effect of making the replacement $x \rightarrow -x$): (a) $x^3 - kx$, (b) $\cos kx$, (c) $x^2 + 3x - 1$. State the eigenvalue of i when relevant.

11.12 Which of the functions in Problem 11.10 are (a) also eigenfunctions of d^2/dx^2 and (b) only eigenfunctions of d^2/dx^2? Give the eigenvalues where appropriate.

11.13 A particle is in a state described by the wavefunction

$$\psi = (\cos\chi)e^{ikx} + (\sin\chi)e^{-ikx}$$

where χ is a parameter. What is the probability that the particle will be found with a linear momentum (a) $+k\hbar$, (b) $-k\hbar$? (c) What form would the wavefunction have if it were 90 per cent certain that the particle had linear momentum $+k\hbar$?

11.14 Evaluate the kinetic energy of the particle with wavefunction given in Problem 11.13.

11.15 Calculate the average linear momentum of a particle described by the following wavefunctions: (a) e^{ikx}, (b) $\cos kx$, (c) $e^{-\alpha x^2}$, where in each one x ranges from $-\infty$ to $+\infty$.

11.16 Evaluate the expectation values of r and r^2 for a hydrogen atom with wavefunctions given in Problem 11.9.

11.17 Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the ground state of a hydrogenic atom.

11.18 Write a computer program, or use mathematical software, for constructing superpositions of cosine functions and explore how the wavefunction becomes more localized as more components are included. Include routines that determine the probability that a given momentum will be observed. If you plot the superposition (which you should), set $x = 0$ at the centre of the screen and build the superposition there. Include a routine that includes the evaluation of the root mean square location of the packet, $\langle x^2\rangle^{1/2}$.

11.19 Determine the commutators (that is, the value of $\hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1$) of the operators (a) d/dx and x, (b) d/dx and x^2, (c) a and $a^\dagger$, where $a = (x + ip)/2^{1/2}$ and $a^\dagger = (x - ip)/2^{1/2}$.

Additional problems supplied by Carmen Giunta and Charles Trapp

11.20 Demonstrate explicitly that the Planck distribution reduces to the Rayleigh–Jeans law at long wavelengths.

11.21 The temperature of the Sun's surface is approximately 5800 K. On the assumption that the human eye evolved to be most sensitive at the wavelength of light corresponding to the maximum in the Sun's radiant energy distribution, determine the colour of light to which the eye is the most sensitive.

11.22 Solar energy strikes the top of the Earth's atmosphere at a rate of 343 W m^{-2}. About 30 per cent of this energy is reflected directly back into space by the Earth or the atmosphere. The Earth–atmosphere system absorbs the remaining energy and re-radiates it into space as black-body radiation. What is the average black-body temperature of the Earth? What is the wavelength of the most plentiful of the Earth's black-body radiation?

11.23 A star too small and cold to shine has been found by B.R. Oppenheimer, S. Kulkarni, K. Matthews, and T. Nakajima (*Science* 270, 1478, (1995)). The spectrum of the object shows the presence of methane which, according to the authors, would not exist at temperatures much above 1000 K. The mass of the object, as determined from its gravitational effect upon a companion star, is roughly 20 times the mass of Jupiter. With this mass, it is very unlikely that the object formed as a planet; hence it is considered a brown dwarf star, the coolest ever found. (a) From available thermodynamic data test the stability of methane at temperatures above 1000 K. (b) What is $\lambda_{\max}$ for this star? (c) What are the energy density and excitance of this star relative to that of the Sun (6000 K)? (d) To determine whether the star will shine, estimate the fraction of the energy density of the star that appears in the visible portion of the spectrum.

11.24 Max Planck was the first to determine the Boltzmann constant, k, and the value of the constant now known by his name from the experimental data on black-body radiation. Calculate values for k and h from the following data. The excitance, $\mathcal{M}$, from a surface of area 1.000 m^2 at 2000 K is 904.48 kW; at this temperature $\lambda_{\max} = 1.451 \times 10^{-6}$ m. *Hint.* Obtain $\lambda_{\max}$ from the Planck distribution by differentiation with respect to λ.

12

Quantum theory: techniques and applications

To find the properties of systems according to quantum mechanics we need to solve the appropriate Schrödinger equation. This chapter presents the essentials of the solutions for three basic types of motion: translation, vibration, and rotation. We shall see that only certain wavefunctions and their corresponding energies are acceptable. Hence, quantization emerges as a natural consequence of the equation and the conditions imposed on it. The solutions bring to light a number of highly nonclassical, and therefore surprising, features of particles, particularly their ability to tunnel into and through regions where classical physics would forbid them to be found. We shall also encounter a property of the electron, its spin, that has no classical counterpart.

The three basic modes of motion—translation (motion through space), vibration, and rotation—all play an important role in chemistry because they are ways in which molecules store energy. Gas-phase molecules, for instance, undergo translational motion, and their kinetic energy is a contribution to the total internal energy of a sample. Molecules can also store energy as rotational kinetic energy, and transitions between their rotational energy states can be observed spectroscopically. Energy is also stored as molecular vibration, and transitions between vibrational states are responsible for the appearance of infrared spectra.

Translational motion

The quantum mechanical description of free motion in one dimension was introduced in Section 11.5. We saw there that the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=E\psi \qquad (1a)$$

or more succinctly

$$H\psi=E\psi \qquad H=-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \qquad (1b)$$

The general solutions are

$$\psi_k = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx} \qquad E_k = \frac{k^2\hbar^2}{2m} \tag{2}$$

Note that we are now labelling both the wavefunctions and the energies (that is, the eigenfunctions and eigenvalues of H) with the index k. That these functions are solutions can be verified by substituting ψ_k into the left-hand side of eqn 1*a* and showing that the result is equal to $E_k\psi_k$. In this case, all values of k, and therefore all values of the energy, are permitted. It follows that the translational energy of a free particle is not quantized.

We saw in Section 11.5c that a wavefunction of the form $\mathrm{e}^{\mathrm{i}kx}$ describes a particle with linear momentum $p_x = +k\hbar$, corresponding to motion towards positive x (to the right), and that a wavefunction of the form $\mathrm{e}^{-\mathrm{i}kx}$ describes a particle with the same magnitude of linear momentum but travelling towards negative x (to the left). That is, $\mathrm{e}^{\mathrm{i}kx}$ is an eigenfunction of the operator $\hat{p}_x$ with eigenvalue $+k\hbar$, and $\mathrm{e}^{-\mathrm{i}kx}$ is an eigenfunction with eigenvalue $-k\hbar$. In either state, $|\psi|^2$ is independent of x, which implies that the position of the particle is completely unpredictable. This conclusion is consistent with the uncertainty principle because, if the momentum is certain, then the position cannot be specified (the operators $\hat{x}$ and $\hat{p}_x$ do not commute, Section 11.5e).

12.1 A particle in a box

In this section, we consider the problem of a **particle in a box**, in which a particle of mass m is confined between two walls at $x = 0$ and $x = L$. In an **infinite square well**, the potential energy is zero inside the box but rises abruptly to infinity at the walls (Fig. 12.1). This potential energy is an idealization of the potential energy of a gas-phase molecule that is free to move in a one-dimensional container.

(a) The Schrödinger equation

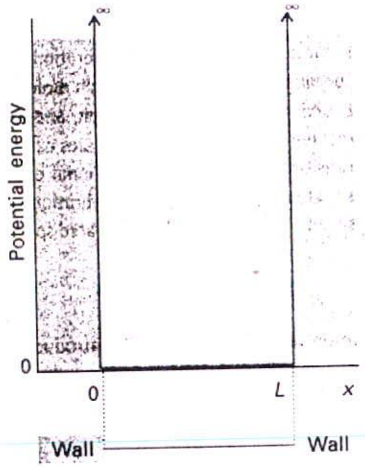
The Schrödinger equation for the region between the walls (where $V = 0$) is the same as for a free particle (eqn 1), so the general solutions given in eqn 2 are also the same. It is convenient to write them as[1]

$$\psi_k(x) = C\sin kx + D\cos kx \qquad E_k = \frac{k^2\hbar^2}{2m} \tag{3}$$

(b) The acceptable solutions

For a free particle, any value of E_k corresponds to an acceptable solution. However, when the particle is confined within a region, the acceptable wavefunctions must satisfy certain **boundary conditions**, or constraints on the function at certain locations. It is physically impossible for the particle to be found with an infinite potential energy, so the wavefunction must be zero where V is infinite, at $x<0$ and $x>L$. The continuity of the wavefunction then requires it to vanish just inside the well at $x = 0$ and $x = L$. That is, the boundary conditions are $\psi_k(0) = 0$ and $\psi_k(L) = 0$.

Consider the wall at $x = 0$. According to eqn 3, $\psi(0) = D$ (because $\sin 0 = 0$ and $\cos 0 = 1$). But because $\psi(0) = 0$ we must have $D = 0$. It follows that the wavefunction must be of the form $\psi_k(x) = C\sin kx$. The value of ψ at the other wall (at $x = L$) is $\psi_k(L) = C\sin kL$, which must also be zero. Taking $C = 0$ would give $\psi_k(x) = 0$ for all x,



12.1 A particle in a one-dimensional region with impenetrable walls. Its potential energy is zero between $x = 0$ and $x = L$, and rises abruptly to infinity as soon as it touches the walls.

---

[1] We use $\mathrm{e}^{\pm\mathrm{i}x} = \cos x \pm \mathrm{i}\sin x$ and absorb all numerical factors into the coefficients C and D.

which would conflict with the Born interpretation (the particle must be somewhere). Therefore, kL must be chosen so that $\sin kL = 0$, which is satisfied by

$$kL = n\pi \qquad n = 1, 2, \ldots \tag{4}$$

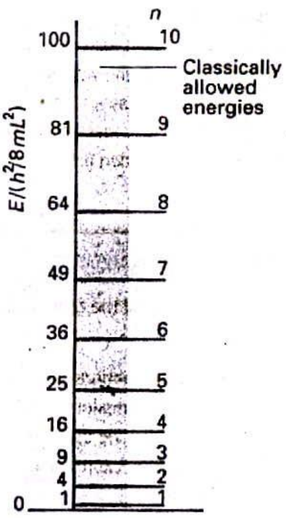
The value $n = 0$ is ruled out, because it implies $k = 0$ and $\psi_k(x) = 0$ everywhere (because $\sin 0 = 0$), which is again unacceptable, and negative values of n merely change the sign of $\sin kL$ (because $\sin(-x) = -\sin x$). The wavefunctions are therefore

$$\psi_n(x) = C \sin \frac{n\pi x}{L} \qquad n = 1, 2, \ldots \tag{5}$$

(At this point we have started to label the solutions with the index n instead of k.) Because k and E_k are related by eqn 3, it follows that the energy of the particle is limited to the values

$$E_n = \frac{(n\pi/L)^2\hbar^2}{2m} = \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, \ldots \tag{6}$$

We see that the energy of the particle is quantized, and that the quantization arises from the boundary conditions that ψ must satisfy if it is to be an acceptable wavefunction. This is a general conclusion: *the need to satisfy boundary conditions implies that only certain wavefunctions are acceptable, and hence restricts observables to discrete values*. So far, only energy has been quantized; shortly we shall see that other physical observables may also be quantized.



12.2 The allowed energy levels for a particle in a box. Note that the energy levels increase as n^2, and that their separation increases as the quantum number increases.

(c) Normalization

Before discussing the solution in more detail, we shall complete the derivation of the wavefunctions (which are real, that is, do not contain i) by finding the normalization constant (here written C). To do so, we look for the value of C that ensures that the integral of ψ^2 over all the space available to the particle (that is, from $x = 0$ to $x = L$) is equal to 1:[2]

$$\int_0^L \psi^2\,\mathrm{d}x = C^2 \int_0^L \sin^2 \frac{n\pi x}{L}\,\mathrm{d}x = C^2 \times \tfrac{1}{2}L = 1, \qquad \text{so } C = \left(\frac{2}{L}\right)^{1/2}$$

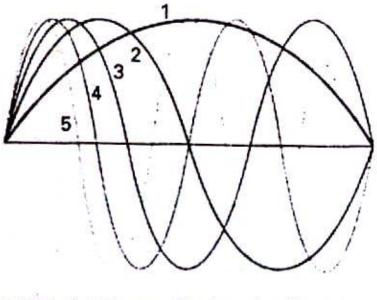
for all n. Therefore, the complete solution to the problem is

$$\begin{aligned} E_n &= \frac{n^2h^2}{8mL^2} \qquad n = 1, 2, \ldots \\ \psi_n(x) &= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad \text{for } 0 \le x \le L \end{aligned} \tag{7}$$

The energies and wavefunctions are labelled with the 'quantum number' n. A **quantum number** is an integer (in some cases, as we shall see, a half-integer) that labels the state of the system. For a particle in a box there is an infinite number of acceptable solutions, and the quantum number n specifies the one of interest (Fig. 12.2). As well as acting as a label, a quantum number can often be used to calculate the energy corresponding to the state and to write down the wavefunction explicitly (in the present example, by using the information in eqn 7).

(d) The properties of the solutions

Figure 12.3 shows some of the wavefunctions of a particle in a box: they are all sine functions with the same amplitude but different wavelengths. With these images in mind, it is easy to see the origin of the quantization: each wavefunction is a standing wave and, to fit



12.3 The first five normalized wavefunctions of a particle in a box. Each wavefunction is a standing wave, and successive functions possess one more half wave and a correspondingly shorter wavelength.

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[2] To evaluate the integral, we use the standard form

$$\int \sin^2 ax\,\mathrm{d}x = \tfrac{1}{2}x - \tfrac{1}{4a}\sin 2ax + \text{constant}$$

into the cavity, successive wavefunctions must possess one more half-wavelength. Shortening the wavelength results in a sharper average curvature of the wavefunction and therefore an increase in the kinetic energy of the particle. Note that the number of nodes (points where the wavefunction *passes through* zero) also increases as n increases, and that the wavefunction ψ_n has $n-1$ nodes. Increasing the number of nodes between walls of a given separation increases the average curvature of the wavefunction and hence the kinetic energy of the particle.

Example 12.1 Deriving the energies of a particle in a box

Derive the energy levels of a particle in a box from the de Broglie relation and the boundary conditions on the wavefunction.

Method We see from Fig. 12.3 that, to fit into the box, successive wavefunctions possess one more half-wavelength. Therefore, the first thing to do is to find an expression for the permitted wavelengths. To convert the permitted wavelengths into energies, we use the de Broglie relation to express wavelength as linear momentum and then use the expression for the kinetic energy in terms of the momentum to find the permitted energies.

Answer The permitted wavelengths satisfy

$$L = n \times \tfrac{1}{2}\lambda \qquad n = 1, 2, \ldots$$

and therefore

$$\lambda = \frac{2L}{n}, \qquad n = 1, 2, \ldots$$

According to the de Broglie relation, these wavelengths correspond to the momenta

$$p = \frac{h}{\lambda} = \frac{nh}{2L}$$

The particle has only kinetic energy inside the box (where $V = 0$), so the permitted energies are

$$E_n = \frac{p^2}{2m} = \frac{n^2h^2}{8mL^2}$$

as obtained more formally earlier.

Self-test 12.1 What is the average value of the linear momentum of a particle in a box with quantum number n?

$[\langle p \rangle = 0]$

The linear momentum of a particle in a box is not well defined because the wavefunction $\sin kx$ is a standing wave and, like the example of $\cos kx$ treated in Section 11.5d, not an eigenfunction of the linear momentum operator. However, each wavefunction is a superposition of momentum eigenfunctions:

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) = \frac{1}{2\mathrm{i}}\left(\frac{2}{L}\right)^{1/2}\left(\mathrm{e}^{\mathrm{i}kx} - \mathrm{e}^{-\mathrm{i}kx}\right) \qquad k = \frac{n\pi}{L} \tag{8}$$

It follows that measurement of the linear momentum will give the value $+k\hbar$ for half the measurements of momentum and $-k\hbar$ for the other half. This detection of opposite directions of travel with equal probability is the quantum mechanical version of the classical picture that a particle in a box rattles from wall to wall, and in any given period spends half its time travelling to the left and half travelling to the right.

Because n cannot be zero, the lowest energy that the particle may possess is not zero (as would be allowed by classical mechanics, corresponding to a stationary particle) but

$$E_1 = \frac{h^2}{8mL^2} \tag{9}$$

This lowest, irremovable energy is called the **zero-point energy**.

The physical origin of the zero-point energy can be explained in two ways. First, the uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region: the particle's location is not completely indefinite, so its momentum cannot be precisely zero. Hence it has nonzero kinetic energy. Second, if the wavefunction is to be zero at the walls, but smooth, continuous, and not zero everywhere, then it must be curved, and curvature in a wavefunction implies the possession of kinetic energy.

The separation between adjacent energy levels with quantum numbers n and $n + 1$ is

$$E_{n+1} - E_n = \frac{(n+1)^2h^2}{8mL^2} - \frac{n^2h^2}{8mL^2} = (2n+1)\frac{h^2}{8mL^2} \tag{10}$$

This separation decreases as the length of the container increases, and is very small when the container has macroscopic dimensions. The separation of adjacent levels becomes zero when the walls are infinitely far apart. Atoms and molecules free to move in normal laboratory-sized vessels may therefore be treated as though their translational energy is not quantized. The translational energy of completely free particles (those not confined by walls) is not quantized.

Illustration

For a container of length $L = 1.0$ nm, $h^2/8m_eL^2 = 6.0 \times 10^{-20}$ J. Therefore, the zero-point energy is $E_1 = 6.0 \times 10^{-20}$ J (corresponding to 0.37 eV). The minimum excitation energy is given by eqn 10 with $n = 1$, and is $3E_1$, or 1.8×10^{-19} J, which corresponds to 1.1 eV.

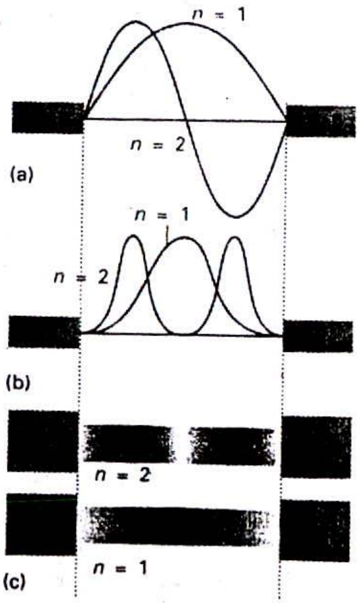
Self-test 12.2 Estimate a typical nuclear excitation energy by calculating the first excitation energy of a proton confined to a one-dimensional infinite square well with a length roughly equal to the diameter of a nucleus (1 fm).

[0.6 GeV]

The probability density for a particle in a box is

$$\psi^2(x) = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right) \tag{11}$$

This probability density varies with position within the box. The nonuniformity is pronounced when n is small (Fig. 12.4), but $\psi^2(x)$ becomes more uniform as n increases. The distribution at high quantum numbers reflects the classical result that a particle bouncing between the walls spends, on the average, equal times at all points. That the quantum result corresponds to the classical prediction at high quantum numbers is an illustration of the **correspondence principle**, which states that classical mechanics emerges from quantum mechanics as high quantum numbers are reached.



12.4 (a) The first two wavefunctions, (b) the corresponding probability distributions, and (c) a representation of the probability distribution in terms of the darkness of shading.

Example 12.2 Using the particle in a box solutions

What is the probability, P of locating the electron between $x = 0$ (the left-hand edge) and $x = 0.2$ nm in its lowest energy state in a box of length 1.0 nm?

Method The value of $\psi^2\,\mathrm{d}x$ is the probability of finding the particle in the small region $\mathrm{d}x$ located at x; therefore, the total probability of finding the electron in the specified region is the integral of $\psi^2\,\mathrm{d}x$ over that region. The wavefunction of the electron is given in eqn 7 with $n = 1$.

Answer The probability of finding the particle in a region between $x = 0$ and $x = l$ is

$$P = \frac{2}{L}\int_0^l \sin^2\left(\frac{n\pi x}{L}\right)\mathrm{d}x = \frac{l}{L} - \frac{1}{2n\pi}\sin\left(\frac{2n\pi l}{L}\right)$$

We then set $n = 1$ and $l = 0.2$ nm, which gives $P = 0.05$.

Comment The result corresponds to a chance of 1 in 20 of finding the electron in the region. As n becomes infinite, the sine term, which is multiplied by $1/n$, makes no contribution to P and the classical result, $P = l/L$, is obtained.

Self-test 12.3 Calculate the probability that a particle in the state with $n = 1$ will be found between $x = 0.25L$ and $x = 0.75L$ in a box of length L (with $x = 0$ at the left-hand wall).

[0.82]

(e) Orthogonality and the bracket notation

A property of wavefunctions first mentioned in *Justification 11.2* can now be illustrated more fully. Two wavefunctions are **orthogonal** if the integral of their product vanishes. Specifically, the functions ψ_n and $\psi_{n'}$ are orthogonal if

$$\int \psi_n^*\psi_{n'}\,\mathrm{d}\tau = 0 \qquad (12a)$$

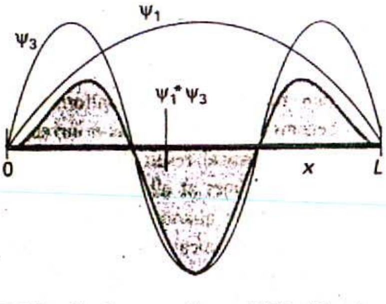
where the integration is over all space. A general feature of quantum mechanics is that wavefunctions corresponding to different energies are orthogonal; therefore, we can be confident that all the wavefunctions of a particle in a box are mutually orthogonal.

Illustration

We can verify the orthogonality of wavefunctions of a particle in a box with $n = 1$ and $n = 3$ (Fig. 12.5):

$$\int_0^L \psi_1^*\psi_3\,\mathrm{d}x = \frac{2}{L}\int_0^L \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi x}{L}\right)\mathrm{d}x = 0$$

from the general properties of integrals over trigonometric functions.



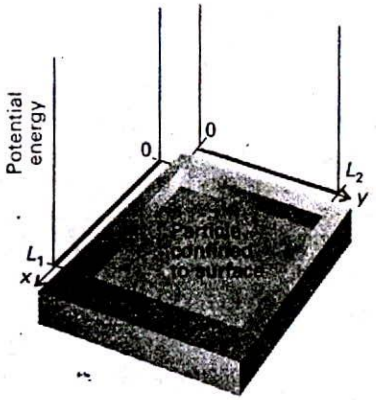
12.5 Two functions are orthogonal if the integral of their product is zero. Here the calculation of the integral is illustrated graphically for two wavefunctions of a particle in a square well. The integral is equal to the total area beneath the graph of the product, and is zero.

The integral in eqn 12*a* is often written

$$\langle n|n'\rangle = 0 \qquad (n' \neq n) \qquad (12b)$$

This Dirac bracket notation is much more succinct than writing out the integral in full. It also introduces the words 'bra' and 'ket' into the language of quantum mechanics. Thus, the **bra** $\langle n|$ corresponds to the complex conjugate of the wavefunction ψ_n and the **ket** $|n'\rangle$ corresponds to the wavefunction $\psi_{n'}$. When the bra and ket are put together as in eqn 12*b*, the integration over all space is understood. Similarly, the normalization condition in eqn 11.20 becomes simply

$$\langle n|n\rangle = 1 \qquad (13)$$



12.6 A two-dimensional square well. The particle is confined to the plane bounded by impenetrable walls. As soon as it touches the walls, its potential energy rises to infinity.

in bracket notation. These two expressions can be combined into a single expression:

$$\langle n|n'\rangle = \delta_{nn'} \tag{14}$$

where $\delta_{nn'}$, which is called the **Kronecker delta**, is 1 when $n' = n$ and 0 when $n' \neq n$. We shall see more of this notation later.

The property of orthogonality is of great importance in quantum mechanics because it enables us to eliminate a large number of integrals from calculations. Orthogonality plays a central role in the theory of chemical bonding (Chapter 14) and spectroscopy (Chapter 17).

12.2 Motion in two dimensions

Next, we consider a two-dimensional version of the particle in a box. Now the particle is confined to a rectangular surface of length L_1 in the x-direction and L_2 in the y-direction; the potential energy is zero everywhere except at the walls, where it is infinite (Fig. 12.6). The wavefunction is now a function of both x and y and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right) = E\psi \tag{15}$$

We need to see how to solve this *partial* differential equation, an equation in more than one variable.

(a) Separation of variables

Some partial differential equations can be simplified by the **separation of variables technique**, which divides the equation into two or more ordinary differential equations, one for each variable. The method works in this case, as can be seen by testing whether a solution of eqn 15 can be found by writing the wavefunction as a product of functions, one depending only on x and the other only on y:

$$\psi(x,y) = X(x)Y(y) \tag{16}$$

The notation $X(x)Y(y)$ reminds us that the two functions into which the wavefunction is factored depend only on x and only on y for X and Y, respectively. We show in the *Justification* below that with this substitution, eqn 15 separates into two ordinary differential equations, one for each coordinate:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_XX \qquad -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_YY \qquad E = E_X + E_Y \tag{17}$$

The quantity E_X is the energy associated with the motion of the particle parallel to the x-axis, and likewise for E_Y and motion parallel to the y-axis.

Justification 12.1

The first step in the justification of the separability of the wavefunction into the product of two functions X and Y is to note that, because X is independent of y and Y is independent of x, we can write

$$\frac{\partial^2\psi}{\partial x^2} = \frac{\partial^2 XY}{\partial x^2} = Y\frac{\mathrm{d}^2X}{\mathrm{d}x^2} \qquad \frac{\partial^2\psi}{\partial y^2} = \frac{\partial^2 XY}{\partial y^2} = X\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}$$

Then eqn 15 becomes

$$-\frac{\hbar^2}{2m}\left(Y\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+X\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right) = EXY$$

When both sides are divided by XY, the resulting equation can be rearranged into

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=-\frac{2mE}{\hbar^2}$$

The first term on the left is independent of y, so if y is varied only the second term can change. But the sum of these two terms is a constant given by the right-hand side of the equation; therefore, even the second term cannot change when y is changed. In other words, the second term is a constant, which we write $-2mE_Y/\hbar^2$. By a similar argument, the first term is a constant when x changes, and we write it $-2mE_X/\hbar^2$, and $E=E_X+E_Y$. Therefore, we can write

$$\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=-\frac{2mE_X}{\hbar^2}\qquad\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=-\frac{2mE_Y}{\hbar^2}$$

which rearrange into the two ordinary (that is, single variable) differential equations in eqn 17.

Each of the two ordinary differential equations in eqn 17 is the same as the one-dimensional square-well Schrödinger equation; hence we can adapt the results in eqn 7 without further calculation:

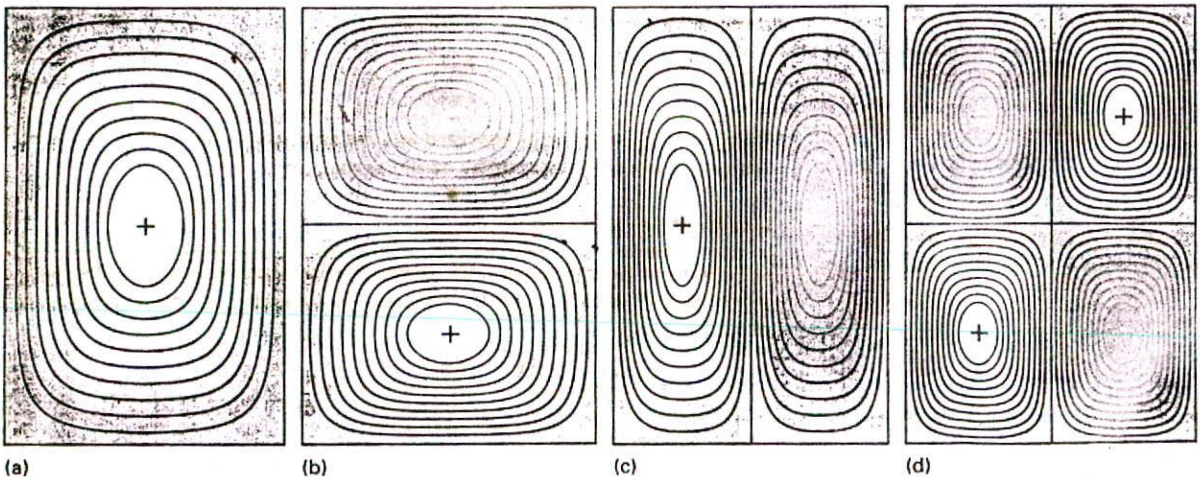
$$X_{n_1}(x)=\left(\frac{2}{L_1}\right)^{1/2}\sin\left(\frac{n_1\pi x}{L_1}\right)\qquad Y_{n_2}(y)=\left(\frac{2}{L_2}\right)^{1/2}\sin\left(\frac{n_2\pi y}{L_2}\right)$$

Then, because $\psi=XY$ and $E=E_X+E_Y$, we obtain

$$\psi_{n_1,n_2}(x,y)=\frac{2}{(L_1L_2)^{1/2}}\sin\left(\frac{n_1\pi x}{L_1}\right)\sin\left(\frac{n_2\pi y}{L_2}\right)\qquad 0\le x\le L_1, 0\le y\le L_2$$

$$E_{n_1n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m}\tag{18}$$

with the quantum numbers taking the values $n_1=1,2,\ldots$ and $n_2=1,2,\ldots$ independently. Some of these functions are plotted in Fig. 12.7. They are the two-dimensional versions of the wavefunctions shown in Fig. 12.3. Note that two quantum numbers are needed in this



12.7 The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1=1$, $n_2=1$, the state of lowest energy, (b) $n_1=1$, $n_2=2$, (c) $n_1=2$, $n_2=1$, and (d) $n_1=2$, $n_2=2$.

two-dimensional problem, and in the Dirac bracket notation we denote the states by the ket $|n_1, n_2\rangle$.

A particle in a three-dimensional box can be treated in the same way. The wavefunctions have another factor (for the z-dependence), and the energy has an additional term in n_3^2/L_3^2.

(b) Degeneracy

An interesting feature of the solutions is obtained when the plane surface is square, when $L_1 = L$ and $L_2 = L$. Then eqn 18 becomes

$$\psi_{n_1 n_2}(x, y) = \frac{2}{L}\sin\left(\frac{n_1 \pi x}{L}\right)\sin\left(\frac{n_2 \pi y}{L}\right) \qquad E_{n_1 n_2} = (n_1^2 + n_2^2)\frac{h^2}{8mL^2} \tag{19}$$

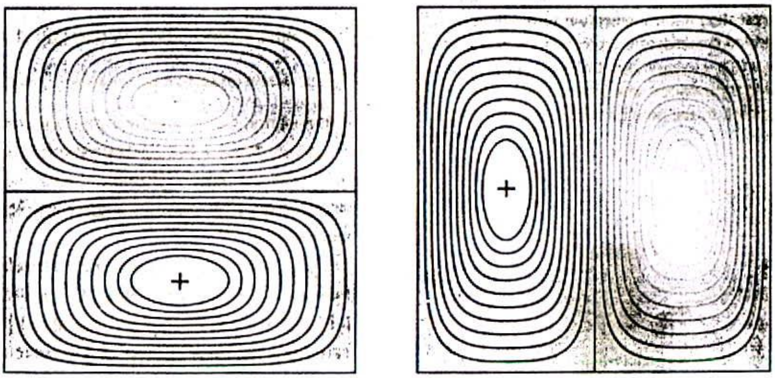
Consider the cases $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$:

$$\psi_{1,2}(x, y) = \frac{2}{L}\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi y}{L}\right) \qquad E_{1,2} = \frac{5h^2}{8mL^2}$$

$$\psi_{2,1}(x, y) = \frac{2}{L}\sin\left(\frac{2\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right) \qquad E_{2,1} = \frac{5h^2}{8mL^2}$$

We see that different wavefunctions correspond to the same energy, the condition called degeneracy. In this case, in which there are two degenerate wavefunctions, we say that the energy level $5(h^2/8mL^2)$ is 'doubly degenerate'. Alternatively, we say that the states $|1, 2\rangle$ and $|2, 1\rangle$ are degenerate.

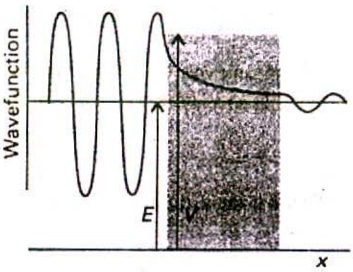
The occurrence of degeneracy is related to the symmetry of the system. Fig. 12.8 shows contour diagrams of the two degenerate functions $\psi_{1,2}$ and $\psi_{2,1}$. Because the box is square, we can convert one wavefunction into the other simply by rotating the plane by 90°. Interconversion by rotation through 90° is not possible when the plane is not square, and $\psi_{1,2}$ and $\psi_{2,1}$ are then not degenerate. We shall see many examples of degeneracy in the pages that follow (for example, in the hydrogen atom), and all of them can be traced to the symmetry properties of the system (see Section 15.4b).



12.8 The wavefunctions for a particle confined to a square surface. Note that one wavefunction can be converted into the other by a rotation of the box by 90°. The two functions correspond to the same energy. Degeneracy and symmetry are closely related.

12.3 Tunnelling

If the potential energy of a particle does not rise to infinity when it is in the walls of the container, and $E < V$, the wavefunction does not decay abruptly to zero. If the walls are thin (so that the potential energy falls to zero again after a finite distance), the wavefunction oscillates inside the box, varies smoothly inside the region representing the wall, and oscillates again on the other side of the wall outside the box (Fig. 12.9). Hence the particle might be found on the outside of a container even though according to classical mechanics



12.9 A particle incident on a barrier from the left has an oscillating wavefunction, but inside the barrier there are no oscillations (for $E<V$). If the barrier is not too thick, the wavefunction is nonzero at its opposite face, and so oscillations begin again there. (Only the real component of the wavefunction is shown.)

it has insufficient energy to escape. Such leakage by penetration through classically forbidden zones is called **tunnelling**.

The Schrödinger equation can be used to calculate the probability of tunnelling of a particle of mass m incident on a finite barrier from the left. On the left of the barrier (for $x<0$) the wavefunctions are those of a particle with $V=0$, so from eqn 2 we can write

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad k\hbar = (2mE)^{1/2} \tag{20}$$

The Schrödinger equation for the region representing the barrier (for $0 \le x \le L$), where the potential energy is the constant V, is

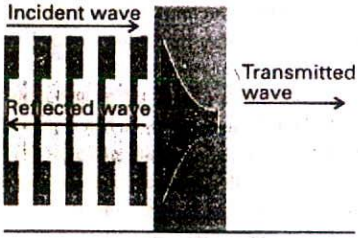
$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi \tag{21}$$

We shall consider particles that have $E<V$, so $V-E$ is positive. The general solutions of this equation are then

$$\psi = Ce^{\kappa x} + De^{-\kappa x} \qquad \kappa\hbar = \{2m(V-E)\}^{1/2} \tag{22}$$

as can readily be verified by differentiating ψ twice with respect to x. The important feature to note is that the two exponentials are now *real* functions (as distinct from the complex, oscillating functions for the region where $V=0$).[3] To the right of the barrier ($x>L$), where $V=0$ again, the wavefunctions are

$$\psi = A'e^{ikx} + B'e^{-ikx} \qquad k\hbar = (2mE)^{1/2} \tag{23}$$



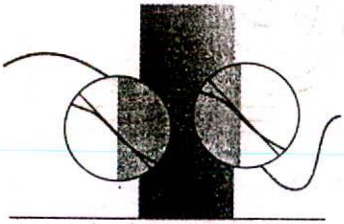
12.10 When a particle is incident on a barrier from the left, the wavefunction consists of a wave representing linear momentum to the right, a reflected component representing momentum to the left, a varying but not oscillating component inside the barrier, and a (weak) wave representing motion to the right on the far side of the barrier.

The complete wavefunction for a particle incident from the left consists of an incident wave, a wave reflected from the barrier, the exponentially changing amplitudes inside the barrier, and an oscillating wave representing the propagation of the particle to the right after tunnelling through the barrier successfully (Fig. 12.10). The *acceptable* wavefunctions have to obey the conditions set out in Section 11.4b. In particular, they must be continuous at the edges of the barrier (at $x=0$ and $x=L$, remembering that $e^0=1$):

$$A+B = C+D \qquad Ce^{\kappa L} + De^{-\kappa L} = A'e^{ikL} + B'e^{-ikL} \tag{24}$$

Their slopes (their first derivatives) must also be continuous there (Fig. 12.11):

$$ikA - ikB = \kappa C - \kappa D \qquad \kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA'e^{ikL} - ikB'e^{-ikL} \tag{25}$$



12.11 The wavefunction and its slope must be continuous at the edges of the barrier. The conditions for continuity enable us to connect the wavefunctions in the three zones and hence to obtain relations between the coefficients that appear in the solutions of the Schrödinger equation.

At this stage, we have four equations for the six unknown coefficients. If the particles are shot towards the barrier from the left, there can be no particles travelling to the left on the *right* of the barrier. Therefore, we can set $B'=0$, which removes one more unknown. We cannot set $B=0$ because some particles may be reflected back from the barrier toward negative x.

The probability that a particle is travelling towards positive x (to the right) on the left of the barrier is proportional to $|A|^2$, and the probability that it is travelling to the right on the right of the barrier is proportional to $|A'|^2$. The ratio of these two probabilities is called the **transmission probability**, T. After some algebra we find

$$T = \left\{1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1} \tag{26}$$

where $\varepsilon = E/V$. This function is plotted in Fig. 12.12; the transmission coefficient for $E>V$ is shown there too. For high, wide barriers (in the sense that $\kappa L \gg 1$), eqn 26 simplifies to

$$T \approx 16\varepsilon(1-\varepsilon)e^{-2\kappa L} \tag{27}$$

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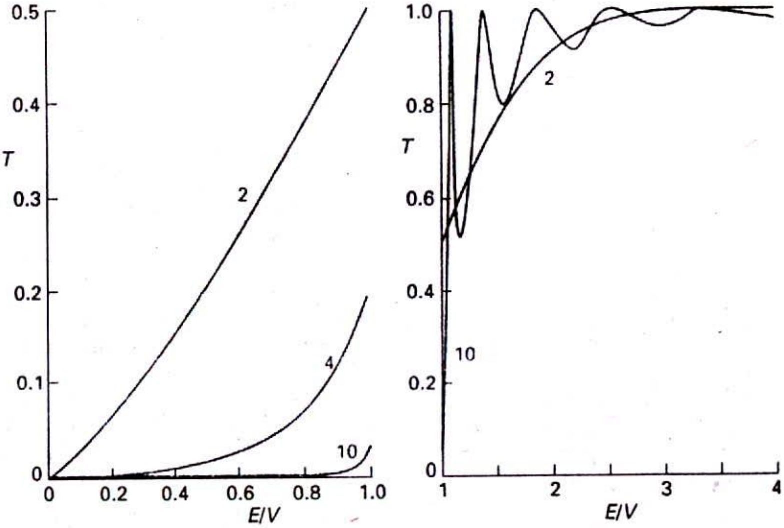
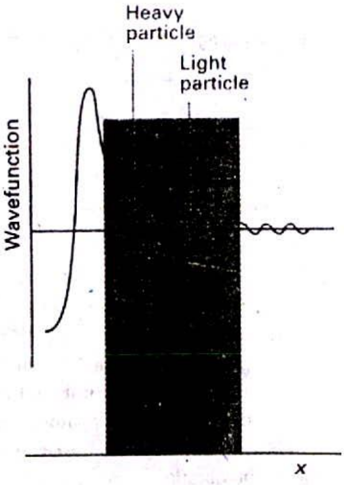
[3] Oscillating functions would be obtained if $E>V$.



12.12 The transition probabilities for passage through a barrier. The horizontal axis is the energy of the incident particle expressed as a multiple of the barrier height. The curves are labelled with the value of $L(2mV)^{1/2}/\hbar$. The graph on the left is for $E<V$ and that on the right for $E>V$. Note that $T>0$ for $E<V$, whereas classically T would be zero. However, $T<1$ for $E>V$, whereas classically T would be 1.

The transmission probability decreases exponentially with the thickness of the barrier and with $m^{1/2}$. It follows that particles of low mass are more able to tunnel through barriers than heavy ones (Fig. 12.13). Tunnelling is very important for electrons and muons, and moderately important for protons; for heavier particles it is less important. A number of effects in chemistry (for example, the isotope-dependence of some reaction rates) depend on the ability of the proton to tunnel more readily than the deuteron. The very rapid equilibration of proton transfer reactions (which were discussed in Chapter 9) is also a manifestation of the ability of protons to tunnel through barriers and transfer quickly from an acid to a base. The important technique of 'scanning tunnelling microscopy' (STM), which is described in more detail in Section 28.2f, relies on the exponential dependence of electron tunnelling on the thickness of the region between a point and a surface.



12.13 The wavefunction of a heavy particle decays more rapidly inside a barrier than that of a light particle. Consequently, a light particle has a greater probability of tunnelling through the barrier.

Illustration

To estimate the relative probabilities that a proton and a deuteron can tunnel through the same barrier of height 1.00 eV (1.60×10^{-19} J) and length 100 pm when their energy is 0.9 eV, so $E-V=0.10$ eV, we first evaluate

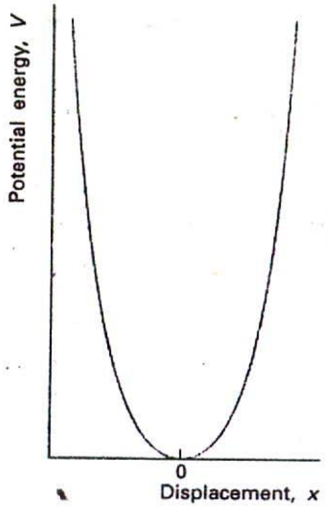
$$\kappa=\left\{\frac{2(m/\mathrm{u})\times(1.67\times10^{-27}\ \mathrm{kg})\times(1.6\times10^{-20}\ \mathrm{J})}{(1.055\times10^{-34}\ \mathrm{J\,s})^2}\right\}^{1/2}$$

$$=\frac{(m/\mathrm{u})^{1/2}}{14\ \mathrm{pm}}$$

The values of κ for a proton ($m=1.0$ u) and a deuteron ($m=2.0$ u) are $1/(14\ \mathrm{pm})$ and $1/(9.9\ \mathrm{pm})$, respectively, so $\kappa L\gg1$ and eqn 27 can be used. The ratio of transmission probabilities is then

$$\frac{T_{\mathrm{H}}}{T_{\mathrm{D}}}=\mathrm{e}^{-2(\kappa_{\mathrm{H}}-\kappa_{\mathrm{D}})L}=3.7\times10^2$$

(The ratio is very sensitive to rounding errors.) The result shows that the tunnelling probability of a proton (in the system specified) is about 370 times greater than that of a deuteron.



12.14 The parabolic potential energy $V = \frac{1}{2}kx^2$ of a harmonic oscillator, where x is the displacement from equilibrium. The narrowness of the curve depends on the force constant k: the larger the value of k, the narrower the well.

Self-test 12.4 Calculate the relative tunnelling probabilities when the barrier is twice as long, the other conditions being unchanged.

$[1.4 \times 10^5]$

Vibrational motion

A particle undergoes **harmonic motion** if it experiences a restoring force proportional to its displacement:

$$F = -kx \tag{28}$$

where k is the **force constant**: the stiffer the 'spring', the greater the value of k. Because force is related to potential energy by $F = -\mathrm{d}V/\mathrm{d}x$ (see *Further information* 4), the force in eqn 28 corresponds to a potential energy

$$V = \tfrac{1}{2}kx^2 \tag{29}$$

This expression, which is the equation of a parabola (Fig. 12.14), is the origin of the term 'parabolic potential energy' for the potential energy characteristic of a harmonic oscillator. The Schrödinger equation for the particle is therefore

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \tfrac{1}{2}kx^2\psi = E\psi \tag{30}$$

12.4 The energy levels

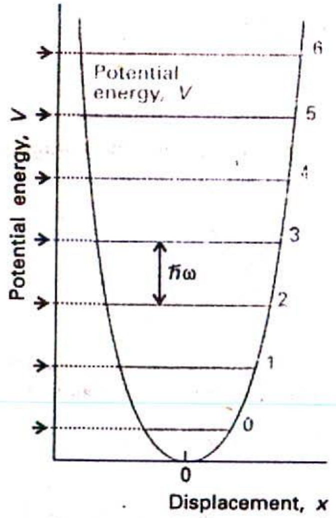
Equation 30 is a standard equation in the theory of differential equations and its solutions are well known to mathematicians (see below).[4] When the boundary conditions, that the oscillator will not be found with infinitely large compressions or extensions, are applied, it is found that the permitted energy levels are

$$E_v = (v + \tfrac{1}{2})\hbar\omega \qquad \omega = \left(\frac{k}{m}\right)^{1/2} \qquad v = 0, 1, 2, \ldots \tag{31}$$

Note that ω increases with increasing force constant and decreasing mass. It follows that the separation between adjacent levels is

$$E_{v+1} - E_v = \hbar\omega \tag{32}$$

which is the same for all v. Therefore, the energy levels form a **uniform ladder** of spacing $\hbar\omega$ (Fig. 12.15). The energy separation $\hbar\omega$ is negligibly small for macroscopic objects (with large mass), but is of great importance for objects with mass similar to that of atoms.



12.15 The energy levels of a harmonic oscillator are evenly spaced with separation $\hbar\omega$, with $\omega = (k/m)^{1/2}$. Even in its lowest state, an oscillator has an energy greater than zero.

Illustration

The force constant of a typical X–H chemical bond is around 500 $\mathrm{N\,m^{-1}}$. Because the mass of a proton is about 1.7×10^{-27} kg, $\omega \approx 5 \times 10^{14}\ \mathrm{s^{-1}}$ and the separation of adjacent levels is $\hbar\omega \approx 6 \times 10^{-20}$ J (about 0.4 eV). This energy separation corresponds to 30 $\mathrm{kJ\,mol^{-1}}$, which is chemically significant. The excitation of the vibration of the bond from one level to the level immediately above requires 6×10^{-20} J. Therefore, if it is caused by a photon, the excitation requires radiation of frequency $\nu = \Delta E/h = 9 \times 10^{13}$ Hz and wavelength $\lambda = c/\nu = 3\ \mu\mathrm{m}$. It follows that transitions between adjacent vibrational energy levels of molecules are stimulated by or emit infrared radiation (Chapter 16).

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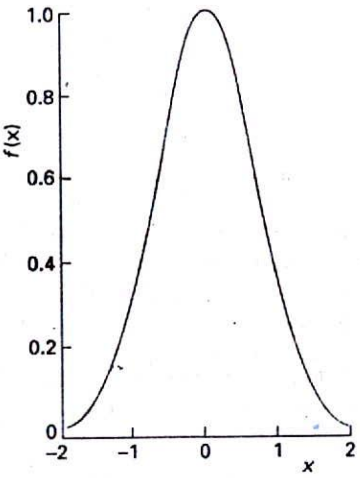
[4] For the details of the solution, see *Further reading*.



12.16 The graph of the Gaussian function, $f(x) = e^{-x^2}$.

Because the smallest permitted value of v is 0, it follows from eqn 31 that a harmonic oscillator has a zero-point energy

$$E_0 = \tfrac{1}{2}\hbar\omega \tag{33}$$

For the typical molecular oscillator specified in the *Illustration*, the zero-point energy is about 3×10^{-20} J, which corresponds to 0.2 eV, or 15 kJ mol^{-1}. The mathematical reason for the zero-point energy is that v cannot take negative values, for if it did the wavefunction would be ill-behaved. The physical reason is the same as for the particle in a square well: the particle is confined, its position is not completely uncertain, and therefore its momentum, and hence its kinetic energy, cannot be exactly zero. We can picture this zero-point state as one in which the particle fluctuates incessantly around its equilibrium position; classical mechanics would allow the particle to be perfectly still.

12.5 The wavefunctions

It is helpful at the outset to identify the similarities between the harmonic oscillator and the particle in a box, for then we shall be able to anticipate the form of the oscillator wavefunctions without detailed calculation. Like the particle in a box, a particle undergoing harmonic motion is trapped in a symmetrical well in which the potential energy rises to large values (and ultimately to infinity) for sufficiently large displacements (compare Figs 12.1 and 12.14). However, there are two important differences. First, because the potential energy climbs towards infinity only as x^2 and not abruptly, the wavefunction approaches zero more slowly at large displacements than for the particle in a box. Second, as the kinetic energy of the oscillator depends on the displacement in a more complex way (on account of the variation of the potential energy), the curvature of the wavefunction also varies in a more complex way.

(a) The form of the wavefunctions

The detailed solution of eqn 30 shows that the wavefunction for a harmonic oscillator has the form

$$\psi(x) = N \times (\text{polynomial in } x) \times (\text{bell-shaped Gaussian function})$$

where N is a normalization constant. A Gaussian function is a function of the form e^{-x^2} (Fig. 12.16). The precise form of the wavefunctions is

$$\psi_v(x) = N_v H_v(y) e^{-y^2/2} \qquad y = \frac{x}{\alpha} \qquad \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4} \tag{34}$$

The factor $H_v(y)$ is a Hermite polynomial (Table 12.1). For instance, because $H_0(y) = 1$, the wavefunction for the ground state (the lowest energy state, with $v = 0$) of the harmonic oscillator is

$$\psi_0(x) = N_0 e^{-y^2/2} = N_0 e^{-x^2/2\alpha^2} \tag{35}$$

It follows that the probability density is the bell-shaped Gaussian function

$$\psi_0^2(x) = N_0^2 e^{-x^2/\alpha^2} \tag{36}$$

The wavefunction and the probability distribution are shown in Fig. 12.17. Both curves have their largest values at zero displacement (at $x = 0$), so they capture the classical picture of the zero-point energy as arising from the ceaseless fluctuation of the particle about its equilibrium position.

Table 12.1 The Hermite polynomials $H_v(y)$

v	H_v
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$
6	$64y^6 - 480y^4 + 720y^2 - 120$

The Hermite polynomials (which continue up to infinite v) satisfy the equation

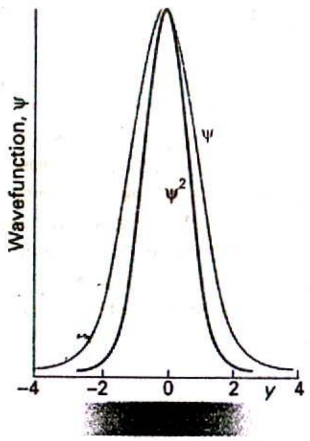
$$H_v'' - 2yH_v' + 2vH_v = 0$$

and the recursion relation

$$H_{v+1} = 2yH_v - 2vH_{v-1}$$

An important integral is

$$\int_{-\infty}^{\infty} H_{v'} H_v e^{-y^2}\, dy = \begin{cases} 0 & \text{if } v' \neq v \\ \pi^{1/2} 2^v v! & \text{if } v' = v \end{cases}$$



12.17 The normalized wavefunction and probability distribution (shown also by shading) for the lowest energy state of a harmonic oscillator.

The wavefunction for the first excited state of the oscillator, the state with $v = 1$, is obtained by noting that $H_1(y) = 2y$ (note that some of the Hermite polynomials are very simple functions!):

$$\psi_1(x) = N_1 \times 2y\mathrm{e}^{-y^2/2} = \frac{2N_1}{\alpha} x\mathrm{e}^{-x^2/2\alpha^2} \tag{37}$$

This function has a node at zero displacement ($x = 0$), and the probability density has maxima at $x = \pm\alpha$, corresponding to $y = \pm 1$ (Fig. 12.18).

The shapes of several wavefunctions are shown in Fig. 12.19. The shading in Fig. 12.20 that represents the probability density is based on the squares of these functions. At high quantum numbers, harmonic oscillator wavefunctions have their largest amplitudes near the turning points of the classical motion (the locations at which $V = E$, so the kinetic energy is zero). We see classical properties emerging in the correspondence limit of high quantum numbers, for a classical particle is most likely to be found at the turning points (where it travels most slowly) and is least likely to be found at zero displacement (where it travels most rapidly).

Example 12.3 Normalizing a harmonic oscillator wavefunction

Find the normalization constant for the harmonic oscillator wavefunctions.

Method Normalization is always carried out by evaluating the integral of $|\psi|^2$ over all space and then finding the normalization factor from eqn 11.17. The normalized wavefunction is then equal to $N\psi$. In this one-dimensional problem, the volume element is $\mathrm{d}x$ and the integration is from $-\infty$ to $+\infty$. The wavefunctions are expressed in terms of the dimensionless variable $y = x/\alpha$, so begin by expressing the integral in terms of y by using $\mathrm{d}x = \alpha\,\mathrm{d}y$. The integrals required are given in Table 12.1.

Answer The unnormalized wavefunction is

$$\psi_v(x) = H_v(y)\mathrm{e}^{-y^2/2}$$

It follows from the integrals given in Table 12.1 that

$$\int_{-\infty}^{\infty} \psi_v^*\psi_v\,\mathrm{d}x = \alpha\int_{-\infty}^{\infty} \psi_v^*\psi_v\,\mathrm{d}y = \alpha\int_{-\infty}^{\infty} H_v^2(y)\mathrm{e}^{-y^2}\,\mathrm{d}y$$
$$= \alpha\pi^{1/2}2^v v!$$

where $v! = v(v-1)(v-2)\cdots 1$. Therefore,

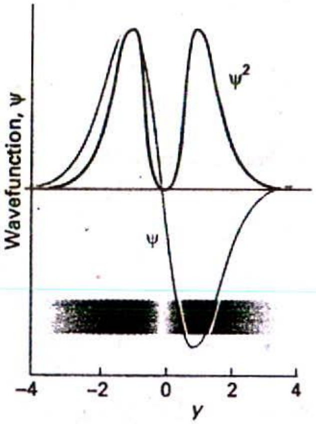
$$N_v = \frac{1}{(\alpha\pi^{1/2}2^v v!)^{1/2}}$$

Note that for a harmonic oscillator N_v is different for each value of v.

Comment The Hermite polynomials are members of a class of functions called *orthogonal polynomials*. These polynomials have a wide range of important properties which allow a number of quantum mechanical calculations to be done with relative ease. See *Further reading* for a reference to their properties.

Self-test 12.5 Confirm, by explicit evaluation of the integral, that ψ_0 and ψ_1 are orthogonal.

[Evaluate the integral $\int_{-\infty}^{\infty} \psi_0^*\psi_1\,\mathrm{d}x$ by using the information in Table 12.1.]



12.18 The normalized wavefunction and probability distribution (shown also by shading) for the first excited state of a harmonic oscillator.

(b) The properties of oscillators

With the wavefunctions that are available, we can start calculating the properties of a harmonic oscillator. For instance, we can calculate the expectation values of an observable Ω by evaluating integrals of the type

$$\langle\Omega\rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, \mathrm{d}x \tag{38}$$

(Here and henceforth, the wavefunctions are all taken to be normalized.) A tidier expression is obtained by using Dirac bracket notation, in which an integral is replaced by a bracket labelled with the quantum numbers of the states:

$$\langle v'|\hat{\Omega}|v\rangle = \int_{-\infty}^{\infty} \psi_{v'}^* \hat{\Omega} \psi_v \, \mathrm{d}x \qquad [39]$$

This bracket is also called a **matrix element** of the operator $\hat{\Omega}$. Note how the operator stands between the bra and the ket (which may denote different states), in the place of the c in ⟨bra|c|ket⟩. An integration is implied whenever a complete bracket is written. In this notation, the expectation value is

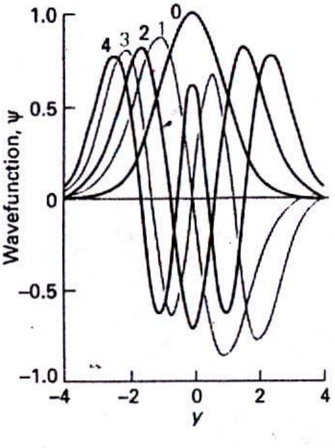
$$\langle\Omega\rangle = \langle v|\hat{\Omega}|v\rangle \tag{40}$$

with the bra and the ket corresponding to the same state (with quantum number v and wavefunction ψ_v).

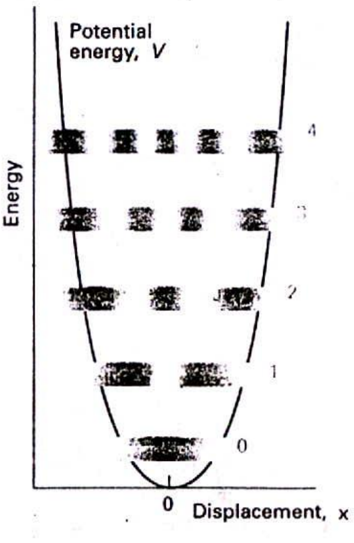
When the explicit wavefunctions are substituted, the integrals look fearsome, but the Hermite polynomials have many simplifying features. For instance, we show in the following example that the mean displacement, $\langle x\rangle$, and the mean square displacement, $\langle x^2\rangle$, of the oscillator when it is in the state with quantum number v are

$$\langle x\rangle = 0 \qquad \langle x^2\rangle = (v+\tfrac{1}{2})\frac{\hbar}{(mk)^{1/2}} \tag{41}$$

The result for $\langle x\rangle$ shows that the oscillator is equally likely to be found on either side of $x = 0$ (like a classical oscillator). The result for $\langle x^2\rangle$ shows that the mean square displacement increases with v. This increase is apparent from the probability densities in Fig. 12.20, and corresponds to the classical amplitude of swing increasing as the oscillator becomes more highly excited.



12.19 The normalized wavefunctions for the first five states of a harmonic oscillator. Even values of v are black; odd values are green. Note that the number of nodes is equal to v and that alternate wavefunctions are symmetrical or antisymmetrical about $y = 0$ (zero displacement).



12.20 The probability distributions for the first five states of a harmonic oscillator represented by the density of shading. Note how the regions of highest probability (the regions of densest shading) move towards the turning points of the classical motion as v increases.

Example 12.4 Calculating properties of a harmonic oscillator

Calculate the mean displacement of the oscillator when it is in a quantum state v.

Method Normalized wavefunctions must be used to calculate the expectation value. The operator for position along x is multiplication by the value of x (Section 11.5c). The resulting integral can be evaluated either by inspection (the integrand is the product of an odd and an even function), or by explicit evaluation using the formulas in Table 12.1. To give practice in this type of calculation, we illustrate the latter procedure. We shall need the relation $x = \alpha y$, which implies that $\mathrm{d}x = \alpha\,\mathrm{d}y$.

Answer The integral we require is

$$\begin{aligned}\langle x\rangle &= \int_{-\infty}^{\infty} \psi_v^* x \psi_v \, \mathrm{d}x = N_v^2 \int_{-\infty}^{\infty} (H_v \mathrm{e}^{-y^2/2}) x (H_v \mathrm{e}^{-y^2/2}) \, \mathrm{d}x \\ &= \alpha^2 N_v^2 \int_{-\infty}^{\infty} (H_v \mathrm{e}^{-y^2/2}) y (H_v \mathrm{e}^{-y^2/2}) \, \mathrm{d}y \\ &= \alpha^2 N_v^2 \int_{-\infty}^{\infty} H_v y H_v \mathrm{e}^{-y^2} \, \mathrm{d}y\end{aligned}$$

Now use the recursion relation in Table 12.1 to form

$$yH_v = vH_{v-1} + \tfrac{1}{2}H_{v+1}$$

which turns the integral into

$$\int_{-\infty}^{\infty} H_v y H_v \mathrm{e}^{-y^2}\,\mathrm{d}y = v\int_{-\infty}^{\infty} H_{v-1}H_v \mathrm{e}^{-y^2}\,\mathrm{d}y + \tfrac{1}{2}\int_{-\infty}^{\infty} H_{v+1}H_v \mathrm{e}^{-y^2}\,\mathrm{d}y$$

Both integrals are zero (Table 12.1), so $\langle x\rangle = 0$.

Self-test 12.6 Calculate the mean square displacement $\langle x^2\rangle$ of the particle from its equilibrium position. (Use the recursion relation twice.)

[eqn 41]

The mean potential energy of an oscillator, the expectation value of $V = \tfrac{1}{2}kx^2$, can now be calculated very easily:

$$\langle V\rangle = \langle \tfrac{1}{2}kx^2\rangle = \tfrac{1}{2}(v+\tfrac{1}{2})\hbar\left(\frac{k}{m}\right)^{1/2} = \tfrac{1}{2}(v+\tfrac{1}{2})\hbar\omega \qquad (42)$$

Because the total energy in the state with quantum number v is $(v+\tfrac{1}{2})\hbar\omega$, it follows that

$$\langle V\rangle = \tfrac{1}{2}E_v \qquad (43)$$

The total energy is the sum of the potential and kinetic energies, so it follows at once that the mean kinetic energy of the oscillator is

$$\langle E_{\mathrm{K}}\rangle = \tfrac{1}{2}E_v \qquad (44)$$

The result that the mean potential and kinetic energies of a harmonic oscillator are equal (and therefore that both are equal to half the total energy) is a special case of the **virial theorem**:

> **If the potential energy of a particle has the form $V=ax^b$ then its mean potential and kinetic energies are related by**

$$2\langle E_{\mathrm{K}}\rangle = b\langle V\rangle \qquad (45)$$

For a harmonic oscillator $b = 2$, so $\langle E_{\mathrm{K}}\rangle = \langle V\rangle$, as we have found. The virial theorem is a short cut to the establishment of a number of useful results, and we shall use it again.

An oscillator may be found at extensions with $V>E$ that are forbidden by classical physics, for they correspond to negative kinetic energy. For example, it follows from the shape of the wavefunction (see the *Justification* below) that in its lowest energy state there is about an 8 per cent chance of finding an oscillator stretched beyond its classical limit and an 8 per cent chance of finding it with a classically forbidden compression. These tunnelling probabilities are independent of the force constant and mass of the oscillator. The probability of being found in classically forbidden regions decreases quickly with increasing v, and vanishes entirely as v approaches infinity, as we would expect from the correspondence principle. Macroscopic oscillators (such as pendulums) are in states with very high quantum numbers, so the probability that they will be found in a classically forbidden region is wholly negligible. Molecules, however, are normally in their vibrational ground states, and for them the probability is very significant.

Table 12.2* The error function

z	erf z
0	0
0.01	0.0113
0.05	0.0564
0.10	0.1125
0.50	0.5205
1.00	0.8427
1.50	0.9661
2.0	0.9953

*More values are given in the *Data section* at the end of this volume.

Justification 12.2

According to classical mechanics, the turning point, x_{tp}, of an oscillator occurs when its kinetic energy is zero, which is when its potential energy $\frac{1}{2}kx^2$ is equal to its total energy E. This equality occurs when

$$x_{tp}^2 = \frac{2E}{k} \qquad \text{or } x_{tp} = \pm\left(\frac{2E}{k}\right)^{1/2}$$

with E given by eqn 31. The probability of finding the oscillator stretched beyond a displacement x_{tp} is the sum of the probabilities $\psi^2\,dx$ of finding it in any of the intervals dx lying between x_{tp} and infinity:

$$P = \int_{x_{tp}}^{\infty} \psi_v^2\,dx$$

The variable of integration is best expressed in terms of $y = x/\alpha$ with α specified in eqn 34, and then the turning point on the right lies at

$$y_{tp} = x_{tp}/\alpha = \left(\frac{2(v+\frac{1}{2})\hbar\omega}{\alpha^2 k}\right)^{1/2} = (2v+1)^{1/2}$$

For the state of lowest energy ($v = 0$), $y_{tp} = 1$ and the probability is

$$P = \int_{x_{tp}}^{\infty} \psi_0^2\,dx = \alpha N_0^2 \int_1^{\infty} e^{-y^2}\,dy$$

The integral is a special case of the **error function**, erf z, which is defined as follows:

$$\text{erf } z = 1 - \frac{2}{\pi^{1/2}}\int_z^{\infty} e^{-y^2}\,dy \qquad [46]$$

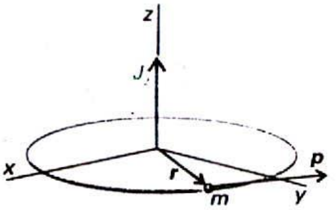
The values of this function are tabulated (just like sine and cosine functions), and a small selection of values is given in Table 12.2. In the present case

$$P = \tfrac{1}{2}(1 - \text{erf } 1) = \tfrac{1}{2}(1 - 0.843) = 0.079$$

It follows that in 7.9 per cent of a large number of observations, any oscillator in the state $v = 0$ will be found stretched to a classically forbidden extent. There is the same probability of finding the oscillator with a classically forbidden compression. The total probability of finding the oscillator tunnelled into a classically forbidden region (stretched or compressed) is about 16 per cent.

Rotational motion

The treatment of rotational motion can be broken down into two parts. The first deals with motion in two dimensions and the second with rotation in three dimensions. It may be helpful to review the classical description of rotational motion given in *Further information 4*, particularly the concepts of moment of inertia and angular momentum.



12.21 The angular momentum of a particle of mass m on a circular path of radius r in the xy-plane is represented by a vector of magnitude pr perpendicular to the plane.

12.6 Rotation in two dimensions

We consider a particle of mass m constrained to move in a circular path of radius r in the xy-plane (Fig. 12.21). The total energy is equal to the kinetic energy, because $V = 0$ everywhere. We can therefore write $E = p^2/2m$. According to classical mechanics, the angular momentum, J_z, around the z-axis (which lies perpendicular to the xy-plane) is $J_z = \pm pr$, so the energy can be expressed as $J_z^2/2mr^2$. Because mr^2 is the moment of inertia, I, of the mass on its path, it follows that

$$E = \frac{J_z^2}{2I} \tag{47}$$

We shall now see that not all the values of the angular momentum are permitted in quantum mechanics, and therefore that both angular momentum and rotational energy are quantized.

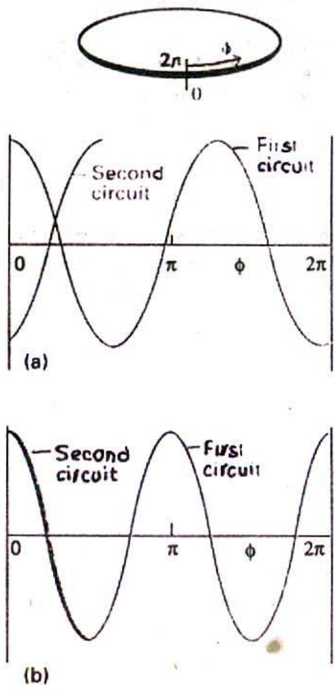
(a) The qualitative origin of quantized rotation

Because $J_z = \pm pr$ and, from the de Broglie relation, $p = h/\lambda$, the angular momentum about the z-axis is

$$J_z = \pm \frac{hr}{\lambda}$$

Opposite signs correspond to opposite directions of travel. This equation shows that, the shorter the wavelength of the particle on a circular path of given radius, the greater the angular momentum of the particle. It follows that, if we can see why the wavelength is restricted to discrete values, then we shall understand why the angular momentum is quantized.

Suppose for the moment that λ can take an arbitrary value. In that case, the wavefunction depends on the azimuthal angle ϕ as shown in Fig. 12.22a. When ϕ increases beyond 2π, the wavefunction continues to change, but for an arbitrary wavelength it gives rise to a different value at each point, which is unacceptable (Section 11.4b). An acceptable solution is obtained only if the wavefunction reproduces itself on successive circuits, as in Fig. 12.22b. Because only some wavefunctions have this property, it follows that only some angular momenta are acceptable, and therefore that only certain rotational energies exist. Hence, the energy of the particle is quantized. Specifically, the only allowed wavelengths are



12.22 Two solutions of the Schrödinger equation for a particle on a ring. The circumference has been opened out into a straight line; the points at $\phi = 0$ and 2π are identical. The solution in (a) is unacceptable because it is not single-valued. Moreover, on successive circuits it interferes destructively with itself, and does not survive. The solution in (b) is acceptable: it is single-valued, and on successive circuits it reproduces itself.

$$\lambda = \frac{2\pi r}{m_l}$$

with m_l, the conventional notation for this quantum number, taking integral values including 0.[5] The angular momentum is therefore limited to the values

$$J_z = \pm \frac{hr}{\lambda} = \frac{m_l hr}{2\pi r} = \frac{m_l h}{2\pi}$$

where we have allowed m_l to have positive or negative values. That is,

$$J_z = m_l \hbar \qquad m_l = 0, \pm 1, \pm 2, \ldots \tag{48}$$

Positive values of m_l correspond to rotation in a clockwise sense around the z-axis (as viewed in the direction of z, Fig. 12.23) and negative values of m_l correspond to counter-clockwise rotation around z. It then follows from eqn 47 that the energy is limited to the values

$$E = \frac{J_z^2}{2I} = \frac{m_l^2 \hbar^2}{2I} \tag{49}$$

We shall see shortly that the corresponding normalized wavefunctions are

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}} \tag{50}$$

The wavefunction with $m_l = 0$ is $\psi_0(\phi) = 1/(2\pi)^{1/2}$, and has the same value at all points on the circle.

We have arrived at a number of conclusions about rotational motion by cobbling together some classical notions and the de Broglie relation. Such a procedure can be very

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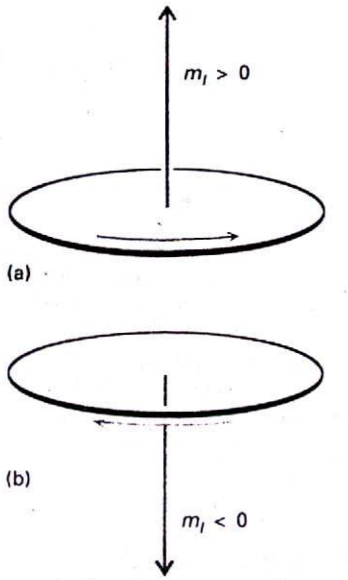
[5] The value $m_l = 0$ corresponds to $\lambda = \infty$; a 'wave' of infinite wavelength has a constant height at all values of ϕ.



12.23 The angular momentum of a particle confined to a plane can be represented by a vector of length $|m_l|$ units along the z-axis and with an orientation that indicates the direction of motion of the particle. The direction is given by the right-hand screw rule.

useful for establishing the general form (and, as in this case, the exact energies) for a quantum mechanical system. However, to be sure that the correct solutions have been obtained, and to obtain practice for more complex problems where this less formal approach is inadequate, we need to solve the Schrödinger equation explicitly. The formal solution is described in the *Justification* that follows.

Justification 12.3

The hamiltonian for a particle of mass m in a plane (with $V = 0$) is the same as that given in eqn 15:

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

and the Schrödinger equation is $H\psi = E\psi$, with the wavefunction a function of the angle ϕ. It is always a good idea to use coordinates that reflect the full symmetry of the system, so we introduce the coordinates r and ϕ (Fig. 12.24), where $x = r\cos\phi$ and $y = r\sin\phi$. By standard manipulations we can write

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} \tag{51}$$

However, because the radius of the path is fixed, the derivative with respect to r can be discarded; the hamiltonian then becomes

$$H = -\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$$

The moment of inertia $I = mr^2$ has appeared automatically, so H may be written

$$H = -\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2} \tag{52}$$

and the Schrödinger equation is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\phi^2} = -\frac{2IE}{\hbar^2}\psi \tag{53}$$

The normalized general solutions of the equation are

$$\psi_{m_l}(\phi) = \frac{\mathrm{e}^{\mathrm{i}m_l\phi}}{(2\pi)^{1/2}} \qquad m_l = \pm\frac{(2IE)^{1/2}}{\hbar}$$

The quantity m_l is just a dimensionless number at this stage.

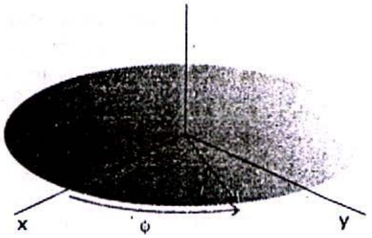
We now select the acceptable solutions from among these general solutions by imposing the condition that the wavefunction should be single-valued. That is, the wavefunction ψ must satisfy a cyclic boundary condition, and match at points separated by a complete revolution: $\psi(\phi + 2\pi) = \psi(\phi)$. On substituting the general wavefunction into this condition, we find

$$\psi_{m_l}(\phi + 2\pi) = \frac{\mathrm{e}^{\mathrm{i}m_l(\phi+2\pi)}}{(2\pi)^{1/2}} = \frac{\mathrm{e}^{\mathrm{i}m_l\phi}\mathrm{e}^{2\mathrm{i}m_l\pi}}{(2\pi)^{1/2}} = \psi(\phi)\mathrm{e}^{2\mathrm{i}m_l\pi}$$

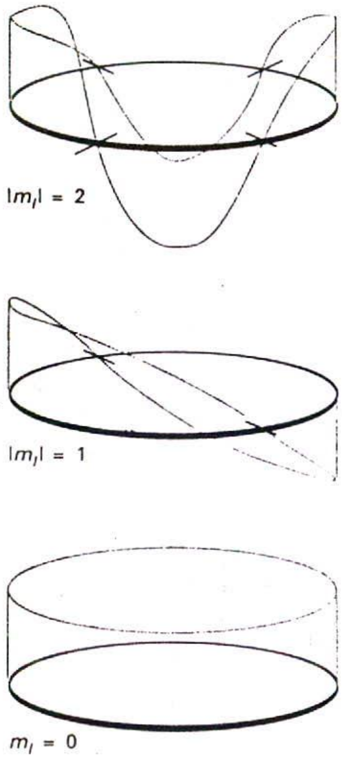
As $\mathrm{e}^{\mathrm{i}\pi} = -1$, this relation is equivalent to

$$\psi_{m_l}(\phi + 2\pi) = (-1)^{2m_l}\psi(\phi) \tag{54}$$

Because we require $(-1)^{2m_l} = 1$, $2m_l$ must be a positive or negative even integer (including 0), and therefore m_l must be an integer: $m_l = 0, \pm 1, \pm 2, \ldots$.



12.24 The cylindrical coordinates r and ϕ for discussing systems with axial (cylindrical) symmetry.



12.25 The real parts of the wavefunctions of a particle on a ring. As shorter wavelengths are achieved, the magnitude of the angular momentum around the z-axis grows in steps of $\hbar$

(b) Quantization of rotation

We can summarize the conclusions so far as follows. The energy is quantized and restricted to the values given in eqn 49 ($E = m_l^2\hbar^2/2I$). The occurrence of m_l as its square means that the energy of rotation is independent of the sense of rotation (the sign of m_l), as we expect physically. In other words, states with a given value of $|m_l|$ are doubly degenerate, except for $m_l = 0$, which is non-degenerate. Although the result has been derived for the rotation of a single mass point, it also applies to any body of moment of inertia I constrained to rotate about one axis.

We have also seen that the angular momentum is quantized and confined to the values given in eqn 48 ($J_z = m_l\hbar$). The increasing angular momentum is associated with the increasing number of nodes in the real and imaginary parts of the wavefunction:[6] the wavelength decreases stepwise as $|m_l|$ increases, so the momentum with which the particle travels round the ring increases (Fig. 12.25). As shown in the following *Justification*, the same conclusion can be obtained formally by using the argument about the relations between eigenvalues and the values of observables that were established in Section 11.5.

Justification 12.4

In the discussion of translational motion in one dimension, we saw that the opposite signs in the wavefunctions e^{ikx} and e^{-ikx} correspond to opposite directions of travel, and that the linear momentum is given by the eigenvalue of the linear momentum operator. The same conclusions can be drawn here, but now we need the eigenvalues of the *angular* momentum operator. In classical mechanics the orbital angular momentum l_z about the z-axis is defined as[7]

$$l_z = xp_y - yp_x \qquad [55]$$

where p_x is the component of linear motion parallel to the x-axis and p_y is the component parallel to the y-axis. The operators for the two linear momentum components are given in eqn 11.32, so the operator for angular momentum about the z-axis, which we denote $\hat{l}_z$, is

$$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \qquad (56)$$

When expressed in terms of the coordinates r and ϕ, this equation becomes

$$\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \qquad (57)$$

With the angular momentum operator available, we can test the wavefunction in eqn 50. Disregarding the normalization constant, we find

$$\hat{l}_z\psi_{m_l} = \frac{\hbar}{i}\frac{d\psi_{m_l}}{d\phi} = im_l\frac{\hbar}{i}e^{im_l\phi} = m_l\hbar\psi_{m_l} \qquad (58)$$

That is, ψ_{m_l} is an eigenfunction of $\hat{l}_z$, and corresponds to an angular momentum $m_l\hbar$. When m_l is positive, the angular momentum is positive (clockwise when seen from below); when m_l is negative, the angular momentum is negative (counter-clockwise when seen from below). These features are the origin of the vector representation of angular momentum, in which the magnitude is represented by the length of a vector and the direction of motion by its orientation (Fig. 12.26).

12.26 **The basic ideas of the vector representation of angular momentum: the magnitude of the angular momentum is represented by the length of the vector, and the orientation of the motion in space by the orientation of the vector (using the right-hand screw rule).**

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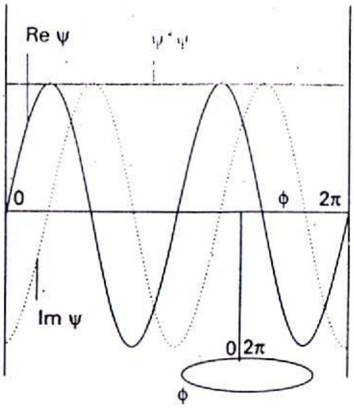
[6] The complex function $e^{im_l\phi}$ does not have nodes, however, it may be written as $\cos m_l\phi + i\sin m_l\phi$, and the real ($\cos m_l\phi$) and imaginary ($\sin m_l\phi$) components do have nodes

[7] The angular momentum in three dimensions is defined as $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$, to obtain eqn 55, expand the vector product and identify the z-component.



12.27 The probability density for a particle in a definite state of angular momentum is uniform, so there is an equal probability of finding the particle anywhere on the ring.

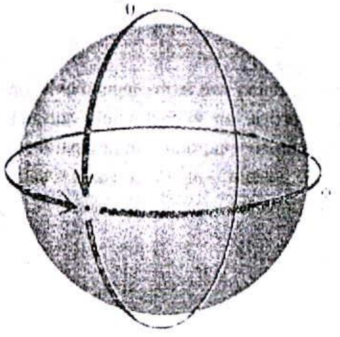
To locate the particle given its wavefunction in eqn 50, we form the probability density:

$$\begin{aligned}\psi^*_{m_l}\psi_{m_l} &= \left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)^*\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right) = \left(\frac{e^{-im_l\phi}}{(2\pi)^{1/2}}\right)\left(\frac{e^{im_l\phi}}{(2\pi)^{1/2}}\right)\\ &= \frac{1}{2\pi}\end{aligned} \tag{59}$$

Because this probability density is independent of ϕ, the probability of locating the particle somewhere on the ring is also independent of ϕ (Fig. 12.27). Hence the location of the particle is completely indefinite, and knowing the angular momentum precisely eliminates the possibility of specifying the particle's location. Angular momentum and angle are a pair of complementary observables (in the sense defined in Section 11.5e), and the inability to specify them simultaneously with arbitrary precision is another example of the uncertainty principle.

12.7 Rotation in three dimensions

We now consider a particle of mass m that is free to move anywhere on the surface of a sphere of radius r. We shall need the results of this calculation when we come to describe the states of electrons in atoms (Chapter 13) and of rotating molecules (Chapter 16). The latter application arises from the fact that the rotation of a solid body of moment of inertia I can be represented by a single point of mass m rotating at a radius r, which is defined so that $I = mr^2$. The requirement that the wavefunction should match as a path is traced over the poles as well as round the equator of the sphere surrounding the central point introduces a second cyclic boundary condition and therefore a second quantum number (Fig. 12.28).



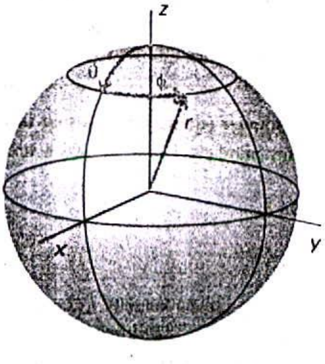
12.28 The wavefunction of a particle on the surface of a sphere must satisfy two cyclic boundary conditions; this requirement leads to two quantum numbers for its state of angular momentum.

(a) The Schrödinger equation

The hamiltonian for motion in three dimensions (Table 11.1) is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{60}$$

The symbol ∇^2 is a convenient abbreviation for the sum of the three second derivatives; it is called the **laplacian**, and read either 'del squared' or 'nabla squared'. For the particle confined to a spherical surface, $V = 0$ wherever it is free to travel, and the radius r is a constant. The wavefunction is therefore a function of the **colatitude**, θ, and the **azimuth**, ϕ (Fig. 12.29), and we write it $\psi(\theta, \phi)$. The Schrödinger equation is



12.29 Spherical polar coordinates. For a particle confined to the surface of a sphere, only the colatitude, θ, and the azimuth, ϕ, can change.

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \tag{61}$$

This partial differential equation can be simplified by the separation of variables procedure by expressing the wavefunction (for constant r) as the product

$$\psi(\theta, \phi) = \Theta(\theta)\Phi(\phi) \tag{62}$$

where Θ is a function only of θ and Φ is a function only of ϕ.

Justification 12.5

The laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 \tag{63}$$

where the **legendrian**, Λ^2, is

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \tag{64}$$

Because r is constant, we can discard the part of the laplacian that involves differentiation with respect to r, and so write the Schrödinger equation as

$$\frac{1}{r^2}\Lambda^2\psi = -\frac{2mE}{\hbar^2}\psi$$

or, because $I = mr^2$, as

$$\Lambda^2\psi = -\varepsilon\psi \qquad \varepsilon = \frac{2IE}{\hbar^2}$$

To verify that this expression is separable, we substitute $\psi = \Theta\Phi$:

$$\frac{\Theta}{\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\Phi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} = -\varepsilon\Theta\Phi$$

We have made use of the fact that Θ and Φ are each functions of one variable, so the partial derivatives become complete derivatives. Division through by $\Theta\Phi$ and multiplication by $\sin^2\theta$ give

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} = -\varepsilon\sin^2\theta$$

The first term on the left depends only on ϕ and the remaining two terms depend only on θ. We met a similar situation when discussing a particle on a rectangular surface (*Justification 12.1*) and, by the same argument, the complete equation can be separated. Thus, if we set the first term equal to the numerical constant $-m_l^2$ (a constant clearly chosen with an eye to the future), the separated equations are

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m_l^2$$

$$\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta} + \varepsilon\sin^2\theta = m_l^2$$

The first of these two equations is the same as in *Justification 12.3*, so it has the same solutions (eqn 50). The second is much more complicated to solve, but the solutions are tabulated as the **associated Legendre functions**. The cyclic boundary conditions on θ result in the introduction of a second quantum number, l, which identifies the acceptable solutions. The presence of the quantum number m_l in the second equation implies, as we see below, that the range of acceptable values of m_l is restricted by the value of l.

As indicated in the *Justification*, solution of the Schrödinger equation shows that the acceptable wavefunctions are specified by two quantum numbers l and m_l which are restricted to the values

$$l = 0, 1, 2, \ldots \qquad m_l = l, l-1, \ldots, -l \tag{65}$$

Note that the quantum number l is non-negative and that, for a given value of l, there are $2l+1$ permitted values of m_l. The normalized wavefunctions are usually denoted $Y_{l,m_l}(\theta,\phi)$ and are called the **spherical harmonics**. Some of the spherical harmonics are listed in Table 12.3, and their amplitudes at different points on the spherical surface are illustrated in Fig. 12.30.

Table 12.3 The spherical harmonics $Y_{l,m_l}(\theta,\phi)$

l	m_l	Y_{l,m_l}
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\,\mathrm{e}^{\pm2\mathrm{i}\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\,\mathrm{e}^{\pm2\mathrm{i}\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\,\mathrm{e}^{\pm3\mathrm{i}\phi}$

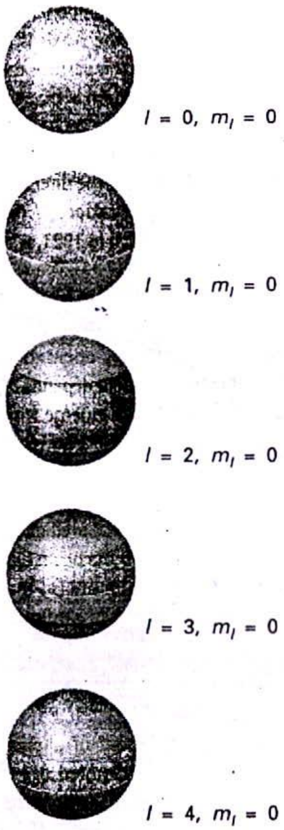
Normalization and orthogonality:

$$\int_0^\pi\int_0^{2\pi} Y^*_{l',m_l'}Y_{l,m_l}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \delta_{l'l}\delta_{m_l'm_l}$$

Triple integral

$$\int_0^\pi\int_0^{2\pi} Y^*_{l'',m_l''}Y_{l',m_l'}Y_{l,m_l}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = 0$$

unless $m_l'' = m_l + m_l'$ and l'', l', l can form a triangle.



12.30 A representation of the wavefunctions of a particle on the surface of a sphere. Note that the number of nodes increases as the value of l increases. All these wavefunctions correspond to $m_l = 0$; a path around the vertical z-axis of the sphere does not cut through any nodes.

It also follows from the solution of the Schrödinger equation that the energy E of the particle is restricted to the values

$$E = l(l+1)\frac{\hbar^2}{2I} \qquad l = 0, 1, 2, \ldots \tag{66}$$

We see that the energy is quantized, and that it is independent of m_l. Because there are $2l+1$ different wavefunctions (one for each value of m_l) that correspond to the same energy, it follows that a level with quantum number l is $(2l+1)$-fold degenerate.

(b) Angular momentum

The energy of a rotating particle is related classically to its angular momentum J by $E = J^2/2I$ (see *Further information 4*). Therefore, by comparing this equation with eqn 66, we can deduce that, because the energy is quantized, then so too is the magnitude of the angular momentum, and confined to the values

$$\text{magnitude of angular momentum} = \{l(l+1)\}^{1/2}\hbar \qquad l = 0, 1, 2, \ldots \tag{67a}$$

We have already seen (in the context of rotation in a plane) that the angular momentum about the z-axis is quantized, and that it has the values

$$z\text{-component of angular momentum} = m_l\hbar \qquad m_l = l, l-1, \ldots, -l \tag{67b}$$

A feature of the (real or imaginary parts of the) wavefunction $\psi_{l,m_l}(\theta,\phi)$ is that, the higher the value of l, the larger the number of nodal lines in the wavefunction (the positions at which ψ passes through 0). This feature reflects the fact that higher angular momentum implies higher kinetic energy, and therefore a more sharply buckled wavefunction. We can also see that the states corresponding to high angular momentum around the z-axis are those in which most nodal lines cut the equator: a high kinetic energy now arises from motion parallel to the equator because the curvature is greatest in that direction.

Illustration

The moment of inertia of H_2 is $4.603 \times 10^{-48}\ \text{kg m}^2$. It follows that

$$\frac{\hbar^2}{2I} = \frac{(1.05457 \times 10^{-34}\ \text{J s})^2}{2 \times (4.603 \times 10^{-48}\ \text{kg m}^2)} = 1.208 \times 10^{-21}\ \text{J}$$

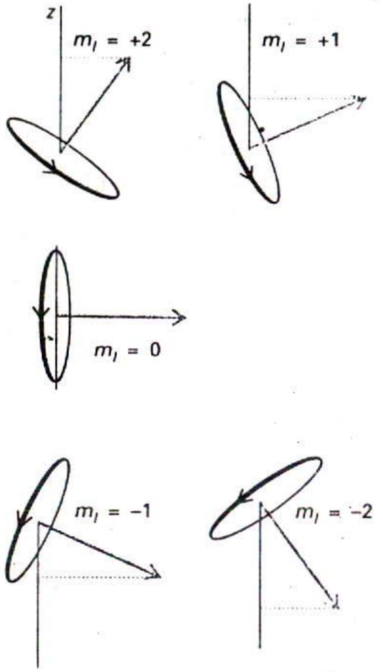
or 1.208 zJ (where z is the little-used but useful SI prefix zepto, denoting 10^{-21}). This energy corresponds to $0.727\ \text{kJ mol}^{-1}$. The first few rotational energy levels are therefore 0 ($l = 0$), 2.416 zJ ($l = 1$), 7.248 zJ ($l = 2$), and 14.496 zJ ($l = 3$). The degeneracies of these levels are 1, 3, 5, and 7, respectively (from $2l+1$) and the magnitudes of the angular momentum of the molecule are 0, $2^{1/2}\hbar$, $6^{1/2}\hbar$, and $(12)^{1/2}\hbar$ (from eqn 67*a*).

Self-test 12.7 Repeat the calculation for a deuterium molecule (same bond length, approximately twice the mass).

[Energies smaller by a factor of two; same angular momenta and numbers of components]

(c) Space quantization

The result that m_l is confined to the values $l, l-1, \ldots, -l$ for a given value of l means that the component of angular momentum about the z-axis may take only $2l+1$ values. If the angular momentum is represented by a vector of length proportional to its magnitude (that is, of length $\{l(l+1)\}^{1/2}$ units), then to represent correctly the value of the component of angular momentum, the vector must be oriented so that its projection on the z-axis is of length m_l units. In classical terms, this means that the plane of rotation of the particle can take only a discrete range of orientations (Fig. 12.31). The remarkable implication is that the orientation of a rotating body is quantized.



12.31 The permitted orientations of angular momentum when $l = 2$. We shall see soon that this representation is too specific because the azimuthal orientation of the vector (its angle around z) is indeterminate.

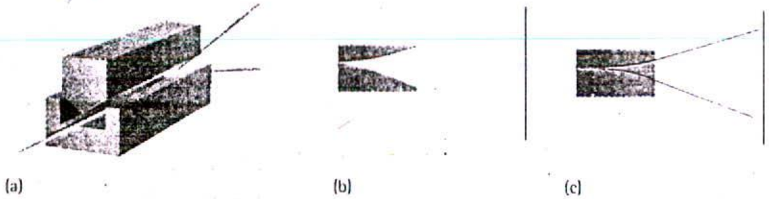
The quantum mechanical result that a rotating body may not take up an arbitrary orientation with respect to some specified axis (for example, an axis defined by the direction of an externally applied electric or magnetic field) is called **space quantization**. It was confirmed by an experiment first performed by Otto Stern and Walther Gerlach in 1921, who shot a beam of silver atoms through an inhomogeneous magnetic field (Fig. 12.32). The idea behind the experiment was that a rotating charged body behaves like a magnet and interacts with the applied field. According to classical mechanics, because the orientation of the angular momentum can take any value, the associated magnet can take any orientation. Because the direction in which the magnet is driven by the inhomogeneous field depends on the magnet's orientation, it follows that a broad band of atoms is expected to emerge from the region where the magnetic field acts. According to quantum mechanics, however, because the angular momentum is quantized, the associated magnet lies in a number of discrete orientations, and so several sharp bands of atoms are expected.

In their first experiment, Stern and Gerlach appeared to confirm the classical prediction. However, the experiment is difficult because collisions between the atoms in the beam blur the bands. When the experiment was repeated with a beam of very low intensity (so that collisions were less frequent), Stern and Gerlach observed discrete bands, and so confirmed the quantum prediction.

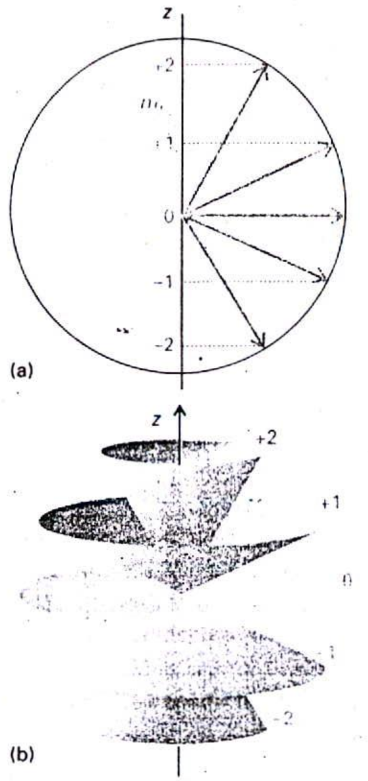
(d) The vector model

Throughout the preceding discussion, we have referred to the z-component of angular momentum (the component about an arbitrary axis, which is conventionally denoted z), and have made no reference to the x- and y-components (the components about the two axes perpendicular to z). The reason for this omission is that, because the operators for the three components do not commute with one another (Section 11.5e), the uncertainty principle forbids the simultaneous, exact specification of more than one component (unless $l = 0$). Therefore, if l_z is known, it is impossible to ascribe values to the other two components. It follows that the illustration in Fig. 12.31, which is summarized in Fig. 12.33a, gives a false impression of the state of the system, because it suggests definite values for the x- and y-components. A better picture must reflect the impossibility of specifying l_x and l_y if l_z is known.

The vector model of angular momentum uses pictures like that in Fig. 12.33b. The cones are drawn with side $\{l(l+1)\}^{1/2}$ units, and represent the magnitude of the angular momentum. Each cone has a definite projection (of m_l units) on the z-axis, representing the system's precise value of l_z. The l_x and l_y projections, however, are indefinite. The vector



12.32 (a) The experimental arrangement for the Stern–Gerlach experiment: the magnet provides an inhomogeneous field. (b) The classically expected result. (c) The observed outcome using silver atoms.



12.33 (a) A summary of Fig. 12.31. However, because the azimuthal angle of the vector around the z-axis is indeterminate, a better representation is as in (b), where each vector lies at an unspecified azimuthal angle on its cone.

representing the state of angular momentum can be thought of as lying with its tip on any point on the mouth of the cone. At this stage it should not be thought of as sweeping round the cone; that aspect of the model will be added later when we allow the picture to convey more information.

12.8 Spin

Stern and Gerlach observed *two* bands of Ag atoms in their experiment. This observation seems to conflict with one of the predictions of quantum mechanics, because an angular momentum l gives rise to $2l+1$ orientations, which is equal to 2 only if $l=\frac{1}{2}$, contrary to the conclusion that l must be an integer. The conflict was resolved by the suggestion that the angular momentum they were observing was not due to orbital angular momentum (the motion of an electron around the atomic nucleus) but arose instead from the motion of the electron about its own axis. This intrinsic angular momentum of the electron is called its spin.

The spin of an electron does not have to satisfy the same boundary conditions as those for a particle circulating around a central point, so the quantum number for spin angular momentum is subject to different restrictions. To distinguish this spin angular momentum from orbital angular momentum we use the quantum number s (in place of l; like l, s is a non-negative number) and m_s for the projection on the z-axis. The magnitude of the spin angular momentum is $\{s(s+1)\}^{1/2}\hbar$ and the component $m_s\hbar$ is restricted to the $2s+1$ values

$$m_s = s, s-1, \ldots, -s \tag{68}$$

The detailed analysis of the spin of a particle is sophisticated (it is rooted in special relativity), and shows that the property should not be taken to be an actual spinning motion. However, that picture can be very useful when used with care. For an electron it turns out that only one value of s is allowed, namely $s=\frac{1}{2}$, corresponding to an angular momentum of magnitude $\frac{1}{2}\sqrt{3}\hbar = 0.866\hbar$. This spin angular momentum is an intrinsic property of the electron, like its rest mass and its charge, and every electron has exactly the same value: the magnitude of the spin angular momentum of an electron cannot be changed. The spin may lie in $2s+1=2$ different orientations (Fig. 12.34). One orientation corresponds to $m_s=+\frac{1}{2}$ (this state is often denoted α or $\uparrow$); the other orientation corresponds to $m_s=-\frac{1}{2}$ (this state is denoted β or $\downarrow$).

The outcome of the Stern–Gerlach experiment can now be explained if we suppose that each Ag atom possesses an angular momentum due to the spin of a single electron, because the two bands of atoms then correspond to the two spin orientations. Why the atoms behave like this will be explained in Chapter 13.[8]

Like the electron, other elementary particles have characteristic, constant spin angular momenta. For example, protons and neutrons are spin-$\frac{1}{2}$ particles (that is, $s=\frac{1}{2}$) and invariably spin with angular momentum $(\frac{3}{4})^{1/2}\hbar$. Because the masses of a proton and a neutron are so much greater than the mass of an electron, yet they all have the same spin angular momentum, the classical picture would be of these two particles spinning much more slowly than an electron. Some elementary particles have $s=1$, and so have an intrinsic angular momentum of magnitude $2^{1/2}\hbar$. Some mesons are spin-1 particles (as are some atomic nuclei), but for our purposes the most important spin-1 particle is the photon.[9] We shall see the importance of photon spin in the next chapter.

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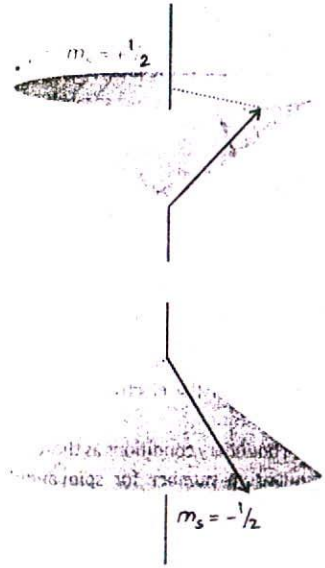
[8] It is already probably familiar from introductory chemistry that the ground-state configuration of a silver atom is $[\mathrm{Kr}]4d^{10}5s^1$, a single unpaired electron outside a closed shell.

[9] A photon has zero rest mass, zero charge, an energy $h\nu$, a linear momentum h/λ or $h\nu/c$, an intrinsic angular momentum of $2^{1/2}\hbar$, and travels at the speed c.



12.34 An electron spin ($s = \frac{1}{2}$) can take only two orientations with respect to a specified axis. An α electron (top) is an electron with $m_s = +\frac{1}{2}$; a β electron (bottom) is an electron with $m_s = -\frac{1}{2}$. The vector representing the magnitude of the spin angular momentum lies at an angle of 55° to the z-axis (more precisely, at $\arccos(1/3^{1/2})$).

Particles with half-integral spin are called **fermions** and those with integral spin (including 0) are called **bosons**. Thus, electrons and protons are fermions and photons are bosons. It is a very deep feature of nature that all the elementary particles that constitute matter are fermions whereas the fundamental particles that are responsible for the forces that bind fermions together are all bosons. (Photons, for example, transmit the electromagnetic force that binds together electrically charged particles.) Matter, therefore, is an assembly of fermions held together by forces conveyed by bosons.

The properties of angular momentum that we have developed are set out in Table 12.4. As mentioned there, when we use the quantum numbers l and m_l we shall mean orbital angular momentum (circulation in space); when we use s and m_s we shall mean spin angular momentum (intrinsic angular momentum); and when we use j and m_j we shall mean either (or, in some contexts to be described in Chapter 13, a combination of orbital and spin momenta).

Table 12.4 Angular momentum

The quantum numbers:
  Orbital angular momentum quantum number: $l = 0, 1, 2, \ldots$
  Orbital magnetic quantum number: $m_l = 0, \pm 1, \ldots, \pm l$
  Spin angular momentum quantum number: $s = \frac{1}{2}$
  Spin magnetic quantum number: $m_s = \pm\frac{1}{2}$

In general:
  Angular momentum quantum number: j
  Magnetic quantum number: m_j

The magnitude of the angular momentum is equal to $\{j(j+1)\}^{1/2}\hbar$ and the z-component of angular momentum is equal to $m_j\hbar$ with the $2j + 1$ values $j, j-1, \ldots, -j$.

For the total angular momentum of a composite system see Section 13.8.

Checklist of key ideas

Translational motion

12.1 A particle in a box

☐ particle in a box
☐ infinite square well
☐ boundary conditions
☐ quantum number
☐ zero-point energy (9)
☐ correspondence principle
☐ orthogonal (12*a*)
☐ Dirac bracket notation (12*b*, 39)
☐ Kronecker delta
☐ energy levels (7)
☐ wavefunctions (7)

12.2 Motion in two dimensions

☐ separation of variables technique
☐ degeneracy

12.3 Tunnelling

☐ tunnelling
☐ transmission probability

Vibrational motion

☐ harmonic motion
☐ force constant
☐ parabolic potential

12.4 The energy levels

☐ energy levels (31)
☐ wavefunctions (34)

12.5 The wavefunctions

☐ matrix element
☐ Gaussian function
☐ Hermite polynomial
☐ virial theorem (45)
☐ error function (46)

Rotational motion

12.6 Rotation in two dimensions

☐ cyclic boundary condition
☐ vector representation
☐ energy levels (48)
☐ wavefunctions (50)

12.7 Rotation in three dimensions

☐ laplacian (60)
☐ colatitude
☐ azimuth
☐ legendrian (64)
☐ associated Legendre function
☐ spherical harmonics
☐ space quantization
☐ energy levels (66)

12.8 Spin

☐ spin
☐ fermion
☐ boson

Further reading

Articles of general interest

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Exercises

12.1 (a) Calculate the energy separations in joules, kilojoules per mole, electronvolts, and reciprocal centimetres between the levels (a) $n = 2$ and $n = 1$, (b) $n = 6$ and $n = 5$ of an electron in a box of length 1.0 nm.

12.1 (b) Calculate the energy separations in joules, kilojoules per mole, electronvolts, and reciprocal centimetres between the levels (a) $n = 3$ and $n = 1$, (b) $n = 7$ and $n = 6$ of an electron in a box of length 1.50 nm.

12.2 (a) Calculate the probability that a particle will be found between $0.49L$ and $0.51L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this range.

12.2 (b) Calculate the probability that a particle will be found between $0.65L$ and $0.67L$ in a box of length L when it has (a) $n = 1$, (b) $n = 2$. Take the wavefunction to be a constant in this range.

12.3 (a) Calculate the expectation values of p and p^2 for a particle in the state $n = 1$ in a square-well potential.

12.3 (b) Calculate the expectation values of p and p^2 for a particle in the state $n = 2$ in a square-well potential.

12.4 (a) What are the most likely locations of a particle in a box of length L in the state $n = 3$?

12.4 (b) What are the most likely locations of a particle in a box of length L in the state $n = 5$?

12.5 (a) Consider a particle in a cubic box. What is the degeneracy of the level that has an energy three times that of the lowest level?

12.5 (b) Consider a particle in a cubic box. What is the degeneracy of the level that has an energy $\frac{14}{3}$ times that of the lowest level?

12.6 (a) Calculate the percentage change in a given energy level of a particle in a cubic box when the length of the edge of the cube is decreased by 10 per cent in each direction.

12.6 (b) A nitrogen molecule is confined in a cubic box of volume 1.00 m^3. Assuming that the molecule has an energy equal to $\frac{3}{2}kT$ at $T = 300$ K, what is the value of $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ for this particle? What is the energy separation between the levels n and $n + 1$? What is its de Broglie wavelength? Would it be appropriate to describe this particle as classical?

12.7 (a) Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass 2.33×10^{-26} kg and force constant 155 N m^{-1}.

12.7 (b) Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass 5.16×10^{-26} kg and force constant 285 N m^{-1}.

12.8 (a) For a harmonic oscillator consisting of a particle of mass 1.33×10^{-25} kg, the difference in adjacent energy levels is 4.82×10^{-21} J. Calculate the force constant of the oscillator.

12.8 (b) For a harmonic oscillator consisting of a particle of mass 2.88×10^{-25} kg, the difference in adjacent energy levels is 3.17 zJ. Calculate the force constant of the oscillator.

12.9 (a) Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a harmonic oscillator of mass equal to that of a proton (1.0078 u) and force constant 855 N m^{-1}.

12.9 (b) Calculate the wavelength of a photon needed to excite a transition between neighbouring energy levels of a harmonic oscillator of mass equal to that of an oxygen atom (15.9949 u) and force constant 544 N m^{-1}.

12.10 (a) Refer to Exercise 12.9a and calculate the wavelength that would result from doubling the mass of the particle.

12.10 (b) Refer to Exercise 12.9b and calculate the wavelength that would result from doubling the mass of the particle.

12.11 (a) Calculate the minimum excitation energies of (a) a pendulum of length 1.0 m on the surface of the Earth, (b) the balance-wheel of a clockwork watch ($\nu = 5$ Hz).

12.11 (b) Calculate the minimum excitation energies of (a) the 33 kHz quartz crystal of a watch, (b) the bond between two O atoms in O_2, for which $k = 1177$ N m^{-1}.

12.12 (a) Confirm that the wavefunction for the ground state of a one-dimensional linear harmonic oscillator given in Table 12.1 is a solution of the Schrödinger equation for the oscillator and that its energy is $\frac{1}{2}\hbar\omega$.

12.12 (b) Confirm that the wavefunction for the first excited state of a one-dimensional linear harmonic oscillator given in Table 12.1 is a solution of the Schrödinger equation for the oscillator and that its energy is $\frac{3}{2}\hbar\omega$.

12.13 (a) Assuming that the vibrations of a $^{35}Cl_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k = 329$ N m^{-1}, what is the zero-point energy of vibration of this molecule? The mass of a ^{35}Cl atom is 34.9688 u.

12.13 (b) Assuming that the vibrations of a $^{14}N_2$ molecule are equivalent to those of a harmonic oscillator with a force constant $k = 2293.8$ N m^{-1}, what is the zero-point energy of vibration of this molecule? The mass of a ^{14}N atom is 14.0031 u.

12.14 (a) The wavefunction, $\psi(\phi)$, for the motion of a particle in a ring is of the form $\psi = Ne^{im_l\phi}$. Determine the normalization constant, N.

12.14 (b) Confirm that wavefunctions for a particle in a ring with different values of the quantum number m_l are orthogonal.

12.15 (a) A point mass rotates in a circle with $l = 1$. Calculate the magnitude of its angular momentum and the possible projections of the angular momentum on an arbitrary axis.

12.15 (b) A point mass rotates in a circle with $l = 2$. Calculate the magnitude of its angular momentum and the possible projections of the angular momentum on an arbitrary axis.

12.16 (a) Draw scale vector diagrams to represent the states (a) $s = \frac{1}{2}$, $m_s = +\frac{1}{2}$, (b) $l = 1$, $m_l = +1$, (c) $l = 2$, $m_l = 0$.

12.16 (b) Draw the vector diagram for all the permitted states of a particle with $l = 6$.

Problems

Numerical problems

12.1 Calculate the separation between the two lowest levels for an O_2 molecule in a one-dimensional container of length 5.0 cm. At what value of n does the energy of the molecule reach $\frac{1}{2}kT$ at 300 K, and what is the separation of this level from the one immediately below?

12.2 To a crude first approximation, a π electron in a linear polyene may be considered to be a particle in a one-dimensional box. The polyene β-carotene contains 22 conjugated C atoms, and the average internuclear distance is 140 pm. Each state up to $n = 11$ is occupied by two electrons. Calculate (a) the separation in energy between the ground state and the first excited state in which one electron occupies the state with $n = 12$, (b) the frequency of the radiation required to produce a transition between these two states, and (c) the total probability of finding an electron between C atoms 11 and 12 in the ground state of the 22-electron molecule.

12.3 The mass to use in the expression for the vibrational frequency of a diatomic molecule is the effective mass $\mu = m_A m_B/(m_A + m_B)$, where m_A and m_B are the masses of the individual atoms. The following data on the infrared absorption wavenumbers (in cm^{-1}) of molecules is taken from *Spectra of diatomic molecules*, G. Herzberg, van Nostrand (1950):

$H^{35}Cl$	$H^{81}Br$	HI	CO	NO
2990	2650	2310	2170	1904

Calculate the force constants of the bonds and arrange them in order of increasing stiffness.

12.4 The rotation of an $^1H^{127}I$ molecule can be pictured as the orbital motion of an H atom at a distance 160 pm from a stationary I atom. (This is quite a good picture; to be precise, both atoms rotate around their common centre of mass, which is very close to the I nucleus.) Suppose that the molecule rotates only in a plane. Calculate the energy needed to excite the molecule into rotation. What, apart from 0, is the minimum angular momentum of the molecule?

12.5 Calculate the energies of the first four rotational levels of $^1H^{127}I$ free to rotate in three dimensions, using for its moment of inertia $I = \mu R^2$, with $\mu = m_H m_I/(m_H + m_I)$ and $R = 160$ pm.

Theoretical problems

12.6 Set up the Schrödinger equation for a particle of mass m in a three-dimensional square well with sides L_1, L_2, and L_3. Show that the wavefunction is defined by three quantum numbers and that the Schrödinger equation is separable. Find the energy levels, and specialize the result to a cubic box of side L.

12.7 The wavefunction inside a long barrier of height V is $\psi = Ne^{-\kappa x}$. Calculate (a) the probability that the particle is inside the barrier and (b) the average penetration depth of the particle into the barrier.

12.8 Confirm that a function of the form e^{-gx^2} is a solution of the Schrödinger equation for the ground state of a harmonic oscillator and find an expression for g in terms of the mass and force constant of the oscillator.

12.9 Calculate the mean kinetic energy of a harmonic oscillator using the relations in Table 12.1.

12.10 Calculate the values of $\langle x^3 \rangle$ and $\langle x^4 \rangle$ for a harmonic oscillator using the relations in Table 12.1.

12.11 Determine the values of $\Delta x = \{\langle x^2 \rangle - \langle x \rangle^2\}^{1/2}$ and $\Delta p = \{\langle p^2 \rangle - \langle p \rangle^2\}^{1/2}$ for (a) a particle in a box of length L and (b) a harmonic oscillator. Discuss these quantities with reference to the uncertainty principle.

12.12 We shall see in Chapter 16 that the intensities of spectroscopic transitions between the vibrational states of a molecule are proportional to the square of the integral $\int \psi_{v'} x \psi_v \, dx$ over all space. Use the relations between Hermite polynomials given in Table 12.1 to show that the only permitted transitions are those for which $v' = v \pm 1$ and evaluate the integral in these cases.

12.13 Use the virial theorem to obtain an expression for the relation between the mean kinetic and potential energies of an electron in a hydrogen atom.

12.14 Evaluate the z-component of the angular momentum and the kinetic energy of a particle on a ring that is described by the (unnormalized) wavefunctions (a) $e^{i\phi}$, (b) $e^{-2i\phi}$, (c) $\cos\phi$, and (d) $(\cos\chi)e^{i\phi} + (\sin\chi)e^{-i\phi}$.

12.15 Confirm that the spherical harmonics (a) $Y_{0,0}$, (b) $Y_{2,-1}$, and (c) $Y_{3,+3}$ satisfy the Schrödinger equation for a particle free to rotate in three dimensions, and find its energy and angular momentum in each case.

12.16 Confirm that $Y_{3,+3}$ is normalized to 1. (The integration required is over the surface of a sphere.)

12.17 Derive an expression in terms of l and m_l for the half-angle of the apex of the cone used to represent an angular momentum according to the vector model. Evaluate the expression for an α spin. Show that the minimum possible angle approaches 0 as $l \to \infty$.

12.18 Show that the function $f = \cos ax \cos by \cos cz$ is an eigenfunction of ∇^2, and determine its eigenvalue.

12.19 Derive (in Cartesian coordinates) the quantum mechanical operators for the three components of angular momentum starting from the classical definition of angular momentum, $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$. Show that any two of the components do not mutually commute, and find their commutator.

12.20 Starting from the definition $l_z = xp_y - yp_x$, prove that in spherical polar coordinates $\hat{l}_z = -i\hbar\partial/\partial\phi$.

Additional problems supplied by Carmen Giunta and Charles Trapp

12.21 Scanning tunnelling microscopy is an imaging technique based on detecting electrons tunnelling across the vacuum between a conducting sample and a conducting probe tip. The tunnelling current is very sensitive to the distance between the tip and the sample, so sensitive that imaging of atoms has been accomplished through this technique. To get an idea of the distance dependence of this tunnelling current, suppose that the wavefunction of the electron in the gap between sample and tip is given by $\psi = Be^{-\kappa x}$, where $\kappa = \{2m_e(V - E)/\hbar^2\}^{1/2}$; take $V - E$ to be 2.0 eV. By what factor would the current drop if the probe is moved from 0.50 nm to 0.60 nm from the surface?

12.22 A particle is confined to move in a one-dimensional box of length L. (a) If the particle is classical, show that the average value of x is equal to $\frac{1}{2}L$, and that the root mean square value is $L/3^{1/2}$. (b) Show that, for large values of n, a quantum particle approaches the classical values. This result is an example of a very general principle called the *correspondence principle*, which states that, for very large values of the quantum numbers, quantum mechanics approaches classical mechanics.

13

Atomic structure and atomic spectra

The principles of quantum mechanics introduced in the preceding two chapters are now used to describe the internal structures of atoms. We see what experimental information is available from a study of the spectrum of atomic hydrogen. Then we set up the Schrödinger equation for an electron in an atom and separate it into angular and radial parts. The wavefunctions obtained are the 'atomic orbitals' of hydrogenic atoms. Next, we use these hydrogenic atomic orbitals to describe the structures of many-electron atoms. In conjunction with the Pauli exclusion principle, we account for the periodicity of atomic properties. The spectra of many-electron atoms are more complicated than those of hydrogen, but the same principles apply. We see in the closing sections of the chapter how such spectra are described in terms of term symbols, the origin of the finer details of their appearance, and the effects on them of an applied magnetic field.

In this chapter we see how to use quantum mechanics to describe the **electronic structure** of an atom, the arrangement of electrons around a nucleus. The concepts we meet are of central importance for understanding the structures and reactions of atoms and molecules, and hence have extensive chemical applications. We need to distinguish between two types of atoms. A **hydrogenic atom** is a one-electron atom or ion of general atomic number Z; examples of hydrogenic atoms are H, He^+, Li^{2+}, and U^{91+}. A **many-electron atom** is an atom or ion with more than one electron; examples include all neutral atoms other than H. So even He, with only two electrons, is a many-electron atom. Hydrogenic atoms are important because their Schrödinger equations can be solved exactly. They also provide a set of concepts that are used to describe the structures of many-electron atoms and, as we shall see in the next chapter, the structures of molecules too.

One of the principal experimental techniques for determining the electronic structures of atoms is **spectroscopy**, the detection and analysis of the electromagnetic radiation absorbed or emitted by a species. The record of spectral intensity as a function of frequency (ν), wavelength (λ), or wavenumber ($\tilde{\nu}$)[1] of the radiation emitted or absorbed by an atom or a

---

[1] The relation between these quantities was described in the *Introduction*: $\nu = c/\lambda$, $\tilde{\nu} = 1/\lambda = \nu/c$.

molecule is called its **spectrum** (from the Greek word for appearance; plural 'spectra'). The spectrum of an atom consists of a series of 'lines', or sharply defined emission or absorption peaks.

The structure and spectra of hydrogenic atoms

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules are dissociated and the energetically excited H atoms that are produced emit light of discrete frequencies (Fig. 13.1). The first important contribution to the interpretation of this spectrum was made by the Swiss schoolteacher Johann Balmer, who pointed out in 1885 that (in modern terms) the wavenumbers of the lines in the visible region fit the expression

$$\tilde{\nu} \propto \frac{1}{2^2} - \frac{1}{n^2} \qquad n = 3, 4, \ldots$$

The transitions this formula describes are now called the **Balmer series**. When further lines were discovered in the ultraviolet, giving the **Lyman series**, and in the infrared, the **Paschen series**, the Swedish spectroscopist Johannes Rydberg noted (in 1890) that all of them could be fitted to the expression

$$\tilde{\nu} = \mathcal{R}_{\mathrm{H}}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \mathcal{R}_{\mathrm{H}} = 109\,677\ \mathrm{cm}^{-1} \tag{1}$$

with $n_1 = 1$ (the Lyman series), 2 (the Balmer series), and 3 (the Paschen series), and that in each case $n_2 = n_1 + 1, n_1 + 2, \ldots$. The constant $\mathcal{R}_{\mathrm{H}}$ is now called the **Rydberg constant** for the hydrogen atom.

Illustration

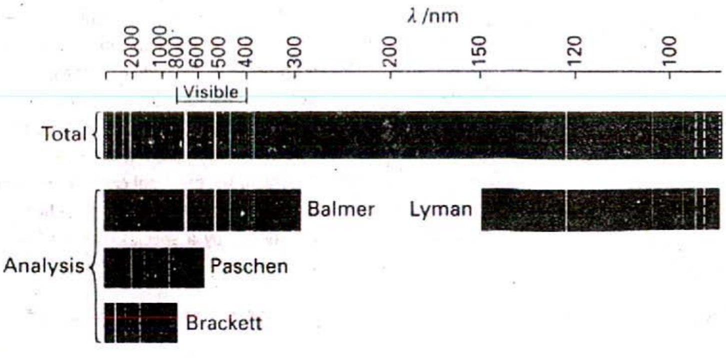
The transition with the longest wavelength (lowest wavenumber) in the Lyman series ($n_1 = 1$) is the one with $n_2 = 2$; its wavenumber is

$$\tilde{\nu} = \mathcal{R}_{\mathrm{H}}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = (109\,677\ \mathrm{cm}^{-1}) \times \tfrac{3}{4} = 82\,258\ \mathrm{cm}^{-1}$$

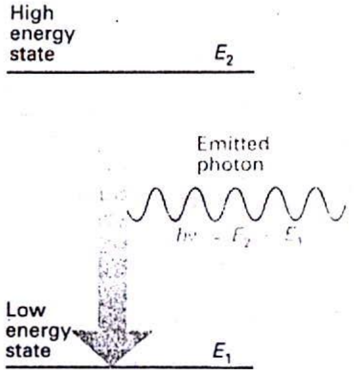
Its wavelength is therefore

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{8.2258 \times 10^{6}\ \mathrm{m}^{-1}} = 1.2157 \times 10^{-7}\ \mathrm{m}$$

or 121.57 nm, in the vacuum ultraviolet region of the spectrum.



13.1 **The spectrum of atomic hydrogen.** Both the observed spectrum and its resolution into overlapping series are shown. Note that the Balmer series lies in the visible region.



13.2 **Energy is conserved when a photon is emitted, so the difference in energy of the atom before and after the emission event must be equal to the energy of the photon emitted.**

Self-test 13.1 Calculate the shortest wavelength transition in the Paschen series.

[821 nm]

The form of eqn 1 strongly suggests that the wavenumber of each spectral line can be written as the difference of two terms, each of the form

$$T_n = \frac{\mathcal{R}_H}{n^2} \tag{2}$$

The **Ritz combination principle** states that *the wavenumber of any spectral line is the difference between two terms*. We say that two terms T_1 and T_2 'combine' to produce a spectral line of wavenumber

$$\tilde{\nu} = T_1 - T_2 \tag{3}$$

The Ritz combination principle applies to all types of atoms and molecules, but only for hydrogenic atoms do the terms have the simple form (constant)/n^2. The Ritz combination principle is readily explained in terms of photons and the conservation of energy. Thus, a spectroscopic line arises from the transition of an atom from one energy level (a term) to another (another term) with the emission of the difference in energy as a photon (Fig. 13.2). This interpretation leads to the **Bohr frequency condition**, which states that, when an atom changes its energy by ΔE, the difference is carried away as a photon of frequency ν, where

$$\Delta E = h\nu \tag{4}$$

Thus, if each spectroscopic term represents an energy hcT, the difference in energy when the atom undergoes a transition between two terms is $\Delta E = hcT_1 - hcT_2$, and the frequency of the light emitted is given by $\nu = cT_1 - cT_2$. This expression rearranges into the Ritz formula when expressed in terms of wavenumbers (on division by c).

Because spectroscopic observations show that electromagnetic radiation is absorbed and emitted by atoms only at certain wavenumbers, it follows that only certain energy states of atoms are permitted. Our tasks in the first part of this chapter are to determine the origin of this energy quantization, to find the permitted energy levels, and to account for the value of $\mathcal{R}_H$.

13.1 The structure of hydrogenic atoms

The Coulomb potential energy of an electron in a hydrogenic atom of atomic number Z (and nuclear charge Ze) is

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{5}$$

where r is the distance of the electron from the nucleus and ε_0 is the vacuum permittivity. The hamiltonian for the electron and a nucleus of mass m_N is therefore

$$\begin{aligned} H &= \hat{E}_{K,\text{electron}} + \hat{E}_{K,\text{nucleus}} + \hat{V} \\ &= -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \end{aligned} \tag{6}$$

The subscripts on ∇^2 indicate differentiation with respect to the electron or nuclear coordinates.

(a) The separation of internal motion

Physical intuition suggests that the full Schrödinger equation ought to separate into two equations, one for the motion of the atom as a whole through space and the other for the motion of the electron relative to the nucleus. We have already solved the first of these equations, because it corresponds to the free translational motion of a particle of mass $m = m_e + m_N$ (Section 11.5). The initial strategy of the calculation is therefore to separate the relative motion of the electron and the nucleus from the motion of the atom as a whole. As we show in the following *Justification*, the resulting expression for the hamiltonian for the internal motion of the electron relative to the nucleus is

$$H = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_N} \tag{7}$$

The quantity μ is called the **reduced mass**. The reduced mass is very similar to the electron mass because m_N, the mass of the nucleus, is much larger than the mass of an electron, so $1/\mu \approx 1/m_e$. In all except the most precise work, the reduced mass can be replaced by m_e.

Justification 13.1

Consider a one-dimensional system in which the potential energy depends only on the separation of the two particles; the total energy is

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V$$

where $p_1 = m_1\dot{x}_1$ and $p_2 = m_2\dot{x}_2$, the dot signifying differentiation with respect to time. The centre of mass (Fig. 13.3) is located at

$$X = \frac{m_1}{m}x_1 + \frac{m_2}{m}x_2 \qquad m = m_1 + m_2$$

and the separation of the particles is $x = x_1 - x_2$. It follows that

$$x_1 = X + \left(\frac{m_2}{m}\right)x \qquad x_2 = X - \left(\frac{m_1}{m}\right)x$$

The linear momenta of the particles can be expressed in terms of x and X:

$$p_1 = m_1\dot{x}_1 = m_1\dot{X} + \left(\frac{m_1 m_2}{m}\right)\dot{x}$$

$$p_2 = m_2\dot{x}_2 = m_2\dot{X} - \left(\frac{m_1 m_2}{m}\right)\dot{x}$$

Then it follows that

$$\frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \tfrac{1}{2}m\dot{X}^2 + \tfrac{1}{2}\mu\dot{x}^2$$

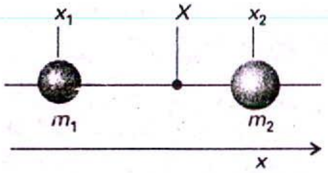
where μ is given in eqn 7. By writing $P = m\dot{X}$ for the linear momentum of the system as a whole and defining p as $\mu\dot{x}$, we find

$$E = \frac{P^2}{2m} + \frac{p^2}{2\mu} + V$$

The corresponding hamiltonian (generalized to three dimensions) is therefore

$$H = -\frac{\hbar^2}{2m}\nabla^2_{\text{c.m.}} - \frac{\hbar^2}{2\mu}\nabla^2 + V$$

where the first term differentiates with respect to the centre of mass coordinates and the second with respect to the relative coordinates.



13.3 The coordinates used for discussing the separation of the relative motion of two particles from the motion of the centre of mass.

Now we write the overall wavefunction as the product $\psi_{\text{total}} = \psi_{\text{c.m.}}\psi$, where the first factor is a function of only the centre of mass coordinates and the second is a function of only the relative coordinates. The overall Schrödinger equation, $H\psi_{\text{total}} = E_{\text{total}}\psi_{\text{total}}$, then separates by the argument that we have used twice already:

$$-\frac{\hbar^2}{2m}\nabla^2_{\text{c.m.}}\psi_{\text{c.m.}} = E_{\text{c.m.}}\psi_{\text{c.m.}}$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi = E\psi$$

with $E_{\text{total}} = E_{\text{c.m.}} + E$.

From now on we consider only the internal, relative coördinates. The Schrödinger equation, $H\psi = E\psi$, is

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi \qquad (8)$$

Because the potential energy is centrosymmetric (independent of angle), we can suspect that the equation is separable into radial and angular components. Therefore, we write

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \qquad (9)$$

and examine whether the Schrödinger equation can be separated into two equations, one for R and the other for Y. As shown in the *Justification* below, the equation does separate, and the equations we have to solve are

$$\Lambda^2 Y = -l(l+1)Y \qquad (10)$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2}{r}\frac{\mathrm{d}R}{\mathrm{d}r}\right) + V_{\text{eff}}R = ER \qquad (11)$$

where

$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2} \qquad (12)$$

Justification 13.2

The laplacian in three dimensions is given in eqn 12.63. It follows that the Schrödinger equation in eqn 8 is

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\mathrm{d}}{\mathrm{d}r} + \frac{1}{r^2}\Lambda^2\right)RY + VRY = ERY$$

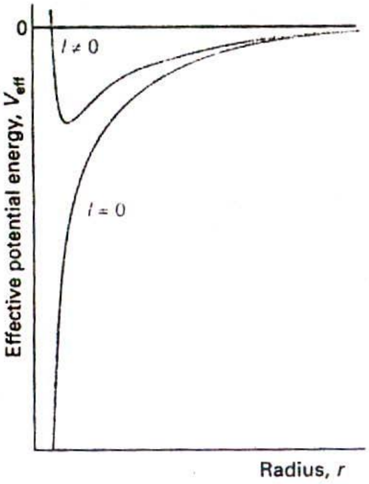
Because R depends only on r and Y depends only on the angular coordinates, this equation becomes

$$-\frac{\hbar^2}{2\mu}\left(Y\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + \frac{2Y}{r}\frac{\mathrm{d}R}{\mathrm{d}r} + \frac{R}{r^2}\Lambda^2 Y\right) + VRY = ERY$$

If we multiply through by r^2/RY, we obtain

$$-\frac{\hbar^2}{2\mu R}\left(r^2\frac{\mathrm{d}^2R}{\mathrm{d}r^2} + 2r\frac{\mathrm{d}R}{\mathrm{d}r}\right) + Vr^2 - \frac{\hbar^2}{2\mu Y}\Lambda^2 Y = Er^2$$

At this point we employ the usual argument. The term in Y is the only one that depends on the angular variables, so it must be a constant. When we write this constant as $\hbar^2 l(l+1)/2\mu$, eqn 12 follows immediately.



13.4 The effective potential energy of an electron in the hydrogen atom. When the electron has zero orbital angular momentum, the effective potential energy is the Coulombic potential energy. When the electron has nonzero orbital angular momentum, the centrifugal effect gives rise to a positive contribution which is very large close to the nucleus. We can expect the $l = 0$ and $l \neq 0$ wavefunctions to be very different near the nucleus.

Equation 10 is the same as the Schrödinger equation for a particle free to move round a central point, and we considered it in Section 12.7. The solutions are the spherical harmonics (Table 12.3), and are specified by the quantum numbers l and m_l. We consider them in more detail shortly. Equation 11 is called the **radial wave equation.** The radial wave equation is the description of the motion of a particle of mass μ in a one-dimensional region where the potential energy is V_{eff}.

(b) The radial solutions

We can anticipate some features of the shapes of the radial wavefunctions by analysing the shape of V_{eff}. The first term in eqn 12 is the Coulomb potential energy of the electron in the field of the nucleus. The second term stems from the centrifugal force that arises from the angular momentum of the electron around the nucleus. When $l = 0$, the electron has no angular momentum, and the effective potential energy is purely Coulombic and attractive at all radii (Fig. 13.4). When $l \neq 0$, the centrifugal term gives a positive contribution to the effective potential energy. When the electron is close to the nucleus ($r \approx 0$), this repulsive term, which is proportional to $1/r^2$, dominates the attractive Coulombic component, which is proportional to $1/r$, and the net effect is an effective repulsion of the electron from the nucleus. The two effective potential energies, the one for $l = 0$ and the one for $l \neq 0$, are qualitatively very different close to the nucleus; however, they are similar at large distances because the centrifugal contribution tends to zero more rapidly than the Coulombic contribution. Therefore, we can expect the solutions with $l = 0$ and $l \neq 0$ to be quite different near the nucleus but similar far away from it.

We shall not go through the technical steps of solving the radial equation (see *Further reading*). It is sufficient to know that acceptable solutions can be found only for integral values of a quantum number n, and that the allowed energies are

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2 n^2} \tag{13}$$

with $n = 1, 2, \ldots$.

The radial wave equation depends on l, and the radial wavefunctions, which depend on the values of both n and l (but not on m_l), all have the form

$$R(r) = (\text{polynomial in } r) \times (\text{decaying exponential in } r) \tag{14}$$

These functions are most simply written in terms of the dimensionless quantity ρ (rho), where

$$\rho = \frac{2Zr}{a_0} \qquad a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} \tag{15}$$

The **Bohr radius,** a_0, has the value 52.9177 pm; it is so called because the same quantity appeared in Bohr's early model of the hydrogen atom as the radius of the electron orbit of lowest energy. Specifically, the radial wavefunctions for an electron with quantum numbers n and l are the (real) functions

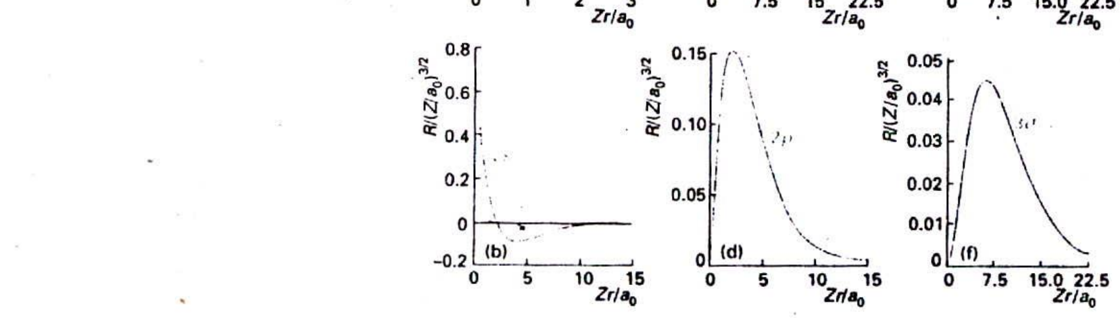
$$R_{n,l}(r) = N_{n,l}\left(\frac{\rho}{n}\right)^l L_{n,l} \mathrm{e}^{-\rho/2n} \tag{16}$$

where L is a polynomial in ρ called an **associated Laguerre polynomial**. Expressions for some radial wavefunctions are given in Table 13.1 and their appearance is illustrated in Fig. 13.5. Note that, because R is proportional to ρ^l, all radial wavefunctions are zero at the nucleus unless $l = 0$.

Table 13 Hydrogenic radial wavefunctions

Orbital	n	l	$R_{n,l}$
1*s*	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2*s*	2	0	$\frac{1}{2(2)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\frac{1}{2}\rho)e^{-\rho/4}$
2*p*	2	1	$\frac{1}{4(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/4}$
3*s*	3	0	$\frac{1}{9(3)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (6-2\rho+\frac{1}{9}\rho^2)e^{-\rho/6}$
3*p*	3	1	$\frac{1}{27(6)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} (4-\frac{1}{3}\rho)\rho e^{-\rho/6}$
3*d*	3	2	$\frac{1}{81(30)^{1/2}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/6}$

The full wavefunction is $\psi = RY$, where Y is given in Table 12.3. In the table, $\rho = 2Zr/a_0$.



13.5 The radial wavefunctions of the first few states of hydrogenic atoms of atomic number Z. Note that the *s* orbitals have a nonzero and finite value at the nucleus. The horizontal scales are different in each case: orbitals with high principal quantum numbers are relatively distant from the nucleus.

Illustration

To calculate the probability density for a $1s$-electron at the nucleus, we set $n = 1$, $l = 0$, $m_l = 0$ and evaluate ψ at $r = 0$:

$$\psi_{1,0,0}(0, \theta, \phi) = R_{1,0}(0)Y_{0,0}(\theta, \phi) = 2\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{1}{4\pi}\right)^{1/2}$$

The probability density is therefore

$$\psi^2_{1,0,0}(0, \theta, \phi) = \frac{Z^3}{\pi a_0^3}$$

which evaluates to 2.15×10^{-6} pm^{-3} when $Z = 1$.

Self-test 13.2 Evaluate the probability density of the electron at the nucleus for a $2s$-electron.

$[(Z/a_0)^3/8\pi]$

13.2 Atomic orbitals and their energies

An **atomic orbital** is a one-electron wavefunction for an electron in an atom. Each hydrogenic atomic orbital is defined by three quantum numbers (Table 13.2), designated n, l, and m_l. When an electron is described by one of these wavefunctions, we say that it 'occupies' that orbital. We could go on to say that the electron is in the state $|n, l, m_l\rangle$. For instance, an electron described by the wavefunction $\psi_{1,0,0}$ and in the state $|1, 0, 0\rangle$ is said to occupy the orbital with $n = 1$, $l = 0$, and $m_l = 0$.

One quantum number, n, is called the **principal quantum number**; it can take the values $n = 1, 2, 3, \ldots$ and determines the energy of the electron:

> **An electron in an orbital with quantum number n has an energy given by eqn 13.**

The two other quantum numbers, l and m_l, come from the angular solutions, and specify the angular momentum of the electron around the nucleus:

> **An electron in an orbital with quantum number l has an angular momentum of magnitude $\{l(l+1)\}^{1/2}\hbar$, with l=0, 1, 2, ..., $n-1$.**
> **An electron in an orbital with quantum number m_l has a z-component of angular momentum $m_l\hbar$, with m_l=0, ±1, ±2, ... ±l.**

Note how the value of the principal quantum number, n, controls the maximum value of l, and how l in turn controls the range of values of m_l.

To define the state of an electron in a hydrogenic atom fully we need to specify not only the orbital it occupies but also its spin state. We saw in Section 12.8 that an electron possesses an intrinsic angular momentum that is described by the two quantum numbers s and m_s (the analogues of l and m_l). The value of s is fixed at $\frac{1}{2}$ for an electron, so we do not need to consider it further at this stage. However, m_s may be either $+\frac{1}{2}$ or $-\frac{1}{2}$, and to specify the electron's state in a hydrogenic atom we need to specify which of these values describes it. It follows that, to specify the state of an electron in a hydrogenic atom, we need to give the values of four quantum numbers, namely n, l, m_l, and m_s.

Table 13.2 Hydrogenic atoms

The wavefunctions of hydrogenic atoms depend on three quantum numbers:

Principal quantum number: $n = 1, 2, 3, \ldots$
Angular momentum quantum number: $l = 0, 1, 2, \ldots, n-1$
Magnetic quantum number: $m_l = l, l-1, l-2, \ldots, -l$

The energy is related to n by

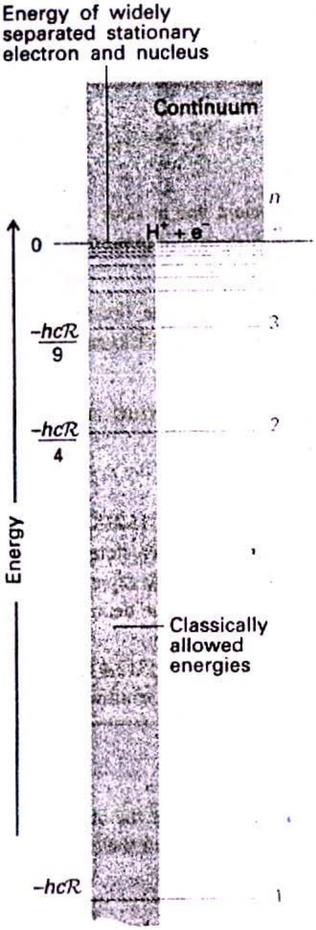
$$E_n = -\frac{hc\mathcal{R}_{\text{atom}}}{n^2} \qquad hc\mathcal{R}_{\text{atom}} = \frac{Z^2\mu e^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

The magnitude of the orbital angular momentum of the electron $\{l(l+1)\}^{1/2}\hbar$ and its component on an arbitrary axis is $m_l\hbar$. Each energy level is n^2-fold degenerate.
The wavefunctions are products of radial and angular components:

$$\psi = R(r)Y(\theta, \phi)$$

The angular wavefunctions Y are the spherical harmonics (Table 12.3) and the radial wavefunctions R are the normalized associated Laguerre polynomials multiplied by an exponential factor (Table 13.1).
The selection rules for spectroscopic transitions are

$$\Delta m_l = 0, \pm 1 \quad \Delta n \text{ unrestricted} \quad \Delta l = \pm 1$$



13.6 The energy levels of a hydrogen atom. The values are relative to an infinitely separated, stationary electron and a proton.

(a) The energy levels

The energy levels predicted by eqn 13 are depicted in Fig. 13.6. The energies, and also the separation of neighbouring levels, are proportional to Z^2, so the levels are four times as widely apart (and the ground state four times deeper in energy) in He^+ ($Z = 2$) than in H ($Z = 1$). All the energies given by eqn 13 are negative. They refer to the **bound states** of the atom, in which the energy of the atom is lower than that of the infinitely separated, stationary electron and nucleus (which corresponds to the zero of energy). There are also solutions of the Schrödinger equation with positive energies. These solutions correspond to **unbound states** of the electron, the states to which an electron is raised when it is ejected from the atom by a high-energy collision or photon. The energies of the unbound electron are not quantized and form the **continuum states** of the atom.

Equation 13 is consistent with the spectroscopic result summarized by eqn 1, and we can identify the Rydberg constant for hydrogen ($Z = 1$) by writing

$$hc\mathcal{R}_{\text{H}} = \frac{\mu_{\text{H}} e^4}{32\pi^2\varepsilon_0^2\hbar^2} \qquad [17]$$

where μ_{H} is the reduced mass for hydrogen. The **Rydberg constant** itself, $\mathcal{R}$, is defined by the same expression except for the replacement of μ by the mass of an electron, m_e:

$$\mathcal{R}_{\text{H}} = \frac{\mu_{\text{H}}}{m_e}\mathcal{R} \qquad \mathcal{R} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c} \qquad [18]$$

Insertion of the values of the fundamental constants into the expression for $\mathcal{R}_{\text{H}}$ gives almost exact agreement with the experimental value. The only discrepancies arise from the neglect of relativistic corrections, which the non-relativistic Schrödinger equation ignores.

(b) Ionization energies

The ionization energy, I, of an element is the minimum energy required to remove an electron from the ground state, the state of lowest energy, of one of its atoms. The ground state of hydrogen is the state with $n = 1$, which has energy

$$E_1 = -hc\mathcal{R}_{\text{H}}$$

The atom is ionized when the electron has been excited to the level corresponding to $n = \infty$ (see Fig. 13.6). Therefore, the energy that must be supplied is

$$I = hc\mathcal{R}_{\mathrm{H}} \tag{19}$$

The value of I is 2.179 aJ (a, for atto, is the prefix that denotes 10^{-18}), which corresponds to 13.60 eV.

Example 13.1 Measuring an ionization energy spectroscopically

The spectrum of atomic hydrogen shows lines at 82 259, 97 492, 102 824, 105 292, 106 632, 107 440 cm^{-1}. Determine (a) the ionization energy of the lower state, (b) the value of the Rydberg constant.

Method The spectroscopic determination of ionization energies depends on the determination of the series limit, the wavenumber at which the series terminates and becomes a continuum. If the upper state lies at an energy $-hc\mathcal{R}_{\mathrm{H}}/n^2$, then, when the atom makes a transition to E_{lower}, a photon of wavenumber

$$\tilde{\nu} = -\frac{\mathcal{R}_{\mathrm{H}}}{n^2} - E_{\mathrm{lower}}/hc$$

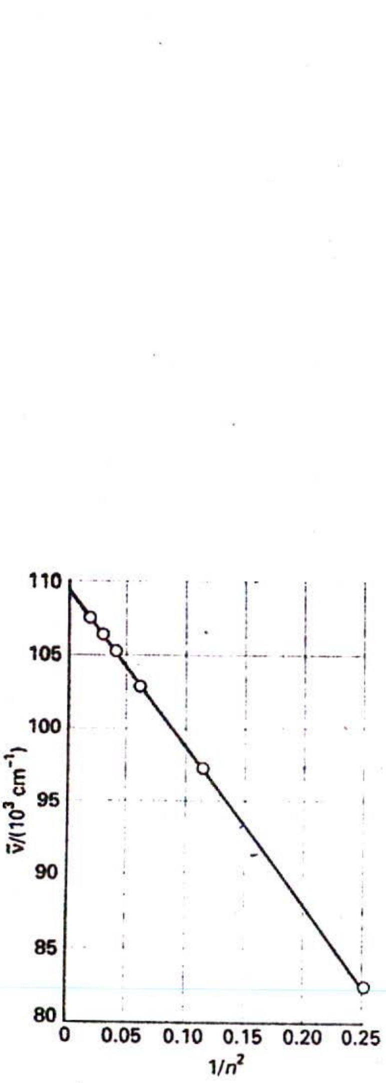
is emitted. However, because $I = -E_{\mathrm{lower}}$, it follows that

$$\tilde{\nu} = I/hc - \frac{\mathcal{R}_{\mathrm{H}}}{n^2}$$

A plot of the wavenumbers against $1/n^2$ should give a straight line of slope $-\mathcal{R}_{\mathrm{H}}$ and intercept I/hc. Use a computer (or a calculator) to make a least-squares fit of the data to get a result that reflects the precision of the data.

Answer The wavenumbers are plotted against $1/n^2$ in Fig. 13.7. The (least-squares) intercept lies at 109 679 cm^{-1}, so the ionization energy is 2.1788 aJ (1312.1 $\mathrm{kJ\,mol^{-1}}$). The slope is, in this instance, numerically the same, so $\mathcal{R}_{\mathrm{H}} = 109\,679\ \mathrm{cm}^{-1}$.

Comment A similar extrapolation procedure can be used for many-electron atoms (see Section 13.6).



13.7 The plot of the data in Example 13.1 used to determine the ionization energy of an atom (in this case, of H).

Self-test 13.3 The spectrum of atomic deuterium shows lines at 15 238, 20 571, 23 039, 24 380 cm^{-1}. Determine (a) the ionization energy of the lower state, (b) the ionization energy of the ground state, (c) the mass of the deuteron (by expressing the Rydberg constant in terms of the reduced mass of the electron and the deuteron, and solving for the mass of the deuteron).

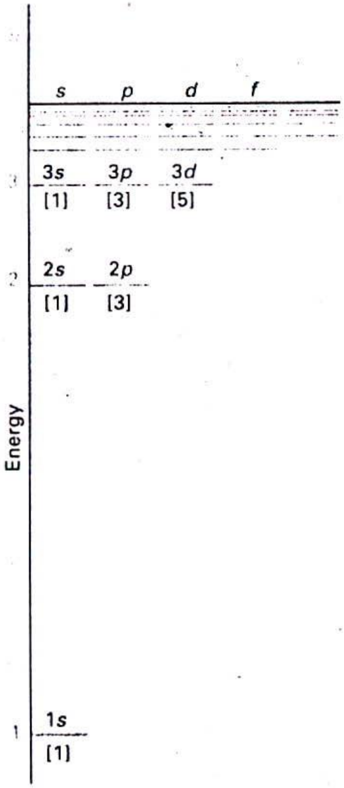
[(a) 328.1 $\mathrm{kJ\,mol^{-1}}$, (b) 1312.4 $\mathrm{kJ\,mol^{-1}}$,
(c) 2.8×10^{-27} kg, a result very sensitive to $\mathcal{R}_{\mathrm{D}}$.]

(c) Shells and subshells

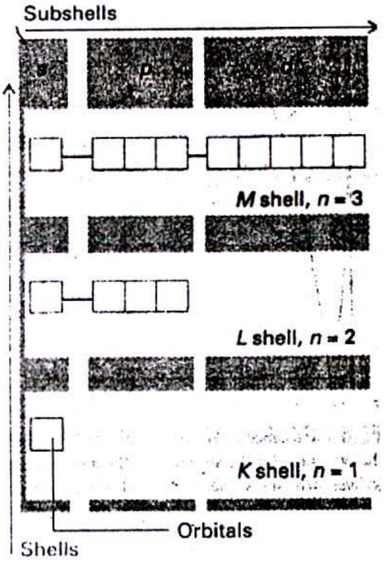
All the orbitals of a given value of n are said to form a single shell of the atom. In a hydrogenic atom, all orbitals of given n, and therefore belonging to the same shell, have the same energy. It is common to refer to successive shells by letters:

$n =$	1	2	3	4	...
	K	L	M	N	...

Thus, all the orbitals of the shell with $n = 2$ form the L shell of the atom, and so on.



13.8 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy.



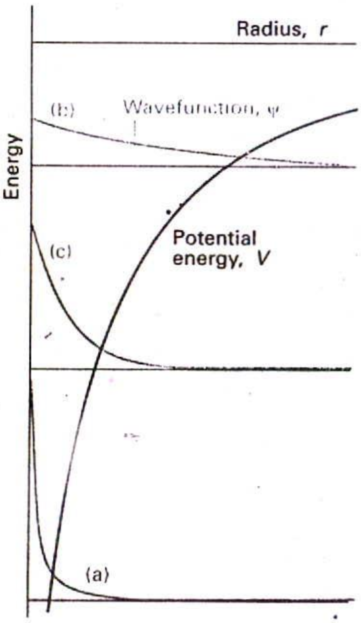
13.9 The organization of orbitals into subshells (characterized by l) and shells (characterized by n).

The orbitals with the same value of n but different values of l are said to form a **subshell** of a given shell. These subshells are generally referred to by letters:

$l =$	0	1	2	3	4	5	6	...
	s	p	d	f	g	h	i	...

The letters then run alphabetically (j is not used). Figure 13.8 is a version of Fig. 13.6 which shows the subshells explicitly. Because l can range from 0 to $n - 1$, giving n values in all, it follows that there are n subshells of a shell with principal quantum number n. Thus, when $n = 1$, there is only one subshell, the one with $l = 0$.

When $n = 2$, there are two subshells, the $2s$ subshell (with $l = 0$) and the $2p$ subshell (with $l = 1$). When $n = 1$ there is only one subshell, that with $l = 0$, and that subshell contains only one orbital, with $m_l = 0$ (the only value of m_l permitted). When $n = 2$, there are four orbitals, one in the s subshell with $l = 0$ and $m_l = 0$, and three in the $l = 1$ subshell with $m_l = +1, 0, -1$. When $n = 3$ there are nine orbitals (one with $l = 0$, three with $l = 1$, and five with $l = 2$). The organization of orbitals in the shells is summarized in Fig. 13.9. In general, the number of orbitals in a shell of principal quantum number n is n^2, so in a hydrogenic atom each shell is n^2-fold degenerate.



13.10 The balance of kinetic and potential energies that accounts for the structure of the ground state of hydrogen (and similar atoms). (a) The sharply curved but localized orbital has high mean kinetic energy, but low mean potential energy; (b) the mean kinetic energy is low, but the potential energy is not very favourable; (c) the compromise of moderate kinetic energy and moderately favourable potential energy.

(d) s orbitals

The orbital occupied in the ground state is the one with $n = 1$ (and therefore with $l = 0$ and $m_l = 0$, the only possible values of these quantum numbers when $n = 1$). From Table 13.1 we can write (for $Z = 1$):

$$\psi = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0} \tag{20}$$

This wavefunction is independent of angle and has the same value at all points of constant radius, that is, the $1s$ orbital is spherically symmetrical. The wavefunction decays exponentially from a maximum value of $1/(\pi a_0^3)^{1/2}$ at the nucleus (at $r = 0$). It follows that the most probable point at which the electron will be found is at the nucleus itself.

We can understand the general form of the ground-state wavefunction by considering the contributions of the potential and kinetic energies to the total energy of the atom. The closer the electron is to the nucleus on average, the lower its average potential energy. This dependence suggests that the lowest potential energy should be obtained with a sharply peaked wavefunction that has a large amplitude at the nucleus and is zero everywhere else (Fig. 13.10). However, this shape implies a high kinetic energy, because such a wavefunction has a very high average curvature. The electron would have very low kinetic energy if its wavefunction had only a very low average curvature. However, such a wavefunction spreads to great distances from the nucleus and the average potential energy of the electron will be high. The actual ground-state wavefunction is a compromise between these two extremes: the wavefunction spreads away from the nucleus (so the expectation value of the potential energy is not as low as in the first example, but nor is it very high) and has a reasonably low average curvature (so the expectation of the kinetic energy is not very low, but nor is it as high as in the first example).

One way of depicting the probability density of the electron is to represent $|\psi|^2$ by density of shading (Fig. 13.11). A simpler procedure is to show only the **boundary surface**, the surface that captures about 90 per cent of the electron probability. For the $1s$ orbital, the boundary surface is a sphere centred on the nucleus (Fig. 13.12).

All s orbitals are spherically symmetric, but differ in the number of radial nodes. For instance, the $2s$ orbital has radial nodes where the polynomial factor (Table 13.1) is equal to zero:

$$2 - \frac{\rho}{2} = 0 \text{ at } \rho = 4, \text{ which implies that } r = \frac{2a_0}{Z}$$

(remember that $\rho = 2Zr/a_0$). Hence, the $2s$ orbital of a hydrogenic atom with atomic number Z has a radial node at $2a_0/Z$ (see Fig. 13.5). Similarly, the $3s$ orbital has two nodes which are found by solving

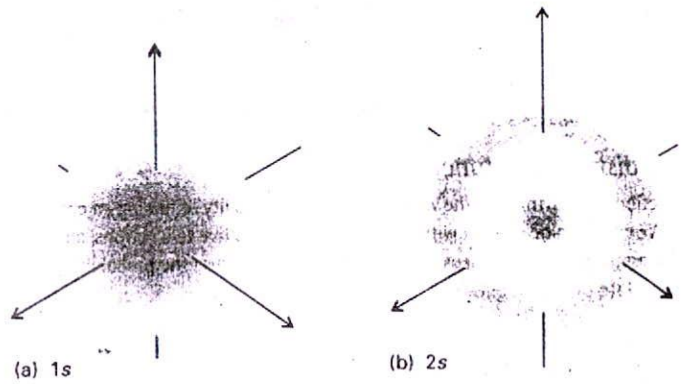
$$6 - 2\rho + (\tfrac{1}{3}\rho)^2 = 0$$

One radial node is at $1.90a_0/Z$ and the other is at $7.10a_0/Z$ (see Fig. 13.5).

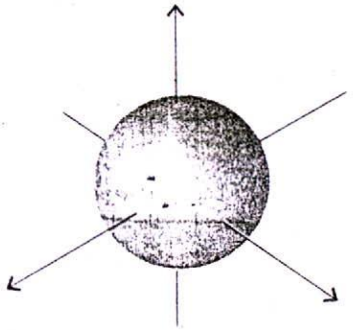
The energies of the s orbitals increase (the electron becomes less tightly bound) as n increases because the average distance of the electron from the nucleus increases. By the virial theorem with $b = -1$ (Section 12.5b, eqn 12.45), $\langle E_K \rangle = -\frac{1}{2}\langle V \rangle$, so, even though the average kinetic energy decreases as n increases, the total energy is equal to $\frac{1}{2}\langle V \rangle$, which becomes less negative as n increases.

Example 13.2 Calculating the mean radius of an orbital

Use hydrogenic orbitals to calculate the mean radius of a $1s$ orbital.



13.11 Representations of the 1*s* and 2*s* hydrogenic atomic orbitals in terms of their electron densities (as represented by the density of shading).



13.12 The boundary surface of an *s* orbital, within which there is a 90 per cent probability of finding the electron.

Method The mean radius is the expectation value

$$\langle r\rangle = \int \psi^{*}\hat{r}\psi\,\mathrm{d}\tau = \int r|\psi|^{2}\,\mathrm{d}\tau$$

We therefore need to evaluate the integral using the wavefunctions given in Table 13.1 and $\mathrm{d}\tau = r^{2}\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$. The angular parts of the wavefunction are normalized in the sense that

$$\int_{0}^{\pi}\int_{0}^{2\pi}|Y_{l,m_l}|^{2}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = 1$$

The integral over r required is given in Example 11.6.

Answer With the wavefunction written in the form $\psi = RY$, the integration is

$$\langle r\rangle = \int_{0}^{\infty}\int_{0}^{\pi}\int_{0}^{2\pi} rR_{n,l}^{2}|Y_{l,m_l}|^{2}r^{2}\,\mathrm{d}r\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi = \int_{0}^{\infty} r^{3}R_{n,l}^{2}\,\mathrm{d}r$$

For a 1*s* orbital,

$$R_{1,0} = 2\left(\frac{Z}{a_0^{3}}\right)^{1/2}\mathrm{e}^{-Zr/a_0}$$

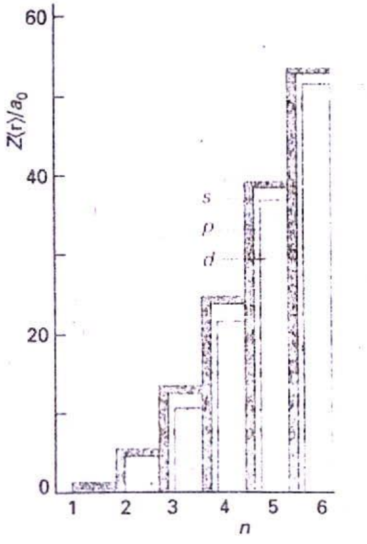
Hence

$$\langle r\rangle = \left(\frac{4Z}{a_0^{3}}\right)\int_{0}^{\infty} r^{3}\mathrm{e}^{-2Zr/a_0}\,\mathrm{d}r = \frac{3a_0}{2Z}$$

Comment The general expression for the mean radius of an orbital with quantum numbers l and n is

$$\langle r\rangle_{n,l} = n^{2}\left\{1 + \tfrac{1}{2}\left(1 - \frac{l(l+1)}{n^{2}}\right)\right\}\frac{a_0}{Z}$$

The variation with n and l is shown in Fig. 13.13. Note that, for a given principal quantum number, the mean radius decreases as l increases.

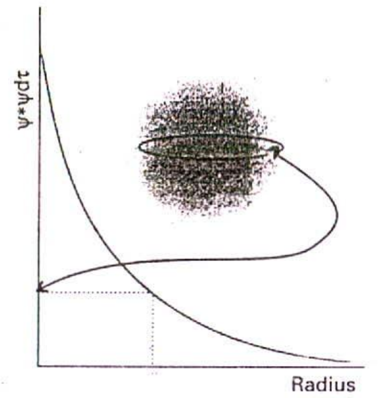


13.13 The variation of the mean radius of a hydrogenic atom with the principal and orbital angular momentum quantum numbers. Note that the mean radius lies in the order $d < p < s$ for a given value of n.

Self-test 13.4 Evaluate the mean radius (a) of a $3s$ orbital by integration, and (b) of a $3p$ orbital by using the general formula.

[(a) $27a_0/2Z$, (b) $25a_0/2Z$]

(e) Radial distribution functions



13.14 A constant-volume electron-sensitive detector (the small cube) gives its greatest reading at the nucleus, and a smaller reading elsewhere. The same reading is obtained anywhere on a circle of given radius: the s orbital is spherically symmetrical.

The wavefunction tells us, through the value of $|\psi|^2$, the probability of finding an electron in any region. We can imagine a probe with a volume $d\tau$ and sensitive to electrons, and which we can move around near the nucleus of a hydrogen atom. Because the probability density in the ground state of the atom is

$$|\psi|^2 \propto e^{-2Zr/a_0}$$

the reading from the detector decreases exponentially as the probe is moved out along any radius but is constant if the probe is moved on a circle of constant radius (Fig. 13.14).

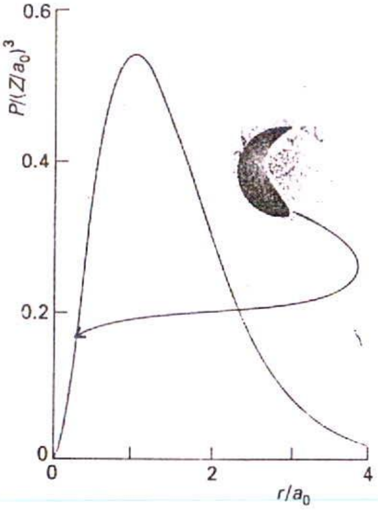
Now consider the probability of finding the electron *anywhere* on a spherical shell of thickness dr at a radius r. The sensitive volume of the probe is now the volume of the shell (Fig. 13.15), which is $4\pi r^2\,dr$. The probability that the electron will be found between the inner and outer surfaces of this shell is the probability density at the radius r multiplied by the volume of the probe, or $|\psi|^2 \times 4\pi r^2\,dr$. This expression has the form $P(r)\,dr$, where

$$P(r) = 4\pi r^2\psi^2 \tag{21}$$

This expression is valid only for spherically symmetric orbitals. For all other orbitals we have to use the more general expression

$$P(r) = r^2R(r)^2 \tag{22}$$

where $R(r)$ is the radial wavefunction for the orbital in question.



13.15 The radial distribution function P gives the probability that the electron will be found anywhere in a shell of radius r. For a $1s$ electron in hydrogen, P is a maximum when r is equal to the Bohr radius a_0. The value of P is equivalent to the reading that a detector shaped like a spherical shell would give as its radius was varied.

Justification [illegible]

The probability of finding an electron in a volume element $d\tau$ when its wavefunction is $\psi = RY$ is $|RY|^2\,d\tau$ with $d\tau = r^2\,dr\sin\theta\,d\theta\,d\phi$. The total probability of finding the electron at any angle at a constant radius is the integral of this probability over the surface of a sphere of radius r, and is written $P(r)dr$, so

$$\begin{aligned} P(r)dr &= \int_0^{2\pi}\int_0^{\pi} R(r)^2|Y(\theta,\phi)|^2 r^2\,dr\sin\theta\,d\theta\,d\phi \\ &= r^2R(r)^2\,dr\int_0^{2\pi}\int_0^{\pi}|Y(\theta,\phi)|^2\sin\theta\,d\theta\,d\phi = r^2R(r)^2\,dr \end{aligned}$$

The last equality follows from the fact that the spherical harmonics are normalized (see Example 13.2). It follows that $P(r) = r^2R(r)^2$, as stated in the text.

The radial distribution function, $P(r)$, is a probability density in the sense that, when it is multiplied by dr, it gives the probability of finding the electron anywhere in a shell of thickness dr at the radius r. For a $1s$ orbital,

$$P(r) = \frac{4Z^3}{a_0^3}r^2e^{-2Zr/a_0} \tag{23}$$

Because r^2 increases with radius from zero at the nucleus, and the exponential term decreases towards zero at infinity, $P(0) = 0$ and $P(r) \to 0$ as $r \to \infty$ and passes through a maximum at an intermediate radius (see Fig. 13.15). The maximum of $P(r)$, which can be found by differentiation, marks the most probable radius at which the electron will be found, and for a 1*s* orbital in hydrogen occurs at $r = a_0$, the Bohr radius. When we carry through the same calculation for the radial distribution function of the 2*s* orbital in hydrogen, we find that the most probable radius is $5.2a_0 = 275$ pm. This larger value reflects the expansion of the atom as its energy increases.

Example 13.3 Calculating the most probable radius

Calculate the most probable radius, r^*, at which an electron will be found when it occupies a 1*s* orbital of a hydrogenic atom of atomic number *Z*, and tabulate the values for the one-electron species from H to Ne^{9+}.

Method We find the radius at which the radial distribution function of the hydrogenic 1*s* orbital has a maximum value by solving $dP/dr = 0$.

Answer The radial distribution function is given in eqn 23. It follows that

$$\frac{dP}{dr} = \frac{4Z^3}{a_0^3}\left(2r - \frac{2Zr^2}{a_0}\right)e^{-2Zr/a_0} = 0$$

at $r = r^*$. Therefore,

$$r^* = \frac{a_0}{Z}$$

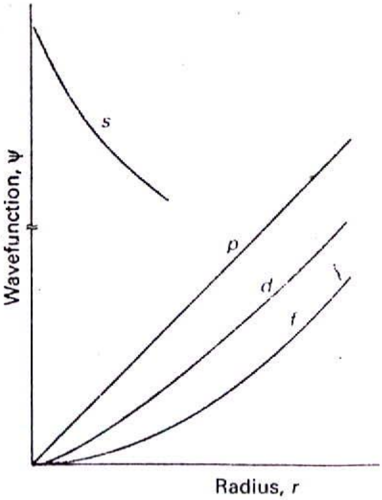
Then, with $a_0 = 52.9$ pm,

	H	He^+	Li^{2+}	Be^{3+}	B^{4+}	C^{5+}	N^{6+}	O^{7+}	F^{8+}	Ne^{9+}
r^*/pm	52.9	26.5	17.6	13.2	10.6	8.82	7.56	6.614	5.88	5.29

Comment Notice how the 1*s* orbital is drawn towards the nucleus as the nuclear charge increases. At uranium the most probable radius is only 0.58 pm, almost 100 times closer than for hydrogen. (On a scale where $r^* = 10$ cm for H, $r^* = 1$ mm for U.) The electron then experiences strong accelerations, and relativistic effects are important.

Self-test 13.5 Find the most probable distance of a 2*s* electron from the nucleus in a hydrogenic atom.

$[(3 + \sqrt{5})a_0/Z]$



13.16 Close to the nucleus, *p* orbitals are proportional to *r*, *d* orbitals are proportional to r^2, and *f* orbitals are proportional to r^3. Electrons are progressively excluded from the neighbourhood of the nucleus as *l* increases. An *s* orbital has a finite, nonzero value at the nucleus.

(f) *p* orbitals

A *p* electron has nonzero angular momentum (its actual magnitude is $2^{1/2}\hbar$). This momentum has a profound effect on the shape of the wavefunction close to the nucleus, for *p* orbitals have zero amplitude at $r = 0$. This difference from *s* orbitals can be understood classically in terms of the centrifugal effect of the angular momentum, which tends to fling the electron away from the nucleus. It is also what we expect from the form of the effective potential energy shown in Fig. 13.4, which rises to infinity as $r \to 0$ and excludes the wavefunction from the nucleus. The same centrifugal effect appears in all orbitals with $l > 0$ (such as the *d* orbitals and the *f* orbitals). We see from eqn 16, in fact, that close to the nucleus a wavefunction is proportional to r^l, so *p* wavefunctions are proportional to *r*, *d* wavefunctions to r^2, and so on (Fig. 13.16). The increasingly strong dependence on *r* as *l* increases can be regarded classically as the outcome of increasing centrifugal effects arising from the angular momentum. As remarked previously, all orbitals with $l > 0$ have zero amplitude at the nucleus, and consequently zero probability of finding the electron there.

The three 2*p* orbitals are distinguished by the three different values that m_l can take when $l = 1$. Because the quantum number m_l tells us the angular momentum around an axis, these different values of m_l denote orbitals in which the electron has different angular momenta around an arbitrary z-axis but the same magnitude of momentum (because l is the same for all three). The orbital with $m_l = 0$, for instance, has zero angular momentum around the z-axis. Its angular variation is proportional to $\cos\theta$, so the probability density, which is proportional to $\cos^2\theta$, has its maximum value on either side of the nucleus along the z-axis (at $\theta = 0$ and $180°$).

The wavefunction of a $2p$ orbital with $m_l = 0$ is

$$p_0 = R_{2,1}(r)Y_{1,0}(\theta,\phi) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta\,\mathrm{e}^{-Zr/2a_0}$$
$$= r\cos\theta f(r)$$

where $f(r)$ is a function only of r. Because in spherical polar coordinates $z = r\cos\theta$, this wavefunction may also be written

$$p_z = zf(r) \tag{24}$$

All p-orbitals with $m_l = 0$ have wavefunctions of this form regardless of the value of n. This way of writing the orbital is the origin of the name 'p_z-orbital': its boundary surface is shown in Fig. 13.17. The wavefunction is zero everywhere in the xy-plane, where $z = 0$, so the xy-plane is a nodal plane of the orbital: the wavefunction changes sign on going from one side of the plane to the other.

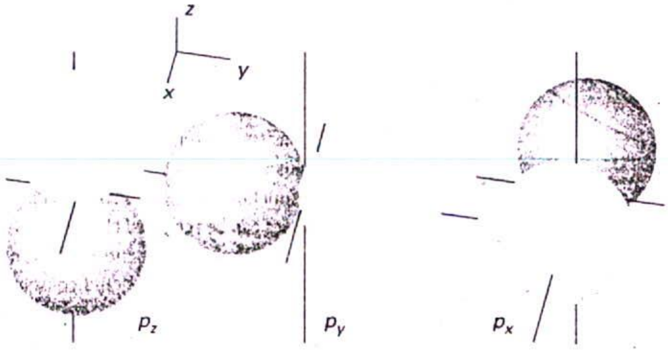
The wavefunctions of $2p$ orbitals with $m_l = \pm1$ have the following form:

$$p_{\pm1} = R_{2,1}(r)Y_{1,\pm1}(\theta,\phi) = \mp\frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r\mathrm{e}^{-Zr/2a_0}\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}$$
$$= \mp\frac{1}{2^{1/2}}r\sin\theta\,\mathrm{e}^{\pm\mathrm{i}\phi}f(r)$$

These functions do have angular momentum about the z-axis: as we have seen (in Section 12.6b), wavefunctions with this ϕ dependence correspond to a particle with angular momentum either clockwise or counter-clockwise around the z-axis: $\mathrm{e}^{+\mathrm{i}\phi}$ corresponds to clockwise rotation when viewed from below, and $\mathrm{e}^{-\mathrm{i}\phi}$ corresponds to counter-clockwise rotation (from the same viewpoint). They have zero amplitude where $\theta = 0$ and $180°$ (along the z-axis) and maximum amplitude at $90°$, which is in the xy-plane. To draw the functions it is usual to take the real linear combinations

$$\begin{aligned} p_x &= -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r\sin\theta\cos\phi f(r) = xf(r) \\ p_y &= \frac{\mathrm{i}}{2^{1/2}}(p_{+1} + p_{-1}) = r\sin\theta\sin\phi f(r) = yf(r) \end{aligned} \tag{25}$$

These linear combinations are standing waves with no net angular momentum around the z-axis, as they are composed of equal and opposite values of m_l. The p_x orbital has the same



13.17 The boundary surfaces of p orbitals. A nodal plane passes through the nucleus and separates the two lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction.

shape as a p_z orbital, but it is directed along the x-axis (see Fig. 13.17); the p_y orbital is similarly directed along the y-axis. The wavefunction of any p orbital of a given shell can be written as a product of x, y, or z and the same radial function (which depends on the value of n).

Justification 13.4

In this remark, we justify the step of taking linear combinations of degenerate orbitals when we want to indicate a particular point. The freedom to do so rests on the fact that, whenever two or more wavefunctions correspond to the same energy, any linear combination of them is an equally valid solution of the Schrödinger equation.

Suppose ψ_1 and ψ_2 are both solutions of the Schrödinger equation with energy E; then we know that

$$H\psi_1 = E\psi_1 \qquad H\psi_2 = E\psi_2$$

Now consider the linear combination

$$\psi = c_1\psi_1 + c_2\psi_2$$

where c_1 and c_2 are arbitrary coefficients. Then it follows that

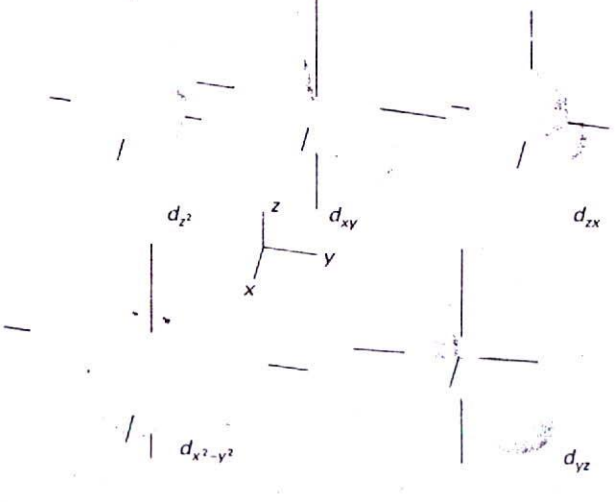
$$\begin{aligned} H\psi &= H(c_1\psi_1 + c_2\psi_2) = c_1 H\psi_1 + c_2 H\psi_2 \\ &= c_1 E\psi_1 + c_2 E\psi_2 = E\psi \end{aligned}$$

Hence, the linear combination is also a solution corresponding to the same energy E.

(g) *d* orbitals

When $n = 3$, l can be 0, 1, or 2. As a result, this shell consists of one $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals. The five d orbitals have $m_l = +2, +1, 0, -1, -2$ and correspond to five different angular momenta around the z-axis (but the same magnitude of angular momentum, because $l = 2$ in each case). As for the p orbitals, d orbitals with opposite values of m_l (and hence opposite senses of motion around the z-axis) may be combined in pairs to give real standing waves, and the boundary surfaces of the resulting shapes are shown in Fig. 13.18. The real combinations have the following forms:

$$\begin{aligned} &d_{xy} = xyf(r) \qquad d_{yz} = yzf(r) \qquad d_{zx} = zxf(r) \\ &d_{x^2-y^2} = \tfrac{1}{2}(x^2 - y^2)f(r) \qquad d_{z^2} = \tfrac{1}{2\sqrt{3}}(3z^2 - r^2)f(r) \end{aligned} \tag{26}$$



13.18 The boundary surfaces of d orbitals. Two nodal planes in each orbital intersect at the nucleus and separate the lobes of each orbital. The dark and light areas denote regions of opposite sign of the wavefunction.

13.3 Spectroscopic transitions and selection rules

The energies of the hydrogenic atoms are given by eqn 13. When the electron undergoes a **transition**, a change of state, from an orbital with quantum numbers n_1, l_1, m_{l1} to another (lower energy) orbital with quantum numbers n_2, l_2, m_{l2}, it undergoes a change of energy ΔE and discards the excess energy as a photon of electromagnetic radiation with a frequency ν given by the Bohr frequency condition (eqn 4).

It is tempting to think that all possible transitions are permissible, and that a spectrum arises from the transition of an electron from any initial orbital to any other orbital. However, this is not so, because a photon has an intrinsic spin angular momentum corresponding to $s = 1$ (Section 12.8). The change in angular momentum of the electron must compensate for the angular momentum carried away by the photon. Thus, an electron in a d orbital ($l = 2$) cannot make a transition into an s orbital ($l = 0$) because the photon cannot carry away enough angular momentum. Similarly, an s electron cannot make a transition to another s orbital, because there would then be no change in the electron's angular momentum to make up for the angular momentum carried away by the photon. It follows that some spectroscopic transitions are **allowed**, meaning that they can occur, whereas others are **forbidden**, meaning that they cannot occur.

A **selection rule** is a statement about which transitions are allowed. They are derived (for atoms) by identifying the transitions that conserve angular momentum when a photon is emitted or absorbed. The selection rules for hydrogenic atoms are

$$\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1 \tag{27}$$

The principal quantum number n can change by any amount consistent with the Δl for the transition, because it does not relate directly to the angular momentum.

Justification 13.5

The formal derivation of a selection rule is based on the evaluation of a **transition dipole moment**, $\boldsymbol{\mu}_{\mathrm{fi}}$, between the initial and final states, where

$$\boldsymbol{\mu}_{\mathrm{fi}} = \langle \mathrm{f}|\boldsymbol{\mu}|\mathrm{i}\rangle \tag*{[28]}$$

and $\boldsymbol{\mu}$ is the electric dipole moment operator. For a one-electron atom it is identified with multiplication by $-e\boldsymbol{r}$ with components $\mu_x = -ex$, $\mu_y = -ey$, and $\mu_z = -ez$. If the transition dipole moment is zero, the transition is forbidden. If it is nonzero, the transition is allowed and its intensity is proportional to the square modulus of the transition dipole moment. Physically, the transition dipole moment is a measure of the dipolar 'kick' that the electron gives to or receives from the electromagnetic field. To evaluate a transition dipole moment, we consider each component in turn. For example, for the z-component,

$$\mu_{z,\mathrm{fi}} = -e\langle \mathrm{f}|z|\mathrm{i}\rangle = -e\int \psi_{\mathrm{f}}^{*} z \psi_{\mathrm{i}}\,\mathrm{d}\tau \tag{29}$$

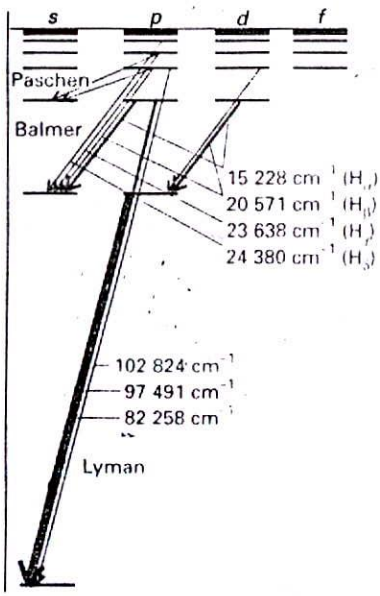
To evaluate the integral, we note from Table 12.3 that $z = (4\pi/3)^{1/2} r Y_{1,0}$, so

$$\int \psi_{\mathrm{f}}^{*} z \psi_{\mathrm{i}}\,\mathrm{d}\tau = \left(\frac{4\pi}{3}\right)^{1/2} \int_0^{\infty} R_{n_{\mathrm{f}},l_{\mathrm{f}}}^{*} r R_{n_{\mathrm{i}},l_{\mathrm{i}}} r^2\,\mathrm{d}r \\ \times \int_0^{\pi}\int_0^{2\pi} Y_{l_{\mathrm{f}},m_{l,\mathrm{f}}}^{*}(\theta,\phi) Y_{1,0}(\theta,\phi) Y_{l_{\mathrm{i}},m_{l,\mathrm{i}}}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

It follows from the properties of the spherical harmonics (Table 12.3) that the integral

$$\int_0^{\pi}\int_0^{2\pi} Y_{l_{\mathrm{f}},m_{l,\mathrm{f}}}^{*}(\theta,\phi) Y_{1,m}(\theta,\phi) Y_{l_{\mathrm{i}},m_{l,\mathrm{i}}}(\theta,\phi)\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

is zero unless $l_f = l_i \pm 1$ and $m_{l,f} = m_{l,i} + m$. Because $m = 0$ in the present case, the angular integral, and hence the z-component of the transition dipole moment, is zero unless $\Delta l = \pm 1$ and $\Delta m_l = 0$, which is a part of the set of selection rules. The same procedure, but considering the x- and y-components, results in the complete set of rules.



13.19 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. The thicker the line, the more intense the transition.

Illustration

To identify the orbitals to which a $4d$ electron may make radiative transitions, we first identify the value of l and then apply the selection rule for this quantum number. Because $l = 2$, the final orbital must have $l = 1$ or 3. Thus, an electron may make a transition from a $4d$ orbital to any np orbital (subject to $\Delta m_l = 0, \pm 1$) and to any nf orbital (subject to the same rule). However, it cannot undergo a transition to any other orbital, so a transition to any ns orbital or to another nd orbital is forbidden.

Self-test 13.6 To what orbitals may a $4s$-electron make radiative transitions?

[To np orbitals only]

The selection rules account for the structure of a **Grotrian diagram** (Fig. 13.19), which summarizes the energies of the states and the transitions between them. The thicknesses of the transition lines in the diagram denote their relative intensities in the spectrum.

The structures of many-electron atoms

The Schrödinger equation for a many-electron atom is highly complicated because all the electrons interact with one another. Even for a helium atom, with its two electrons, no analytical expression for the orbitals and energies can be given, and we are forced to make approximations. We shall adopt a simple approach based on what we already know about the structure of hydrogenic atoms. Later we shall see the kind of numerical computations that are currently used to obtain accurate wavefunctions and energies.

13.4 The orbital approximation

The wavefunction of a many-electron atom is a very complicated function of the coordinates of all the electrons, and we should write it $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$, where $\boldsymbol{r}_i$ is the vector from the nucleus to electron i. However, in the **orbital approximation** we suppose that a reasonable first approximation to this exact wavefunction is obtained by thinking of each electron as occupying its 'own' orbital, and writing

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots) = \psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)\ldots \qquad (30)$$

We can think of the individual orbitals as resembling the hydrogenic orbitals, but with nuclear charges that are modified by the presence of all the other electrons in the atom. This description is only approximate, but it is a useful model for discussing the chemical properties of atoms, and is the starting point for more sophisticated descriptions of atomic structure.

Justification 13.6

The orbital approximation would be exact if there were no interactions between electrons. To demonstrate the validity of this remark, we need to consider a system in which the hamiltonian for the energy is the sum of two contributions, one for electron 1 and the other for electron 2:

$$H = H_1 + H_2$$

In an actual atom (such as helium atom), there is an additional term corresponding to the interaction of the two electrons, but we are ignoring that term. We shall now show that, if $\psi(r_1)$ is an eigenfunction of H_1 with energy E_1, and $\psi(r_2)$ is an eigenfunction of H_2 with energy E_2, then the product $\Psi(r_1, r_2) = \psi(r_1)\psi(r_2)$ is an eigenfunction of the combined hamiltonian H. To do so we write

$$\begin{aligned} H\Psi(r_1, r_2) &= (H_1 + H_2)\psi(r_1)\psi(r_2) \\ &= \{H_1\psi(r_1)\}\psi(r_2) + \psi(r_1)\{H_2\psi(r_2)\} \\ &= \{E_1\psi(r_1)\}\psi(r_2) + \psi(r_1)\{E_2\psi(r_2)\} \\ &= (E_1 + E_2)\psi(r_1)\psi(r_2) = E\Psi(r_1, r_2) \end{aligned}$$

where $E = E_1 + E_2$. This is the result we need to prove. However, if the electrons interact (as they do in fact), then the proof fails.

(a) The helium atom

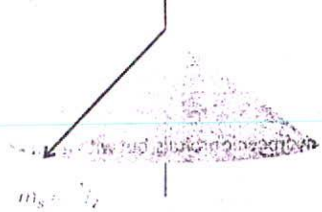
The orbital approximation allows us to express the electronic structure of an atom by reporting its **configuration**, the list of occupied orbitals (usually, but not necessarily, in its ground state). Thus, as the ground state of a hydrogenic atom consists of the single electron in a $1s$ orbital, we report its configuration as $1s^1$.

The He atom has two electrons. We can imagine forming the atom by adding the electrons in succession to the orbitals of the bare nucleus (of charge $2e$). The first electron occupies a $1s$ hydrogenic orbital, but because $Z = 2$ that orbital is more compact than in H itself. The second electron joins the first in the $1s$ orbital, so the electron configuration of the ground state of He is $1s^2$.

(b) The Pauli principle

Lithium, with $Z = 3$, has three electrons. The first two occupy a $1s$ orbital drawn even more closely than in He around the more highly charged nucleus. The third electron, however, does not join the first two in the $1s$ orbital because that configuration is forbidden by the **Pauli exclusion principle**:

> **No more than two electrons may occupy any given orbital and, if two do occupy one orbital, then their spins must be paired.**



13.20 Electrons with paired spins have zero resultant spin angular momentum. They can be represented by two vectors that lie at an indeterminate position on the cones shown here but, wherever one lies on its cone, the other points in the opposite direction; their resultant is zero.

Electrons with paired spins, which we denote ↑↓, have zero net spin angular momentum because the spin of one electron is cancelled by the spin of the other. Specifically, one electron has $m_s = +\frac{1}{2}$, the other has $m_s = -\frac{1}{2}$, and they are orientated on their respective cones so that the resultant spin is zero (Fig. 13.20). The exclusion principle is the key to the structure of complex atoms, to chemical periodicity, and to molecular structure. It was proposed by Wolfgang Pauli in 1924 when he was trying to account for the absence of some lines in the spectrum of helium. Later he was able to derive a very general form of the principle from theoretical considerations.

Justification 13.7

The Pauli exclusion principle in fact applies to any pair of identical fermions (particles with half integral spin). Thus it applies to protons, neutrons, and ^{13}C nuclei (all of which have spin $\frac{1}{2}$) and to ^{35}Cl nuclei (which have spin $\frac{3}{2}$). It does not apply to identical bosons (particles with integral spin), which include photons (spin 1), ^{12}C nuclei (spin 0). Any number of identical bosons may occupy the same orbital.

The Pauli exclusion principle is a special case of a general statement called the Pauli principle:

> **When the labels of any two identical fermions are exchanged, the total wavefunction changes sign. When the labels of any two identical bosons are exchanged, the total wavefunction retains the same sign.**

By 'total wavefunction' is meant the entire wavefunction, including the spin of the particles.

Consider the wavefunction for two electrons $\Psi(1,2)$. The Pauli principle implies that it is a fact of nature (which has its roots in the theory of relativity) that the wavefunction must change sign if we interchange the labels 1 and 2 wherever they occur in the function:

$$\Psi(2,1) = -\Psi(1,2) \tag{31}$$

Suppose the two electrons in an atom occupy an orbital ψ, then in the orbital approximation the overall wavefunction is $\psi(1)\psi(2)$. To apply the Pauli principle, we must deal with the *total* wavefunction, the wavefunction including spin. There are several possibilities for two spins: both α, denoted $\alpha(1)\alpha(2)$, both β, denoted $\beta(1)\beta(2)$, and one α the other β, denoted either $\alpha(1)\beta(2)$ or $\alpha(2)\beta(1)$. Because we cannot tell which electron is α and which is β, in the last case it is appropriate to express the spin states as the (normalized) linear combinations

$$\sigma_+(1,2) = \frac{1}{2^{1/2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} \qquad \sigma_-(1,2) = \frac{1}{2^{1/2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{32}$$

because these allow one spin to be α and the other β with equal probability. The total wavefunction of the system is therefore the product of the orbital part and one of the four spin states:

$$\psi(1)\psi(2)\alpha(1)\alpha(2) \quad \psi(1)\psi(2)\beta(1)\beta(2) \quad \psi(1)\psi(2)\sigma_+(1,2) \quad \psi(1)\psi(2)\sigma_-(1,2)$$

The Pauli principle says that, for a wavefunction to be acceptable (for electrons), it must change sign when the electrons are exchanged. In each case, exchanging the labels 1 and 2 converts the factor $\psi(1)\psi(2)$ into $\psi(2)\psi(1)$, which is the same, because the order of multiplying the functions does not change the value of the product. The same is true of $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$. Therefore, the first two overall products are not allowed, because they do not change sign. The combination $\sigma_+(1,2)$ changes to

$$\sigma_+(2,1) = \frac{1}{2^{1/2}}\{\alpha(2)\beta(1) + \beta(2)\alpha(1)\} = \sigma_+(1,2)$$

because it is simply the original function written in a different order. The third overall product is therefore also disallowed. Finally, consider $\sigma_-(1,2)$:

$$\begin{aligned}\sigma_-(2,1) &= \frac{1}{2^{1/2}}\{\alpha(2)\beta(1) - \beta(2)\alpha(1)\} = -\frac{1}{2^{1/2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}\\ &= -\sigma_-(1,2)\end{aligned}$$

This combination does change sign (it is 'antisymmetric'). The product $\psi(1)\psi(2)\sigma_-(1,2)$ also changes sign under particle exchange, and therefore it is acceptable.

Now we see that only one of the four possible states is allowed by the Pauli principle, and the one that survives has paired α and β spins.[2] This is the content of the Pauli exclusion principle. The exclusion principle is irrelevant when the orbitals occupied by the

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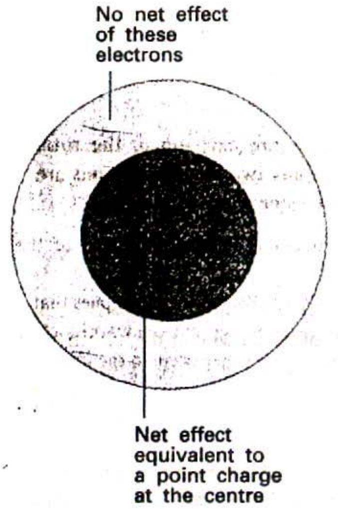
[2] The distinction between σ_+ and σ_-, which both have one α and one β spin, is explained in Section 13.7.

electrons are different, and both electrons may then have (but need not have) the same spin state. Nevertheless, even then the overall wavefunction must still be antisymmetric overall, and must still satisfy the Pauli principle itself.

In Li ($Z = 3$), the third electron cannot enter the $1s$ orbital because that orbital is already full: we say the K shell is **complete** and that the two electrons form a **closed shell.** Because a similar closed shell is characteristic of the He atom, we denote it [He]. The third electron is excluded from the K shell and must occupy the next available orbital, which is one with $n = 2$ and hence belonging to the L shell. However, we now have to decide whether the next available orbital is the $2s$ orbital or a $2p$ orbital, and therefore whether the lowest energy configuration of the atom is [He]$2s^1$ or [He]$2p^1$.



13.21 An electron at a distance r from the nucleus experiences a Coulombic repulsion from all the electrons within a sphere of radius r and which is equivalent to a point negative charge located on the nucleus. The negative charge reduces the effective nuclear charge of the nucleus from Ze to $Z_{\text{eff}}e$.

(c) Penetration and shielding

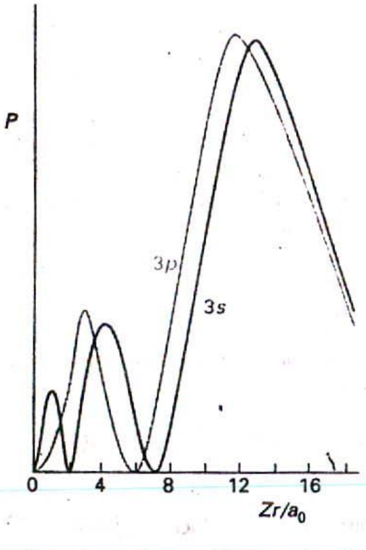
Unlike in hydrogenic atoms, the $2s$ and $2p$ orbitals (and, in general, all subshells of a given shell) are not degenerate in many-electron atoms. For reasons we shall now explain, s orbitals generally lie lower in energy than p orbitals of a given shell, and p orbitals lie lower than d orbitals.

An electron in a many-electron atom experiences a Coulombic repulsion from all the other electrons present. If it is at a distance r from the nucleus, it experiences a repulsion that can be represented by a point negative charge located at the nucleus and equal in magnitude to the total charge of the electrons within a sphere of radius r (Fig. 13.21). The effect of this point negative charge, when averaged over all the locations of the electron, is to reduce the full charge of the nucleus from Ze to $Z_{\text{eff}}e$, the **effective nuclear charge.** We say that the electron experiences a **shielded** nuclear charge, and the difference between Z and Z_{eff} is called the shielding constant, σ:

$$Z_{\text{eff}} = Z - \sigma \qquad [33]$$

The electrons do not actually 'block' the full Coulombic attraction of the nucleus: the shielding constant is simply a way of expressing the net outcome of the nuclear attraction and the electronic repulsions in terms of a single equivalent charge at the centre of the atom.

The shielding constant is different for s and p electrons because they have different radial distributions (Fig. 13.22). An s electron has a greater **penetration** through inner shells than a p electron, in the sense that it is more likely to be found close to the nucleus than a p electron of the same shell (the wavefunction of a p orbital, remember, is zero at the nucleus). Because only electrons inside the sphere defined by the location of the electron (in effect, the core electrons) contribute to shielding, an s electron experiences less shielding than a p electron. Consequently, by the combined effects of penetration and shielding, an s electron is more tightly bound than a p electron of the same shell. Similarly, a d electron penetrates less than a p electron of the same shell (recall that the wavefunction of a d orbital varies as r^2 close to the nucleus, whereas a p orbital varies as r), and therefore experiences more shielding.



13.22 An electron in an s orbital (here a $3s$ orbital) is more likely to be found close to the nucleus than an electron in a p orbital of the same shell (note the closeness of the innermost peak of the $3s$ orbital to the nucleus at $r = 0$). Hence an s electron experiences less shielding and is more tightly bound than a p electron.

Shielding constants for different types of electrons in atoms have been calculated from their wavefunctions obtained by numerical solution of the Schrödinger equation for the atom (Table 13.3). We see that, in general, valence-shell s electrons do experience higher effective nuclear charges than p electrons, although there are some discrepancies. We return to this point shortly.

The consequence of penetration and shielding is that the energies of subshells in a many-electron atom in general lie in the order

$$s < p < d < f$$

Table 13.3* Screening constants for atoms

Element	Z	Orbital	σ
He	2	1*s*	0.3125
C	6	1*s*	0.3273
		2*s*	2.7834
		2*p*	2.8642

*More values are given in the *Data section* at the end of this volume.

The individual orbitals of a given subshell remain degenerate because they all have the same radial characteristics and so experience the same effective nuclear charge.

We can now complete the Li story. Because the shell with $n = 2$ consists of two non-degenerate subshells, with the 2*s* orbital lower in energy than the three 2*p* orbitals, the third electron occupies the 2*s* orbital. This occupation results in the ground-state configuration $1s^2 2s^1$, with the central nucleus surrounded by a complete helium-like shell of two 1*s* electrons, and around that a more diffuse 2*s* electron. The electrons in the outermost shell of an atom in its ground state are called the **valence electrons** because they are largely responsible for the chemical bonds that the atom forms. Thus, the valence electron in Li is a 2*s* electron and its other two electrons belong to its core.

(d) The building-up principle

The extension of the procedure used for H, He, and Li to other atoms is called the **building-up principle**, or the '*Aufbau* principle', from the German word for building up. The building-up principle proposes an order of occupation of the hydrogenic orbitals that accounts for the experimentally determined ground-state configurations of neutral atoms.[3]

We imagine the bare nucleus of atomic number *Z*, and then feed into the orbitals *Z* electrons in succession. The order of occupation is

$$1s \quad 2s \quad 2p \quad 3s \quad 3p \quad 4s \quad 3d \quad 4p \quad 5s \quad 4d \quad 5p \quad 6s \ldots$$

and each orbital may accommodate up to two electrons. This order of occupation is approximately the order of energies of the individual orbitals, because, in general, the lower the energy of the orbital, the lower the total energy of the atom as a whole when that orbital is occupied. However, there are complicating effects arising from electron–electron repulsions that are important when the orbitals have very similar energies (such as the 4*s* and 3*d* orbitals near Ca and Sc), and we must take special care then.

We feed the *Z* electrons in succession into the orbitals subject to the demand of the exclusion principle that no more than two electrons can occupy any one orbital. Because an *s* subshell consists of only one orbital, up to two electrons may occupy it. A *p* subshell consists of three orbitals, so it can accommodate up to six electrons; a *d* subshell consists of five orbitals and can accommodate up to ten electrons.

As an example, consider the carbon atom, for which $Z = 6$ and there are six electrons to accommodate. Two electrons enter and fill the 1*s* orbital, two enter and fill the 2*s* orbital, leaving two electrons to occupy the orbitals of the 2*p* subshell. Hence the ground-state configuration of C is $1s^2 2s^2 2p^2$, or more succinctly $[\mathrm{He}]2s^2 2p^2$, with [He] the helium-like $1s^2$ core. However, we can be more precise: we can expect the last two electrons to occupy different 2*p* orbitals because they will then be further apart on average and repel each other less than if they were in the same orbital. Thus one electron can be thought of as occupying the $2p_x$ orbital and the other the $2p_y$ orbital (the *x*, *y*, *z* designation is arbitrary, and it would be equally valid to use the complex forms of these orbitals), and the lowest energy configuration of the atom is $[\mathrm{He}]2s^2 2p_x^1 2p_y^1$. The same rule applies whenever degenerate orbitals of a subshell are available for occupation. Thus, another rule of the building-up principle is:

> **Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.**

Thus nitrogen ($Z = 7$) has the configuration $[\mathrm{He}]2s^2 2p_x^1 2p_y^1 2p_z^1$, and only when we get to oxygen ($Z = 8$) is a 2*p* orbital doubly occupied, giving $[\mathrm{He}]2s^2 2p_x^2 2p_y^1 2p_z^1$.

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[3] Electron configurations are determined either spectroscopically or by measurements of magnetic properties.

An additional point arises when electrons occupy orbitals singly, for there is then no requirement that their spins should be paired. We need to know whether the lowest energy is achieved when the electron spins are the same (both α, for instance, denoted $\uparrow\uparrow$, if there are two electrons in question, as in C) or when they are paired ($\uparrow\downarrow$). This question is resolved by an empirical observation known as **Hund's rule**:

> **An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.**

The explanation of Hund's rule is subtle, but it reflects the quantum mechanical property of **spin correlation**, that, as demonstrated in the *Justification* below, electrons with parallel spins behave as if they have a tendency to stay well apart, and hence repel each other less.[4] We can now conclude that, in the ground state of the carbon atom, the two $2p$ electrons have the same spin, that all three $2p$ electrons in the N atoms have the same spin, and that the two $2p$ electrons in different orbitals in the O atom have the same spin (the two in the $2p_x$ orbital are necessarily paired).

Justification 13.8

Suppose electron 1 is described by a wavefunction $\psi_a(r_1)$ and electron 2 is described by a wavefunction $\psi_b(r_2)$; then, in the orbital approximation, the joint wavefunction of the electrons is the product $\Psi = \psi_a(r_1)\psi_b(r_2)$. However, this wavefunction is not acceptable, because it suggests that we know which electron is in which orbital, whereas we cannot keep track of electrons. According to quantum mechanics, the correct description is either of the two following wavefunctions:

$$\Psi_{\pm} = \frac{1}{2^{1/2}}\{\psi_a(r_1)\psi_b(r_2) \pm \psi_b(r_1)\psi_a(r_2)\}$$

According to the Pauli principle (*Justification 13.7*), because Ψ_+ is symmetrical under particle interchange, it must be multiplied by an antisymmetric spin function (the one denoted σ_- in *Justification 13.7*). That combination corresponds to a spin-paired state. Conversely, Ψ_- is antisymmetric, so it must be multiplied by one of the three symmetric spin states. These three symmetric states correspond to electrons with parallel spins.[5]

Now consider the values of the two combinations when one electron approaches another, and $r_1 = r_2$. We see that Ψ_- vanishes, which means that there is zero probability of finding the two electrons at the same point in space when they have parallel spins. The other combination does not vanish when the two electrons are at the same point in space. Because the two electrons have different relative spatial distributions depending on whether their spins are parallel or not, it follows that their Coulombic interaction is different, and hence that the two states have different energies.

Neon, with $Z = 10$, has the configuration [He]$2s^2 2p^6$, which completes the L shell. This closed-shell configuration is denoted [Ne], and acts as a core for subsequent elements. The next electron must enter the $3s$ orbital and begin a new shell, so an Na atom, with $Z = 11$, has the configuration [Ne]$3s^1$. Like lithium with the configuration [He]$2s^1$, sodium has a single s electron outside a complete core.

This analysis has brought us to the origin of chemical periodicity. The L shell is completed by eight electrons, so the element with $Z = 3$ (Li) should have similar properties to the

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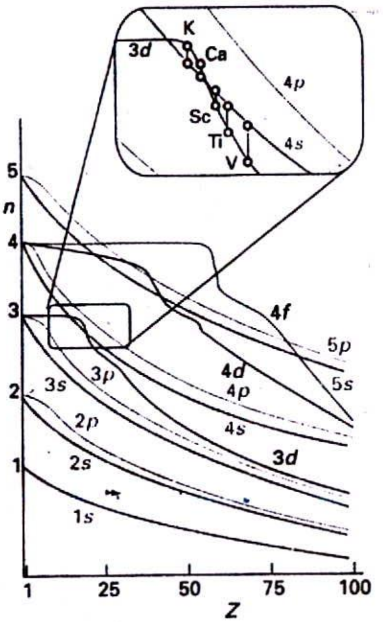
[4] The effect of spin correlation is to allow the atom to shrink slightly, so the electron-nucleus interaction is improved when the spins are parallel.

[5] See Section 13.7 for an explanation of this point.



13.23 The orbital energies of the elements. Note the relative energies of the 3*d* and 4*s* orbitals close to potassium (see inset).

element with $Z = 11$ (Na). Likewise, Be ($Z = 4$) should be similar to $Z = 12$ (Mg), and so on, up to the noble gases He ($Z = 2$), Ne ($Z = 10$), and Ar ($Z = 18$).

Argon has complete 3*s* and 3*p* subshells, and as the 3*d* orbitals are high in energy it counts as having a closed-shell configuration. Indeed, the 3*d* orbitals are so high in energy that the next electron (for K) occupies the 4*s* orbital, and the configuration of a K atom is analogous to that of an Na atom. The same is true of a Ca atom, which has the configuration $[\mathrm{Ar}]4s^2$. However, at this point, the 3*d* orbitals become comparable in energy to the 4*s* orbitals (Fig. 13.23), and they commence to be filled.

Ten electrons can be accommodated in the five 3*d* orbitals, which accounts for the electron configurations of scandium to zinc. However, the building-up principle has less clear-cut predictions about the ground-state configurations of these elements because electron–electron repulsions are comparable to the energy difference between the 4*s* and 3*d* orbitals, and a simple analysis no longer works. At gallium, the energy of the 3*d* orbitals has fallen so far below those of the 4*s* and 4*p* orbitals that the 3*d* orbitals can be largely ignored, and the building-up principle can be used in the same way as in preceding periods. Now the 4*s* and 4*p* subshells constitute the valence shell, and the period terminates with krypton. Because 18 electrons have intervened since argon, this period is the first 'long period' of the periodic table. The existence of the *d*-block elements (the 'transition metals') reflects the stepwise occupation of the 3*d* orbitals, and the subtle shades of energy differences along this series give rise to the rich complexity of inorganic *d*-metal chemistry. A similar intrusion of the *f* orbitals in Periods 6 and 7 accounts for the existence of the *f* block of the periodic table (the lanthanides and actinides).

(e) The configurations of ions

We derive the configurations of cations of elements in the *s*, *p*, and *d* blocks of the periodic table by removing electrons from the ground-state configuration of the neutral atom in a specific order. First, we remove valence *p* electrons, then valence *s* electrons, and then as many *d* electrons as are necessary to achieve the stated charge. For instance, because the configuration of Fe is $[\mathrm{Ar}]3d^6 4s^2$, the Fe^{3+} cation has the configuration $[\mathrm{Ar}]3d^5$.

The configurations of anions are derived by continuing the building-up procedure and adding electrons to the neutral atom until the configuration of the next noble gas has been reached. Thus, the configuration of the O^{2-} ion is achieved by adding two electrons to $[\mathrm{He}]2s^2 2p^4$, giving $[\mathrm{He}]2s^2 2p^6$, the same as the configuration of neon.

(f) Ionization energies and electron affinities

The minimum energy necessary to remove an electron from a many-electron atom is the **first ionization energy**, I_1, of the element.[6] The **second ionization energy**, I_2, is the minimum energy needed to remove a second electron (from the singly charged cation). The variation of the first ionization energy through the periodic table is shown in Fig. 13.24, and some numerical values are given in Table 13.4. In thermodynamic considerations we often need the standard enthalpy of ionization, $\Delta_{\mathrm{ion}}H^{\ominus}$. As shown in the *Justification* below, the two are related by

$$\Delta_{\mathrm{ion}}H^{\ominus}(T) = I + \tfrac{5}{2}RT \tag{34}$$

At 298 K, the difference between the ionization enthalpy and the corresponding ionization energy is 6.20 kJ mol^{-1}.

Table 13.4* First and second ionization energies, $I_1/(\mathrm{kJ\ mol^{-1}})$ and $I_2/(\mathrm{kJ\ mol^{-1}})$

H	1312	
He	2372	5251
Mg	738	1451
Na	496	4562

* More values are given in the *Data section*.

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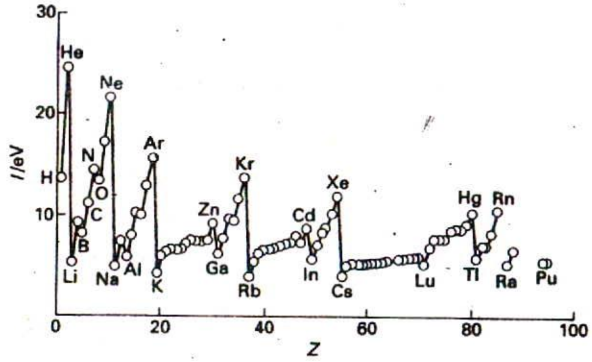
[6] The symbol recommended by IUPAC for ionization energy is E_i; but this notation is open to confusion.



13.24 The first ionization energies of the elements plotted against atomic number.

Justification 13.9

It follows from Kirchhoff's law (Section 2.9 and eqn 2.45) that the reaction enthalpy for

$$\mathrm{M(g)} \longrightarrow \mathrm{M^+(g)} + \mathrm{e^-(g)}$$

at a temperature T is related to the value at $T = 0$ by

$$\Delta_r H^\ominus(T) = \Delta_r H^\ominus(0) + \int_0^T \Delta_r C_p{}^\ominus \, \mathrm{d}T$$

The molar constant-pressure heat capacity of each species in the reaction is $\frac{5}{2}R$, so $\Delta_r C_p^\ominus = +\frac{5}{2}R$. The integral in this expression therefore evaluates to $+\frac{5}{2}RT$. The reaction enthalpy at $T = 0$ is the same as the (molar) ionization energy, I. Equation 34 then follows. The same expression applies to each successive ionization step, so the *overall* ionization enthalpy for the formation of $\mathrm{M^{2+}}$ is

$$\Delta_r H^\ominus(T) = I_1 + I_2 + 5RT$$

Table 13.5* Electron affinities, $E_{ea}/(\mathrm{kJ\ mol^{-1}})$

Cl	349		
F	322		
H	73		
O	141	$\mathrm{O^-}$	−844

*More values are given in the *Data section.*

The **electron affinity**, E_{ea}, is the energy released when an electron attaches to a gas-phase atom (Table 13.5). In a common, logical, but not universal convention (which we adopt), the electron affinity is positive if energy is released when the electron attaches to the atom (that is, $E_{ea} > 0$ implies that electron attachment is exothermic). It follows from a similar argument to that given in the *Justification* above that the **standard enthalpy of electron gain**, $\Delta_{eg}H^\ominus$, at a temperature T is related to the electron affinity by

$$\Delta_{eg}H^\ominus(T) = -E_{ea} - \tfrac{5}{2}RT \tag{35}$$

Note the change of sign. In typical thermodynamic cycles the $\frac{5}{2}RT$ that appears in eqn 35 cancels that in eqn 34, so ionization energies and electron affinities can be used directly. A final preliminary point is that the electron-gain enthalpy of a species X is the negative of the ionization enthalpy of its negative ion:

$$\Delta_{eg}H^\ominus(\mathrm{X}) = -\Delta_{ion}H^\ominus(\mathrm{X^-}) \tag{36}$$

As ionization energy is often easier to measure than electron affinity, this relation can be used to determine numerical values of the latter.

Ionization energies and electron affinities show periodicities, but the former is more regular and we concentrate on it. Lithium has a low first ionization energy: its outermost electron is well-shielded from the nucleus by the core ($Z_{eff} = 1.3$, compared with $Z = 3$) and it is easily removed. Beryllium has a higher nuclear charge than lithium, and its outermost electron (one of the two 2*s* electrons) is more difficult to remove: its ionization energy is higher. The ionization energy decreases between beryllium and boron because in the latter the outermost electron occupies a $2p$ orbital and is less strongly bound than if it had been a $2s$ electron. The ionization energy increases between boron and carbon because the latter's outermost electron is also $2p$ and the nuclear charge has increased. Nitrogen has a still higher ionization energy because of the further increase in nuclear charge.

There is now a kink in the curve which reduces the ionization energy of oxygen below what would be expected by simple extrapolation. The explanation is that at oxygen a $2p$ orbital must become doubly occupied, and the electron–electron repulsions are increased above what would be expected by simple extrapolation along the row. In addition, the loss of a $2p$ electron results in a configuration with a half-filled subshell (like that of N), which is an arrangement of low energy, so the energy of $O^+ + e^-$ is lower than might be expected, and the ionization energy is correspondingly low too. (The kink is less pronounced in the next row, between phosphorus and sulfur because their orbitals are more diffuse.) The values for oxygen, fluorine, and neon fall roughly on the same line, the increase of their ionization energies reflecting the increasing attraction of the more highly charged nuclei for the outermost electrons.

The outermost electron in sodium is $3s$. It is far from the nucleus, and the latter's charge is shielded by the compact, complete neon-like core. As a result, the ionization energy of sodium is substantially lower than that of neon. The periodic cycle starts again along this row, and the variation of the ionization energy can be traced to similar reasons.

Electron affinities are greatest close to fluorine, for the incoming electron enters a vacancy in a compact valence shell and can interact strongly with the nucleus. The attachment of an electron to an anion (as in the formation of O^{2-} from O^-) is invariably endothermic, so E_{ea} is negative. The incoming electron is repelled by the charge already present. Electron affinities are also small, and may be negative, when an electron enters an orbital that is far from the nucleus (as in the heavier alkali metal atoms) or is forced by the Pauli principle to occupy a new shell (as in the noble gas atoms).

13.5 Self-consistent field orbitals

The central difficulty of the Schrödinger equation is the presence of the electron–electron interaction terms. The potential energy of the electrons is

$$V = -\sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \frac{1}{2}\sum_{i,j}{}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{37}$$

The prime on the second sum indicates that $i \neq j$, and the factor of one-half prevents double-counting of electron pair repulsions (1 with 2 is the same as 2 with 1). The first term is the total attractive interaction between the electrons and the nucleus. The second term is the total repulsive interaction; r_{ij} is the distance between electrons i and j. It is hopeless to expect to find analytical solutions of a Schrödinger equation with such a complicated potential energy term, but computational techniques are available that give very detailed and reliable numerical solutions for the wavefunctions and energies. The techniques were originally introduced by D.R. Hartree (before computers were available) and then modified by V. Fock to take into account the Pauli principle correctly. In broad outline, the **Hartree–Fock self-consistent field** (SCF) procedure is as follows.

Imagine that we have a rough idea of the structure of the atom. In the Ne atom, for instance, the orbital approximation suggests the configuration $1s^2 2s^2 2p^6$ with the orbitals approximated by hydrogenic atomic orbitals. Now consider one of the $2p$ electrons. A Schrödinger equation can be written for this electron by ascribing to it a potential energy due to the nuclear attraction and the repulsion from the other electrons. This equation has the form

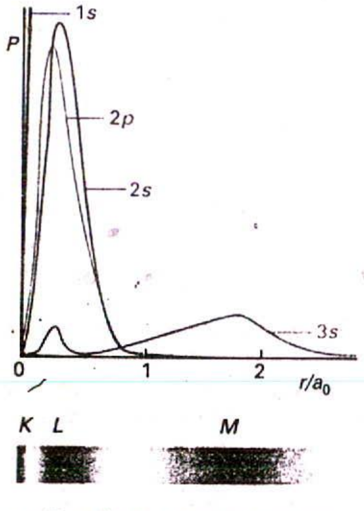
$$\begin{aligned}-\frac{\hbar^2}{2m_e}\nabla_1^2\psi_{2p}(\boldsymbol{r}_1) &- \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{2p}(\boldsymbol{r}_1)\\ &+2\sum_i\left\{\int\frac{\psi_i^*(\boldsymbol{r}_2)\psi_i(\boldsymbol{r}_2)e^2}{4\pi\varepsilon_0 r_{12}}\,\mathrm{d}\tau_2\right\}\psi_{2p}(\boldsymbol{r}_1)\\ &-\sum_i\left\{\int\frac{\psi_i^*(\boldsymbol{r}_2)\psi_{2p}(\boldsymbol{r}_2)e^2}{4\pi\varepsilon_0 r_{12}}\,\mathrm{d}\tau_2\right\}\psi_i(\boldsymbol{r}_1)\\ &= E_{2p}\psi_{2p}(\boldsymbol{r}_1)\end{aligned} \tag{38}$$

The orbitals are labelled i, and the sums on the left are over all the occupied orbitals. A similar equation can be written for the $1s$ and $2s$ orbitals in the atom.

Equation 38 is fearsome, but it can be interpreted by examining each term. The first term on the left is the usual kinetic energy contribution. The second term is the potential energy of attraction of the electron to the nucleus. The third term is the potential energy of the electron of interest due to the charge density $-e|\psi_i(\boldsymbol{r}_2)|^2$ of the electrons in the other occupied orbitals. The fourth term takes into account the spin correlation effects discussed earlier. Note that, although the equation is for the $2p$ orbital in neon, it depends on the wavefunctions of all the other occupied orbitals in the atom.

There is no hope of solving eqn 38 analytically. However, it can be solved numerically if we guess an approximate form of the wavefunctions of all the orbitals except $2p$. The procedure is then repeated for the other orbitals in the atom, the $1s$ and $2s$ orbitals. This sequence of calculations gives the form of the $2p$, $2s$, and $1s$ orbitals, and in general they will differ from the set used initially to start the calculation.[7] These improved orbitals can be used in another cycle of calculation, and a second improved set of orbitals is obtained. The recycling continues until the orbitals and energies obtained are insignificantly different from those used at the start of the current cycle. The solutions are then **self-consistent** and accepted as solutions of the problem.

Plots of some of the self-consistent field (SCF) Hartree–Fock radial distribution functions for sodium are shown in Fig. 13.25. They show the grouping of electron density into shells, as was anticipated by the early chemists, and the differences of penetration as discussed above. These SCF calculations therefore support the qualitative discussions that are used to explain chemical periodicity. They also considerably extend that discussion by providing detailed wavefunctions and precise energies.



13.25 The radial distribution functions for the orbitals of Na based on SCF calculations. Note the shell-like structure, with the $3s$ orbital outside the inner K and L shells.

The spectra of complex atoms

The spectra of atoms rapidly become very complicated as the number of electrons increases, but there are some important and moderately simple features. The general idea is straightforward: lines in the spectrum (in either emission or absorption) occur when the atom undergoes a change of state with a change of energy $|\Delta E|$, and emits or absorbs a photon of frequency $\nu = |\Delta E|/h$ and wavenumber $\tilde{\nu} = |\Delta E|/hc$. Hence, we can expect the spectrum to give information about the energies of electrons in atoms. However, the actual energy levels are not given solely by the energies of the orbitals, because the electrons interact with one another in various ways, and there are contributions to the energy in addition to those we have already considered.

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[7] In practice, much more efficient procedures are used, and the equations for the wavefunctions are solved simultaneously.

13.6 Quantum defects and ionization limits

One application of atomic spectroscopy is to the determination of ionization energies. However, we cannot use the procedure illustrated in Example 13.1 indiscriminately because the energy levels of a many-electron atom do not in general vary as $1/n^2$. If we confine attention to the outermost electrons, then we know that, as a result of penetration and shielding, they experience a nuclear charge of slightly more than $1e$ because in a neutral atom the other $Z-1$ electrons cancel all but about one unit of nuclear charge. Typical values of Z_{eff} are a little more than 1, so we expect binding energies to be given by a term of the form $-hc\mathcal{R}/n^2$, but lying slightly lower in energy than this formula predicts. We therefore introduce a **quantum defect**, δ, and write the energy as $-hc\mathcal{R}/(n-\delta)^2$. The quantum defect is best regarded as a purely empirical quantity.

There are some states that are so diffuse that the $1/n^2$ variation is valid: these states are called **Rydberg states**. In such cases we can write

$$\tilde{\nu} = \frac{I}{hc} - \frac{\mathcal{R}}{n^2} \tag{39}$$

and a plot of wavenumber against $1/n^2$ can be used to obtain I by extrapolation; in practice, one would use a linear regression fit using a computer. If the lower state is not the ground state (a possibility if we wish to generalize the concept of ionization energy), the ionization energy of the ground state can be determined by adding the appropriate energy difference to the ionization energy obtained as described here.

13.7 Singlet and triplet states

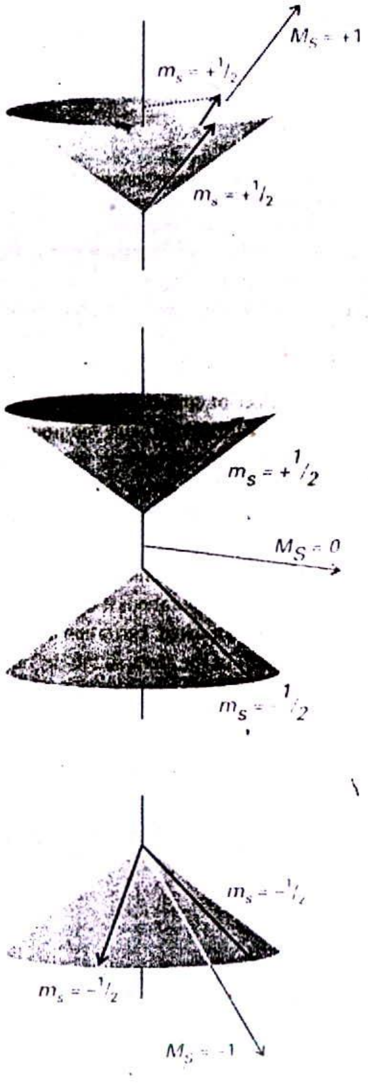
Suppose we were interested in the energy levels of a He atom, with its two electrons. We know that the ground-state configuration is $1s^2$, and can anticipate that an excited configuration will be one in which one of the electrons has been promoted into a $2s$ orbital, giving the configuration $1s^12s^1$. The two electrons need not be paired because they occupy different orbitals. According to Hund's rule, the state of the atom with the spins parallel lies lower in energy than the state in which they are paired. Both states are permissible, and can contribute to the spectrum of the atom.

Parallel and antiparallel (paired) spins differ in their overall spin angular momentum. In the paired case, the two spin momenta cancel each other, and there is zero net spin (as was depicted in Fig. 13.20). The paired-spin arrangement is called a **singlet**. Its spin state is the one we denoted σ_- in the discussion of the Pauli principle:

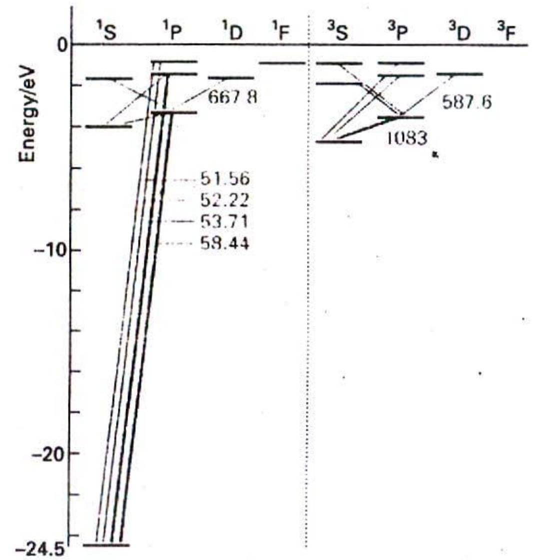
$$\sigma_-(1,2) = \frac{1}{2^{1/2}}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\} \tag{40a}$$

The angular momenta of two parallel spins add together to give a nonzero total spin, and the resulting state is called a **triplet**. As illustrated in Fig. 13.26, there are three ways of achieving a nonzero total spin, but only one way to achieve zero spin. The three spin states are the symmetric combinations introduced earlier:

$$\alpha(1)\alpha(2) \qquad \sigma_+(1,2) = \frac{1}{2^{1/2}}\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\} \qquad \beta(1)\beta(2) \tag{40b}$$



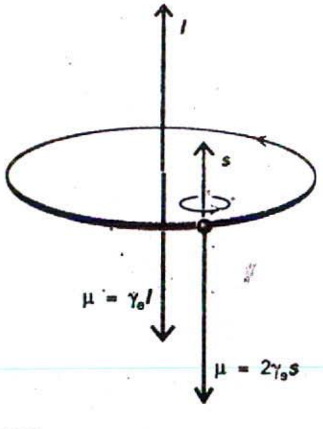
13.26 When two electrons have parallel spins, they have a nonzero total spin angular momentum. There are three ways of achieving this resultant, which are shown by these vector representations. Note that, although we cannot know the orientation of the spin vectors on the cones, the angle between the vectors is the same in all three cases, for all three arrangements have the same total spin angular momentum (that is, the resultant of the two vectors has the same length in each case, but points in different directions). Compare this diagram with Fig. 13.20, which shows the antiparallel case. Note that, whereas two paired spins are precisely antiparallel, two 'parallel' spins are not strictly parallel.



13.27 Part of the Grotrian diagram for a helium atom. Note that there are no transitions between the singlet and triplet levels. Transition wavelengths are given in nanometers.

The fact that the parallel arrangement of spins in the $1s^12s^1$ configuration of the He atom lies lower in energy than the antiparallel arrangement can now be expressed by saying that the triplet state of the $1s^12s^1$ configuration of He lies lower in energy than the singlet state. This is a general conclusion that applies to other atoms (and molecules), and, *for states arising from the same configuration, the triplet state generally lies lower than the singlet state*. The origin of the energy difference lies in the effect of spin correlation on the Coulombic interactions between electrons, as we saw in the case of Hund's rule for ground-state configurations. Because the Coulombic interaction between electrons in an atom is strong, the difference in energies between singlet and triplet states of the same configuration can be large. The two states of $1s^12s^1$ He, for instance, differ by 6421 cm^{-1} (corresponding to 0.7961 eV).

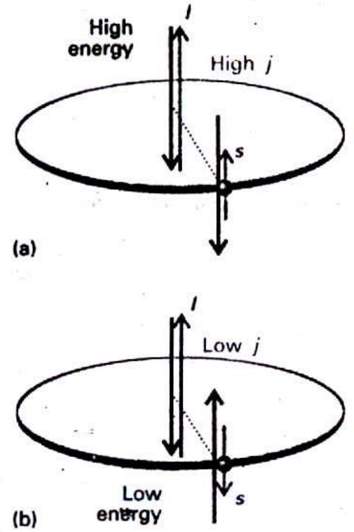
The spectrum of atomic helium is more complicated than that of atomic hydrogen, but there are two simplifying features. One is that the only excited configurations it is necessary to consider are of the form $1s^1nl^1$: that is, only one electron is excited. Excitation of two electrons requires an energy greater than the ionization energy of the atom, so the He$^+$ ion is formed instead of the doubly excited atom. Second, *no transitions take place between singlet and triplet states* because the relative orientation of the two electron spins cannot change during a transition. Thus, there is a spectrum arising from transitions between singlet states (including the ground state) and between triplet states, but not between the two. Spectroscopically, helium behaves like two distinct species, and the early spectroscopists actually thought of helium as consisting of 'parahelium' and 'orthohelium'. The Grotrian diagram for helium in Fig. 13.27 shows the two sets of transitions.



13.28 Angular momentum gives rise to a magnetic moment (μ). For an electron, the magnetic moment is antiparallel to the orbital angular momentum, but proportional to it. For spin angular momentum, there is a factor 2, which increases the magnetic moment to twice its expected value (see Section 13.10).

13.8 Spin–orbit coupling

Electron spin has a further implication for the energies of atoms. Because an electron has spin angular momentum, and because moving charges generate magnetic fields, an electron has a magnetic moment that arises from its spin (Fig. 13.28). Similarly, an electron with orbital angular momentum (that is, an electron in an orbital with $l>0$) is in effect a



13.29 Spin–orbit coupling is a magnetic interaction between spin and orbital magnetic moments. When the angular momenta are parallel, as in (a), the magnetic moments are aligned unfavourably; when they are opposed, as in (b), the interaction is favourable. This magnetic coupling is the cause of the splitting of a configuration into levels.

circulating current, and possesses a magnetic moment that arises from its orbital momentum. The interaction of the spin and orbital magnetic moments is called **spin–orbit coupling.** The strength of the coupling, and its effect on the energy levels of the atom, depends on the relative orientations of the spin and orbital magnetic moments, and therefore on the relative orientations of the two angular momenta (Fig. 13.29).

(a) The total angular momentum

One way of expressing the dependence of the spin–orbit interaction on the relative orientation of the spin and orbital momenta is to say that it depends on the **total angular momentum** of the electron, the vector sum of its spin and orbital momenta. Thus, when the spin and orbital angular momenta are nearly parallel, the total angular momentum is high; when the two angular momenta are opposed, the total angular momentum is low.

The total angular momentum of an electron is described by the quantum numbers j and m_j, with $j = l + \frac{1}{2}$ (when the two angular momenta are in the same direction) or $j = l - \frac{1}{2}$ (when they are opposed, Fig. 13.30). The different values of j that can arise for a given value of l label **levels** of a term. For $l = 0$, the only permitted value is $j = \frac{1}{2}$ (the total angular momentum is the same as the spin angular momentum because there is no other source of angular momentum in the atom). When $l = 1$, j may be either $\frac{3}{2}$ (the spin and orbital angular momenta are in the same sense) or $\frac{1}{2}$ (the spin and angular momenta are in opposite senses).

Example 13.4 Identifying the levels of a configuration

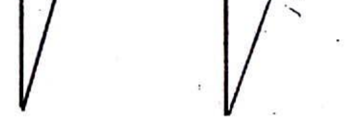
Identify the levels that may arise from the configurations (a) d^1, (b) s^1.

Method In each case, identify the value of l and then the possible values of j. For these one-electron systems, the total angular momentum is the sum or difference of the orbital and spin momenta.

Answer (a) For a d electron, $l = 2$ and there are two levels in the configuration, one with $j = 2 + \frac{1}{2} = \frac{5}{2}$ and the other with $j = 2 - \frac{1}{2} = \frac{3}{2}$. (b) For an s electron $l = 0$, so only one level is possible, and $j = \frac{1}{2}$.

Self-test 13.7 Identify the levels of the configurations (a) p^1 and (b) f^1.

[(a) $\frac{3}{2}, \frac{1}{2}$; (b) $\frac{7}{2}, \frac{5}{2}$]



13.30 The coupling of the spin and orbital angular momenta of a d electron ($l = 2$) gives two possible values of j depending on the relative orientations of the spin and orbital angular momenta of the electron.

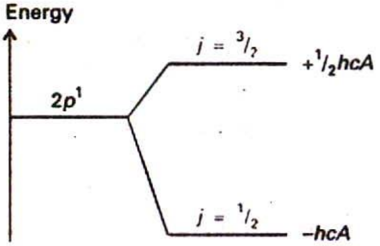
The dependence of the spin–orbit interaction on the value of j is expressed in terms of the **spin–orbit coupling constant**, A (which is typically expressed as a wavenumber). A quantum mechanical calculation leads to the result that the energies of the levels with quantum numbers s, l, and j are given by

$$E_{l,s,j} = \tfrac{1}{2}hcA\{j(j+1) - l(l+1) - s(s+1)\} \tag{41}$$

Justification 13.10

The energy of a magnetic moment $\boldsymbol{\mu}$ in a magnetic field $\boldsymbol{B}$ is equal to their scalar product $-\boldsymbol{\mu}\cdot\boldsymbol{B}$. If the magnetic field arises from the orbital angular momentum of the electron, it is proportional to $\boldsymbol{l}$; if the magnetic moment $\boldsymbol{\mu}$ is that of the electron spin, then it is proportional to $\boldsymbol{s}$. It then follows that the energy of interaction is proportional to the scalar product $\boldsymbol{s}\cdot\boldsymbol{l}$:

$$\text{energy of interaction} = -\boldsymbol{\mu}\cdot\boldsymbol{B} \propto \boldsymbol{s}\cdot\boldsymbol{l}$$



13.31 The levels of a ^{2}P term arising from spin–orbit coupling. Note that the low-j level lies below the high-j level.

Next, we note that the total angular momentum is the vector sum of the spin and orbital momenta: $\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$. The magnitude of the vector $\boldsymbol{j}$ is calculated by evaluating

$$\boldsymbol{j}\cdot\boldsymbol{j} = (\boldsymbol{l}+\boldsymbol{s})\cdot(\boldsymbol{l}+\boldsymbol{s}) = \boldsymbol{l}\cdot\boldsymbol{l} + \boldsymbol{s}\cdot\boldsymbol{s} + 2\boldsymbol{s}\cdot\boldsymbol{l}$$

That is,

$$\boldsymbol{s}\cdot\boldsymbol{l} = \tfrac{1}{2}\{j^2 - l^2 - s^2\}$$

This is a classical result. To make the transition to quantum mechanics, we treat all the quantities as operators, and write

$$\hat{s}\cdot\hat{l} = \tfrac{1}{2}\{\hat{j}^2 - \hat{l}^2 - \hat{s}^2\} \qquad (42)$$

At this point, we evaluate the expectation value:

$$\begin{aligned}\langle j,l,s|\hat{s}\cdot\hat{l}|j,l,s\rangle &= \tfrac{1}{2}\langle j,l,s|\hat{j}^2 - \hat{l}^2 - \hat{s}^2|j,l,s\rangle \\ &= \tfrac{1}{2}\{j(j+1) - l(l+1) - s(s+1)\}\hbar^2\end{aligned} \qquad (43)$$

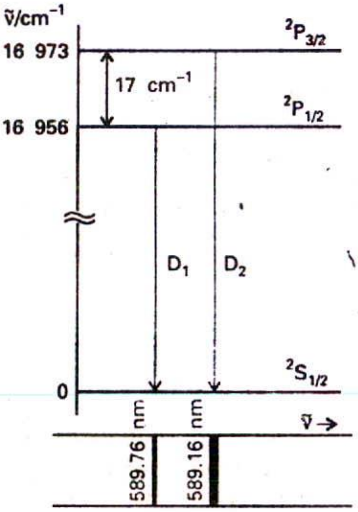
Then, by inserting this expression into the formula for the energy, and writing the constant of proportionality as $hcA/\hbar^2$, we obtain eqn 41. The calculation of A is much more complicated: see *Further reading*.

Illustration

The unpaired electron in the ground state of an alkali metal atom has $l = 0$, so $j = \frac{1}{2}$. Because the orbital angular momentum is zero in this state, the spin–orbit coupling energy is zero (as is confirmed by setting $j = s$ and $l = 0$ in eqn 41). When the electron is excited to an orbital with $l = 1$, it has orbital angular momentum and can give rise to a magnetic field that interacts with its spin. In this configuration the electron can have $j = \frac{3}{2}$ or $j = \frac{1}{2}$, and the energies of these levels are

$$E_{3/2} = \tfrac{1}{2}hcA\{\tfrac{3}{2}\times\tfrac{5}{2} - 1\times 2 - \tfrac{1}{2}\times\tfrac{3}{2}\} = \tfrac{1}{2}hcA$$
$$E_{1/2} = \tfrac{1}{2}hcA\{\tfrac{1}{2}\times\tfrac{3}{2} - 1\times 2 - \tfrac{1}{2}\times\tfrac{3}{2}\} = -hcA$$

The corresponding energies are shown in Fig. 13.31. Note that the 'centre of gravity' of the levels is unchanged, because there are four states of energy $\frac{1}{2}hcA$ and two of energy $-hcA$.



13.32 The energy-level diagram for the formation of the sodium D lines. The splitting of the spectral lines (by 17 cm^{-1}) reflects the splitting of the levels of the ^{2}P term.

The strength of the spin–orbit coupling depends on the nuclear charge. To understand why this is so, imagine riding on the orbiting electron and seeing a charged nucleus apparently orbiting around us (like the sun rising and setting). As a result, we find ourselves at the centre of a ring of current. The greater the nuclear charge, the greater this current, and therefore the stronger the magnetic field we detect. Because the spin magnetic moment of the electron interacts with this orbital magnetic field, it follows that, the greater the nuclear charge, the stronger the spin–orbit interaction. The coupling increases sharply with atomic number (as Z^4 in a hydrogenic atom). Whereas it is only small in H (giving rise to shifts of energy levels of no more than about 0.4 cm^{-1}), in heavy atoms like Pb it is very large (giving shifts of the order of thousands of reciprocal centimetres).

(b) Fine structure

Two spectral lines are observed when the p electron of an electronically excited alkali metal atom undergoes a transition and falls into a lower s orbital. One line is due to a transition starting in a $j = \frac{3}{2}$ level and the other line is due to a transition starting in the $j = \frac{1}{2}$ level of the same configuration. The two lines are an example of **fine structure**. Fine structure can be clearly seen in the emission spectrum from sodium vapour excited by an electric discharge (for example, in one kind of street lighting). The yellow line at 589 nm (close to 17 000 cm^{-1}) is actually a doublet composed of one line at 589.76 nm (16 956.2 cm^{-1}) and another at 589.16 nm (16 973.4 cm^{-1}); the components of this doublet are the 'D lines' of the spectrum (Fig. 13.32). Therefore, in Na, the spin–orbit coupling affects the energies by about 17 cm^{-1}.

Example 13.5 Analysing a spectrum for the spin-orbit coupling constant

The origin of the D lines in the spectrum of atomic sodium is shown in Fig. 13.32. Calculate the spin–orbit coupling constant for the upper configuration of the Na atom.

Method We see from Fig. 13.32 that the splitting of the lines is equal to the energy separation of the $j = \frac{3}{2}$ and $\frac{1}{2}$ levels of the excited configuration. This separation can be expressed in terms of A by using eqn 41. Therefore, set the observed splitting equal to the energy separation calculated from eqn 41 and solve the equation for A.

Answer The two levels are split by

$$\Delta\tilde{\nu} = A\tfrac{1}{2}\{\tfrac{3}{2}(\tfrac{3}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)\} = \tfrac{3}{2}A$$

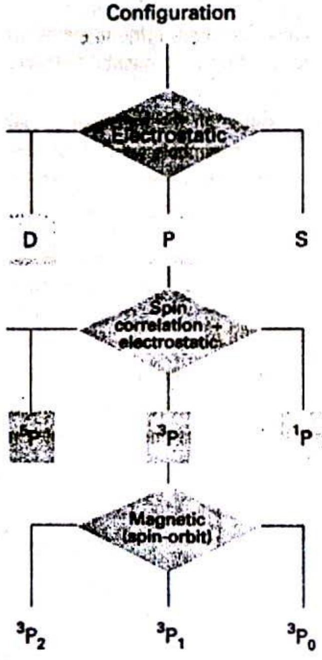
The experimental value is 17.2 cm^{-1}; therefore

$$A = \tfrac{2}{3} \times (17.2\ \text{cm}^{-1}) = 11.5\ \text{cm}^{-1}$$

Comment The same calculation repeated for the other alkali metal atoms gives Li: 0.23 cm^{-1}; K: 38.5 cm^{-1}; Rb: 158 cm^{-1}; Cs: 370 cm^{-1}. Note the increase of A with atomic number (but more slowly than Z^4 for these many-electron atoms).

Self-test 13.8 The configuration . . . $4p^6 5d^1$ of rubidium has two levels at 25 700.56 cm^{-1} and 25 703.52 cm^{-1} above the ground state. What is the spin–orbit coupling constant in this excited state?

[1.18 cm^{-1}]



13.33 A summary of the types of interaction that are responsible for the various kinds of splitting of energy levels in atoms. For light atoms, magnetic interactions are small, but in heavy atoms they may dominate the electrostatic (charge–charge) interactions.

13.9 Term symbols and selection rules

We have used expressions such as 'the $j = \frac{3}{2}$ level of a configuration'. A **term symbol**, which is a symbol looking like $^2P_{3/2}$ or $^3D_2$, conveys this information much more succinctly. The convention of using lower-case letters to label orbitals and upper-case letters to label overall states applies throughout spectroscopy, not just to atoms.

A term symbol gives three pieces of information:

1. The letter (for example, P or D in the examples) indicates the total orbital angular momentum quantum number, L.
2. The left superscript in the term symbol (for example, the 2 in $^2P_{3/2}$) gives the multiplicity of the term.
3. The right subscript on the term symbol (for example, the $\frac{3}{2}$ in $^2P_{3/2}$) is the value of the total angular momentum quantum number, J.

We shall now say what each of these statements means; the contributions to the energies which we are about to discuss are summarized in Fig. 13.33.

(a) The total orbital angular momentum

When several electrons are present, it is necessary to judge how their individual orbital angular momenta add together or oppose each other. The **total orbital angular momentum quantum number**, L, tells us the magnitude of the angular momentum through $\{L(L+1)\}^{1/2}\hbar$. It has $2L+1$ orientations distinguished by the quantum number M_L, which can take the values $L, L-1, \ldots, -L$. Similar remarks apply to the **total spin quantum number**, S, and the quantum number M_S, and the **total angular momentum quantum number**, J, and the quantum number M_J. The value of L (a non-negative integer) is obtained by coupling the individual orbital angular momenta by using the **Clebsch–Gordan series**:

$$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, |l_1 - l_2| \tag{44}$$

The modulus signs are attached to $l_1 - l_2$ because L is non-negative. The maximum value, $L = l_1 + l_2$, is obtained when the two orbital angular momenta are in the same direction; the lowest value, $|l_1 - l_2|$, is obtained when they are in opposite directions. The intermediate values represent possible intermediate relative orientations of the two momenta (Fig. 13.34). For two p electrons (for which $l_1 = l_2 = 1$), $L = 2, 1, 0$. The code for converting the value of L into a letter is the same as for the $s, p, d, f, \ldots$ designation of orbitals, but uses upper-case Roman letters:

L:	0	1	2	3	4	5	6 ...
	S	P	D	F	G	H	I ...

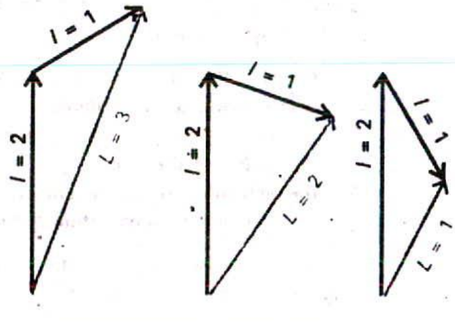
Thus, a p^2 configuration can give rise to D, P, and S terms. The terms differ in energy on account of the different spatial distribution of the electrons and the consequent differences in repulsion between them.

A closed shell has zero orbital angular momentum because all the individual orbital angular momenta sum to zero. Therefore, when working out term symbols, we need consider only the electrons of the unfilled shell. In the case of a single electron outside a closed shell, the value of L is the same as the value of l; so the configuration [Ne]$3s^1$ has only an S term.

Example 13.6 Deriving the total angular momentum of a configuration

Find the terms that can arise from the configurations (a) d^2, (b) p^3.

Method Use the Clebsch–Gordan series and begin by finding the minimum value of L (so that we know where the series terminates). When there are more than two electrons to couple together, use two series in succession: first couple two electrons, and then couple the third to each combined state, and so on.



13.34 The total angular orbital momenta of a p electron and a d electron correspond to $L = 3, 2$, and 1 and reflect the different relative orientations of the two momenta.

Answer (a) Minimum value: $|l_1 - l_2| = |2 - 2| = 0$. Therefore,

$$L = 2+2, 2+2-1, \ldots, 0 = 4, 3, 2, 1, 0$$

corresponding to G, F, D, P, S terms, respectively. (b) First coupling: minimum value: $|1 - 1| = 0$. Therefore,

$$L' = 1+1, 1+1-1, \ldots, 0 = 2, 1, 0$$

Now couple l_3 with $L' = 2$, to give $L = 3, 2, 1$; with $L' = 1$, to give $L = 2, 1, 0$; and with $L' = 0$, to give $L = 1$. The overall result is

$$L = 3, 2, 2, 1, 1, 1, 0$$

giving one F, two D, three P, and one S term.

Self-test 13.9 Repeat the question for the configurations (a) f^1d^1 and (b) d^3.
[(a) H, G, F, D, P; (b) I, 2H, 3G, 4F, 5D, 3P, S]

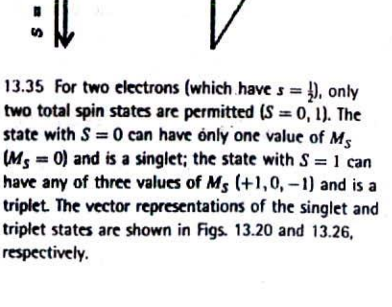
(b) The multiplicity

When there are several electrons to be taken into account, we must assess their total spin angular momentum quantum number, S (a non-negative integer or half integer).[8] Once again, we use the Clebsch–Gordan series in the form

$$S = s_1 + s_2, s_1 + s_2 - 1, \ldots, |s_1 - s_2| \qquad (45)$$

to decide on the value of S, noting that each electron has $s = \frac{1}{2}$, which gives $S = 1, 0$ (Fig. 13.35). If there are three electrons, the total spin angular momentum is obtained by coupling the third spin to each of the values of S for the first two spins, which results in $S = \frac{3}{2}, \frac{1}{2}$ and $S = \frac{1}{2}$.

The multiplicity of a term is the value of $2S + 1$. When $S = 0$ (as for a closed shell) the electrons are all paired and there is no net spin: this arrangement gives a singlet term, such as ^{1}S. A single electron has $S = s = \frac{1}{2}$, so a configuration such as [Ne]$3s^1$ can give rise to a doublet term, ^{2}S. The configuration [Ne]$3p^1$ likewise is a doublet, ^{2}P. When there are two unpaired electrons $S = 1$, so $2S + 1 = 3$, giving a triplet term, such as ^{3}D. We discussed the relative energies of singlets and triplets in Section 13.7 and saw that their energies differ on account of the different effects of spin correlation.



13.35 For two electrons (which have $s = \frac{1}{2}$), only two total spin states are permitted ($S = 0, 1$). The state with $S = 0$ can have only one value of M_S ($M_S = 0$) and is a singlet; the state with $S = 1$ can have any of three values of M_S ($+1, 0, -1$) and is a triplet. The vector representations of the singlet and triplet states are shown in Figs. 13.20 and 13.26, respectively.

(c) The total angular momentum

As we have seen, the quantum number j tells us the relative orientation of the spin and orbital angular momenta of a single electron. The total angular momentum quantum number, J (a non-negative integer or half integer), does the same for several electrons. If there is a single electron outside a closed shell, $J = j$, with j either $l + \frac{1}{2}$ or $|l - \frac{1}{2}|$. The [Ne]$3s^1$ configuration has $j = \frac{1}{2}$ (because $l = 0$ and $s = \frac{1}{2}$), so the ^{2}S term has a single level, which we denote $^2\mathrm{S}_{1/2}$. The [Ne]$3p^1$ configuration has $l = 1$; therefore $j = \frac{3}{2}$ and $\frac{1}{2}$; the ^{2}P term therefore has two levels, $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$. These levels lie at different energies on account of the magnetic spin–orbit interaction.

If there are several electrons outside a closed shell we have to consider the coupling of all the spins and all the orbital angular momenta. This complicated problem can be simplified when the spin–orbit coupling is weak (for atoms of low atomic number), for then we can use the Russell–Saunders coupling scheme. This scheme is based on the view that, if spin–orbit coupling is weak, then it is effective only when all the orbital momenta are operating

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[8] Distinguish italic S, the total spin quantum number, from Roman S, the term label.

cooperatively. We therefore imagine that all the orbital angular momenta of the electrons couple to give a total L, and that all the spins are similarly coupled to give a total S. Only at this stage do we imagine the two kinds of momenta coupling through the spin–orbit interaction to give a total J. The permitted values of J are given by the Clebsch–Gordan series

$$J = L + S, L + S - 1, \ldots, |L - S| \tag{46}$$

For example, in the case of the ^{3}D term of the configuration [Ne]$2p^1 3p^1$, the permitted values of J are 3, 2, 1 (because ^{3}D has $L = 2$ and $S = 1$), so the term has three levels, $^3\mathrm{D}_3$, $^3\mathrm{D}_2$, and $^3\mathrm{D}_1$.

When $L > S$, the multiplicity is equal to the number of levels. For example, a ^{2}P term has the two levels $^2\mathrm{P}_{3/2}$ and $^2\mathrm{P}_{1/2}$, and ^{3}D has the three levels $^3\mathrm{D}_3$, $^3\mathrm{D}_2$, and $^3\mathrm{D}_1$. However, this is not the case when $L < S$: the term ^{2}S, for example, has only the one level $^2\mathrm{S}_{1/2}$.

Example 13.7 Deriving term symbols

Write the term symbols arising from the ground-state configurations of (a) Na and (b) F, and (c) the excited configurations $1s^2 2s^2 2p^1 3p^1$ of C.

Method Begin by writing the configurations, but ignore inner closed shells. Then couple the orbital momenta to find L and the spins to find S. Next, couple L and S to find J. Finally, express the term as $^{2S+1}\{L\}_J$, where $\{L\}$ is the appropriate letter. For F, for which the valence configuration is $2p^5$, treat the single gap in the closed-shell $2p^6$ configuration as a single particle.

Answer (a) For Na, the configuration is [Ne]$3s^1$, and we consider the single $3s$ electron. Because $L = l = 0$ and $S = s = \frac{1}{2}$, it is possible for $J = j = s = \frac{1}{2}$ only. Hence the term symbol is $^2\mathrm{S}_{1/2}$.

(b) For F, the configuration is [He]$2s^2 2p^5$, which we can treat as [Ne]$2p^{-1}$ (where the notation $2p^{-1}$ signifies the absence of a $2p$ electron). Hence $L = 1$, and $S = s = \frac{1}{2}$. Two values of $J = j$ are allowed: $J = \frac{3}{2}, \frac{1}{2}$. Hence, the term symbols for the two levels are $^2\mathrm{P}_{3/2}$, $^2\mathrm{P}_{1/2}$.

(c) For C, the configuration is effectively $2p^1 3p^1$. This is a two-electron problem, and $l_1 = l_2 = 1$, $s_1 = s_2 = \frac{1}{2}$. It follows that $L = 2, 1, 0$ and $S = 1, 0$. The terms are therefore ^{3}D and ^{1}D, ^{3}P and ^{1}P, and ^{3}S and ^{1}S. For ^{3}D, $L = 2$ and $S = 1$; hence $J = 3, 2, 1$ and the levels are $^3\mathrm{D}_3$, $^3\mathrm{D}_2$, and $^3\mathrm{D}_1$. For ^{1}D, $L = 2$ and $S = 0$, so the single level is $^1\mathrm{D}_2$. The triplet of levels of ^{3}P is $^3\mathrm{P}_2$, $^3\mathrm{P}_1$, and $^3\mathrm{P}_0$, and the singlet is $^1\mathrm{P}_1$. For the ^{3}S term there is only one level, $^3\mathrm{S}_1$ (because $J = 1$ only), and the singlet term is $^1\mathrm{S}_0$.

Comment The reason why we have treated an excited configuration of carbon is that in the ground configuration, $2p^2$, the Pauli principle forbids some terms, and deciding which survive (^{1}D, ^{3}P, ^{1}S, in fact) is quite complicated. That is, there is a distinction between 'equivalent electrons', which are electrons that occupy the same orbitals, and 'inequivalent electrons', which are electrons that occupy different orbitals.

Self-test 13.10 Write down the terms arising from the configurations (a) $2s^1 2p^1$, (b) $2p^1 3d^1$.

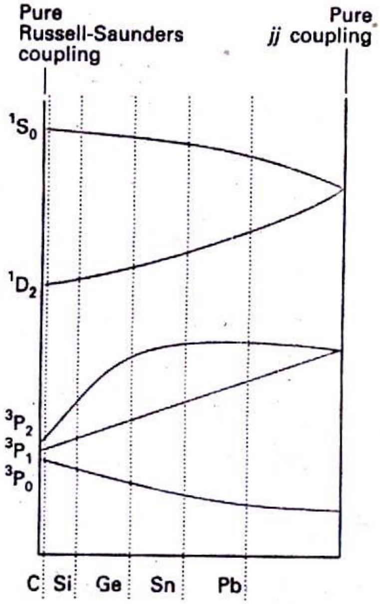
[(a) $^3\mathrm{P}_2$, $^3\mathrm{P}_1$, $^3\mathrm{P}_0$, $^1\mathrm{P}_1$;
(b) $^3\mathrm{F}_4$, $^3\mathrm{F}_3$, $^3\mathrm{F}_2$, $^1\mathrm{F}_3$, $^3\mathrm{D}_3$, $^3\mathrm{D}_2$, $^3\mathrm{D}_1$, $^1\mathrm{D}_2$,
$^3\mathrm{P}_2$, $^3\mathrm{P}_1$, $^3\mathrm{P}_0$, $^1\mathrm{P}_1$]

Russell–Saunders coupling fails when the spin–orbit coupling is large (in heavy atoms). In that case, the individual spin and orbital momenta of the electrons are coupled into individual j values; then these momenta are combined into a grand total, J. This scheme is called **jj-coupling.** For example, in a p^2 configuration, the individual values of j are $\frac{3}{2}$ and $\frac{1}{2}$ for each electron. If the spin and the orbital angular momentum of each electron are coupled together strongly, it is best to consider each electron as a particle with angular momentum $j = \frac{3}{2}$ or $\frac{1}{2}$. These individual total momenta then couple as follows:

$$\begin{array}{ll} j_1 = \frac{3}{2} \text{ and } j_2 = \frac{3}{2} & J = 3, 2, 1, 0 \\ j_1 = \frac{3}{2} \text{ and } j_2 = \frac{1}{2} & J = 2, 1 \\ j_1 = \frac{1}{2} \text{ and } j_2 = \frac{3}{2} & J = 2, 1 \\ j_1 = \frac{1}{2} \text{ and } j_2 = \frac{1}{2} & J = 1, 0 \end{array}$$

For heavy atoms, in which jj-coupling is appropriate, it is best to discuss their energies using these quantum numbers.

Although jj-coupling should be used for assessing the energies of heavy atoms, the term symbols derived from Russell–Saunders coupling can still be used as labels. To see why this procedure is valid, we need to examine how the energies of the atomic states change as the spin–orbit coupling increases in strength. Such a **correlation diagram** is shown in Fig. 13.36. It shows that there is a correspondence between the low spin–orbit coupling (Russell–Saunders coupling) and high spin–orbit coupling (jj-coupling) schemes, so the labels derived by using the Russell–Saunders scheme can be used to label the states of the jj-coupling scheme.



13.36 The correlation diagram for some of the states of a two-electron system. All atoms lie between the two extremes but, the heavier the atom, the closer it lies to the pure jj-coupling case.

(d) Selection rules

Any state of the atom, and any spectral transition, can be specified by using term symbols. For example, the transitions giving rise to the yellow sodium doublet (which were shown in Fig. 13.32) are

$$3p^1\ {}^2P_{3/2} \rightarrow 3s^1\ {}^2S_{1/2} \qquad 3p^1\ {}^2P_{1/2} \rightarrow 3s^1\ {}^2S_{1/2}$$

By convention, the upper term precedes the lower. The corresponding absorptions are therefore denoted

$${}^2P_{3/2} \leftarrow {}^2S_{1/2} \qquad {}^2P_{1/2} \leftarrow {}^2S_{1/2}$$

(The configurations have been omitted.)

We have seen that selection rules arise from the conservation of angular momentum during a transition and from the fact that a photon has a spin of 1. They can therefore be expressed in terms of the term symbols, because the latter carry information about angular momentum. A detailed analysis leads to the following rules:

$$\begin{array}{l} \Delta S = 0 \qquad \Delta L = 0, \pm 1 \qquad \Delta l = \pm 1 \\ \Delta J = 0, \pm 1, \text{ but } J = 0 \nleftrightarrow J = 0 \end{array} \tag{47}$$

The rule about ΔS (no change of overall spin) stems from the fact that the light does not affect the spin directly. The rules about ΔL and Δl express the fact that the orbital angular momentum of an individual electron must change (so $\Delta l = \pm 1$), but whether or not this results in an overall change of orbital momentum depends on the coupling.

The selection rules given above apply when Russell–Saunders coupling is valid (in light atoms). If we insist on labelling the terms of heavy atoms with symbols like ^{3}D, then we shall find that the selection rules progressively fail as the atomic number increases because the quantum numbers S and L become ill defined as jj-coupling becomes more appropriate. As explained above, Russell–Saunders term symbols are only a convenient way of labelling the terms of heavy atoms: they do not bear any direct relation to the actual angular momenta of the electrons in a heavy atom. For this reason, transitions between singlet and triplet states (for which $\Delta S = \pm 1$), while forbidden in light atoms, are allowed in heavy atoms.

13.10 The effect of magnetic fields

Orbital and spin angular momenta give rise to magnetic moments (recall the evidence provided for electron spin by the Stern–Gerlach experiment, Section 12.8). It can be expected that the application of a magnetic field should modify an atom's spectrum. We shall first establish how the energies of an atom depend on the strength of an external field and then see how the spectrum is affected.

(a) The magnetic moment of an electron

The orbital angular momentum of an electron around the z-axis (which we now take as the direction of the applied field) is $m_l\hbar$. Because the component of magnetic moment on the z-axis, μ_z, is proportional to the angular momentum around that axis, we can write

$$\mu_z = \gamma_e m_l \hbar \tag{48}$$

where γ_e is a constant called the **magnetogyric ratio** of the electron. If the magnetic moment is treated as arising from the circulation of an electron of charge $-e$, standard electromagnetic theory gives

$$\gamma_e = -\frac{e}{2m_e} \qquad [49]$$

The negative sign (arising from the sign of the electron's charge) shows that the orbital magnetic moment of the electron is antiparallel to its orbital angular momentum (as was depicted in Fig. 13.28). It follows that the possible values of μ_z are

$$\mu_z = -\frac{e}{2m_e} \times m_l\hbar = -\mu_B m_l \tag{50}$$

where the **Bohr magneton**, μ_B, is

$$\mu_B = \frac{e\hbar}{2m_e} \tag{51}$$

Its numerical value is $9.274 \times 10^{-24}\ \mathrm{J\,T^{-1}}$. The Bohr magneton is often regarded as the fundamental quantum of magnetic moment.

The energy of a magnetic moment in a magnetic field of magnitude B in the z-direction is[9]

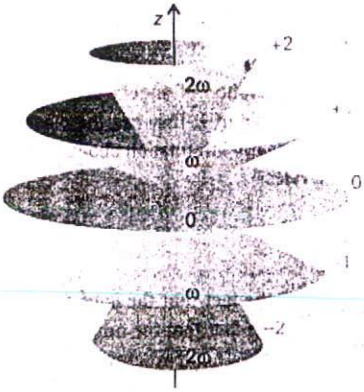
$$E = -\mu_z B \tag{52}$$

Therefore, in the presence of a magnetic field, an electron in a state with quantum number m_l has an additional contribution to its energy given by

$$E_{m_l} = \mu_B m_l B \tag{53}$$

The same expression, but with m_l replaced by M_L, applies when the orbital magnetic moment arises from several electrons.

A p electron has $l = 1$ and $m_l = 0, \pm 1$. In the absence of a magnetic field, these three states are degenerate. When a field is present, the degeneracy is removed: the state with



13.37 The different energies of the m_l states in a magnetic field are represented by different rates of precession of the vectors representing the angular momentum.

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[9] This is a result from standard magnetic theory. B is actually the magnetic induction, and is measured in tesla, T; $1\ \mathrm{T} = 1\ \mathrm{kg\,s^{-2}\,A^{-1}}$. The unit gauss, G, is also occasionally used: $1\ \mathrm{T} = 10^4\ \mathrm{G}$.

$m_l = +1$ moves up in energy by $\mu_B\mathcal{B}$, the state with $m_l = 0$ is unchanged, and the state with $m_l = -1$ moves down by $\mu_B\mathcal{B}$:

$$E_{+1} = +\mu_B\mathcal{B} \qquad E_0 = 0 \qquad E_{-1} = -\mu_B\mathcal{B}$$

The different energies arising from an interaction with an external field are sometimes represented on the vector model by picturing the vectors as precessing, or sweeping round their cones, with the rate of precession proportional to the energy of the state (Fig. 13.37).

The spin magnetic moment of an electron is also proportional to its angular momentum. However, it is not given by $\gamma_e m_s \hbar$ but by about twice this value:

$$\mu_z = g_e\gamma_e m_s\hbar \qquad g_e = 2.002\,319\ldots \qquad (54)$$

The extra factor g_e is called the **g-value** of the electron. The factor 2 (as distinct from 2.0023) is derived from the Dirac equation; the additional 0.0023 arises from interactions of the electron with the electromagnetic fluctuations in the vacuum that surrounds the electron. The energy of an electron in a state m_s in a magnetic field of magnitude $\mathcal{B}$ in the z-direction is

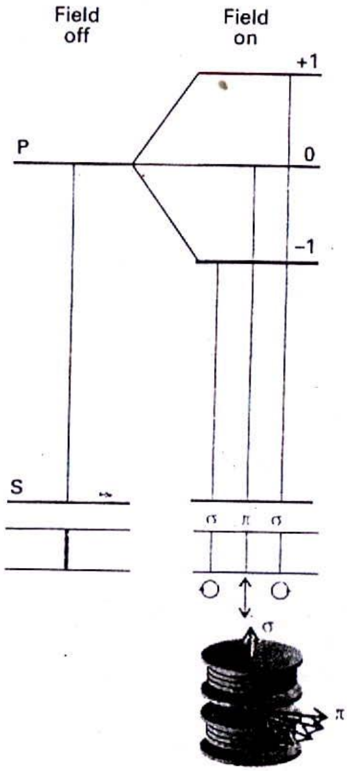
$$E_{m_s} = -g_e\gamma_e m_s\hbar\mathcal{B} = g_e\mu_B m_s\mathcal{B} \qquad (55)$$

The same expression, but with m_s replaced by M_S, applies to the total magnetic moment arising from the spin of several electrons.

(b) The Zeeman effect

The **Zeeman effect** is the modification of an atomic spectrum by the application of a strong magnetic field. In particular, the **normal Zeeman effect** is the observation of three lines in the spectrum where, in the absence of the field, there is only one (Fig. 13.38). The splitting is in fact very small: a field of 2 T (20 kG) is needed to produce a splitting of about 1 cm^{-1}, which should be compared with typical optical transition wavenumbers of 20 000 cm^{-1} and more.

Much more common than the normal Zeeman effect is the **anomalous Zeeman effect**, in which the original line splits into more than three components. The origin of this complexity is the anomalous magnetic moment of electron spin, which results in a more complicated splitting pattern.



13.38 The normal Zeeman effect. On the left, when the field is off, a single spectral line is observed. When the field is on, the line splits into three, with different polarizations. The circularly polarized lines are called the σ-lines; the plane-polarized lines are called π-lines. Which line is observed depends on the orientation of the observer.

Checklist of key ideas

☐ electronic structure
☐ hydrogenic atom
☐ many-electron atom
☐ spectroscopy
☐ spectrum

The structure and spectra of hydrogenic atoms

☐ Balmer series
☐ Lyman series
☐ Paschen series
☐ Rydberg constant
☐ Ritz combination principle
☐ Bohr frequency condition (4)

13.1 The structure of hydrogenic atoms

☐ reduced mass (7)
☐ radial wave equation (11)
☐ Bohr radius (15)
☐ associated Laguerre polynomial (16)

13.2 Atomic orbitals and their energies

☐ atomic orbital
☐ principal quantum number
☐ bound states
☐ unbound states
☐ continuum states

☐ ground state
☐ shell
☐ subshell
☐ boundary surface
☐ radial distribution function
☐ most probable radius
☐ nodal plane

13.3 Spectroscopic transitions and selection rules

☐ transition
☐ allowed transition
☐ forbidden transition
☐ selection rule (27)

☐ transition dipole moment (28)
☐ Grotrian diagram

The structures of many-electron atoms

13.4 The orbital approximation

☐ orbital approximation
☐ configuration
☐ Pauli exclusion principle
☐ Pauli principle
☐ complete shell
☐ closed shell
☐ effective nuclear charge

☐ shielded nuclear charge
☐ shielding constant (33)
☐ penetration
☐ valence electrons
☐ building-up principle
☐ Hund's rule
☐ spin correlation
☐ first ionization energy
☐ second ionization energy
☐ standard enthalpy of ionization (34)
☐ electron affinity
☐ standard enthalpy of electron gain (35)

13.5 Self-consistent field orbitals

☐ Hartree–Fock self-consistent field (SCF)
☐ self-consistent

The spectra of complex atoms

13.6 Quantum defects and ionization limits

☐ quantum defect
☐ Rydberg state

13.7 Singlet and triplet states

☐ singlet
☐ triplet

13.8 Spin–orbit coupling

☐ spin–orbit coupling
☐ total angular momentum
☐ level
☐ spin–orbit coupling constant
☐ fine structure

13.9 Term symbols and selection rules

☐ term symbol
☐ total orbital angular momentum quantum number
☐ total spin quantum number
☐ total angular momentum quantum number
☐ Clebsch–Gordan series (44)
☐ multiplicity
☐ Russell–Saunders coupling
☐ *jj*-coupling
☐ correlation diagram

13.10 The effect of magnetic fields

☐ magnetogyric ratio (49)
☐ Bohr magneton (51)
☐ precessing
☐ *g*-value (54)
☐ Zeeman effect
☐ normal Zeeman effect
☐ anomalous Zeeman effect

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Exercises

13.1 (a) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of krypton, electrons are ejected with a speed of $1.59 \times 10^6\ \mathrm{m\,s^{-1}}$. Calculate the ionization energy of krypton.

13.1 (b) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed on to a sample of xenon, electrons are ejected with a speed of $1.79 \times 10^6\ \mathrm{m\,s^{-1}}$. Calculate the ionization energy of xenon.

13.2 (a) Consider the $2s$ radial wavefunction. Show that it has two extrema in its amplitude, and locate them.

13.2 (b) Consider the $3s$ radial wavefunction. Show that it has three extrema in its amplitude, and locate them.

13.3 (a) Locate the radial nodes in the $3s$ orbital of an H atom.

13.3 (b) Locate the radial nodes in the $3p$ orbital of an H atom.

13.4 (a) The wavefunction for the ground state of a hydrogen atom is Ne^{-r/a_0}. Determine the normalization constant N.

13.4 (b) The wavefunction for the $2s$ orbital of a hydrogen atom is $N(2 - r/a_0)e^{-r/2a_0}$. Determine the normalization constant N.

13.5 (a) Calculate the average kinetic and potential energies of an electron in the ground state of a hydrogen atom.

13.5 (b) Calculate the average kinetic and potential energies of a $2s$ electron in a hydrogenic atom of atomic number Z.

13.6 (a) Write down the expression for the radial distribution function of a $2s$ electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

13.6 (b) Write down the expression for the radial distribution function of a $3s$ electron in a hydrogenic atom and determine the radius at which the electron is most likely to be found.

13.7 (a) What is the orbital angular momentum of an electron in the orbitals (a) $1s$, (b) $3s$, (c) $3d$? Give the numbers of angular and radial nodes in each case.

13.7 (b) What is the orbital angular momentum of an electron in the orbitals (a) $4d$, (b) $2p$, (c) $3p$? Give the numbers of angular and radial nodes in each case.

13.8 (a) Calculate the permitted values of j for (a) a d electron, (b) an f electron.

13.8 (b) Calculate the permitted values of j for (a) a p electron, (b) an h electron.

13.9 (a) An electron in two different states of an atom is known to have $j = \frac{3}{2}$ and $\frac{1}{2}$. What is its orbital angular momentum quantum number in each case?

13.9 (b) What are the allowed total angular momentum quantum numbers of a composite system in which $j_1 = 5$ and $j_2 = 3$?

13.10 (a) State the orbital degeneracy of the levels in a hydrogen atom that have energy (a) $-hc\mathcal{R}_H$; (b) $-\frac{1}{9}hc\mathcal{R}_H$; (c) $-\frac{1}{25}hc\mathcal{R}_H$.

13.10 (b) State the orbital degeneracy of the levels in a hydrogenic atom (Z in parentheses) that have energy (a) $-4hc\mathcal{R}_{\text{atom}}$ (2), (b) $-\frac{1}{4}hc\mathcal{R}_{\text{atom}}$ (4), and (c) $-hc\mathcal{R}_{\text{atom}}$ (5).

13.11 (a) What information does the term symbol $^1\mathrm{D}_2$ provide about the angular momentum of an atom?

13.11 (b) What information does the term symbol $^3\mathrm{F}_4$ provide about the angular momentum of an atom?

13.12 (a) At what radius does the probability of finding an electron at a point in the H atom fall to 50 per cent of its maximum value?

13.12 (b) At what radius in the H atom does the radial distribution function of the ground state have (a) 50 per cent, (b) 75 per cent of its maximum value?

13.13 (a) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $2s \rightarrow 1s$, (b) $2p \rightarrow 1s$, (c) $3d \rightarrow 2p$?

13.13 (b) Which of the following transitions are allowed in the normal electronic emission spectrum of an atom: (a) $5d \rightarrow 2s$, (b) $5p \rightarrow 3s$, (c) $5p \rightarrow 3f$?

13.14 (a) How many electrons can occupy the following subshells: (a) $1s$, (b) $3p$, (c) $3d$, and (d) $6g$?

13.14 (b) How many electrons can occupy the following subshells: (a) $2s$, (b) $4d$, (c) $6f$, and (d) $6h$?

13.15 (a) (a) Write the electronic configuration of the Ni^{2+} ion. (b) What are the possible values of the total spin quantum numbers S and M_S for this ion?

13.15 (b) (a) Write the electronic configuration of the V^{2+} ion. (b) What are the possible values of the total spin quantum numbers S and M_S for this ion?

13.16 (a) Suppose that an atom has (a) 2, (b) 3 electrons in different orbitals. What are the possible values of the total spin quantum number S? What is the multiplicity in each case?

13.16 (b) Suppose that an atom has (a) 4, (b) 5, electrons in different orbitals. What are the possible values of the total spin quantum number S? What is the multiplicity in each case?

13.17 (a) What atomic terms are possible for the electron configuration ns^1nd^1? Which term is likely to lie lowest in energy?

13.17 (b) What atomic terms are possible for the electron configuration np^1nd^1? Which term is likely to lie lowest in energy?

13.18 (a) What values of J may occur in the terms (a) ^{1}S, (b) ^{2}P, (c) ^{3}P? How many states (distinguished by the quantum number M_J) belong to each level?

13.18 (b) What values of J may occur in the terms (a) ^{3}D, (b) ^{4}D, (c) ^{2}G? How many states (distinguished by the quantum number M_J) belong to each level?

13.19 (a) Give the possible term symbols for (a) Li [He]$2s^1$, (b) Na [Ne]$3p^1$.

13.19 (b) Give the possible term symbols for (a) Sc [Ar]$3d^14s^2$, (b) Br [Ar]$3d^{10}4s^24p^5$.

13.20 (a) Calculate the magnetic induction, B, required to produce a splitting of 1.0 cm^{-1} between the states of a ^{1}P term.

13.20 (b) Calculate the magnetic induction, B, required to produce a splitting of 0.784 cm^{-1} between the states of a ^{1}D term.

Problems

Numerical problems

13.1 The Humphreys series is another group of lines in the spectrum of atomic hydrogen. It begins at 12 368 nm and has been traced to 3281.4 nm. What are the transitions involved? What are the wavelengths of the intermediate transitions?

13.2 A series of lines in the spectrum of atomic hydrogen lie at 656.46 nm, 486.27 nm, 434.17 nm, and 410.29 nm. What is the wavelength of the next line in the series? What is the ionization energy of the atom when it is in the lower state of the transitions?

13.3 The Li^{2+} ion is hydrogenic and has a Lyman series at 740 747 cm^{-1}, 877 924 cm^{-1}, 925 933 cm^{-1}, and beyond. Show that the energy levels are of the form $-hc\mathcal{R}/n^2$ and find the value of $\mathcal{R}$ for this ion. Go on to predict the wavenumbers of the two longest-wavelength transitions of the Balmer series of the ion and find the ionization energy of the ion.

13.4 A series of lines in the spectrum of neutral Li atoms rise from combinations of $1s^22p^1$ ^{2}P with $1s^2nd^1$ ^{2}D and occur at 610.36 nm, 460.29 nm, and 413.23 nm. The d orbitals are hydrogenic. It is known that the ^{2}P term lies at 670.78 nm above the ground state, which is $1s^22s^1$ ^{2}S. Calculate the ionization energy of the ground-state atom.

13.5 The characteristic emission from K atoms when heated is purple and lies at 770 nm. On close inspection, the line is found to have two closely spaced components, one at 766.70 nm and the other at 770.11 nm. Account for this observation, and deduce what information you can.

13.6 Calculate the mass of the deuteron given that the first line in the Lyman series of H lies at 82 259.098 cm^{-1} whereas that of D lies at 82 281.476 cm^{-1}. Calculate the ratio of the ionization energies of H and D.

13.7 Positronium consists of an electron and a positron (same mass, opposite charge) orbiting round their common centre of mass. The broad features of the spectrum are therefore expected to be hydrogen-like, the differences arising largely from the mass differences. Predict the wavenumbers of the first three lines of the Balmer series of positronium. What is the binding energy of the ground state of positronium?

13.8 In 1976 it was mistakenly believed that the first of the 'superheavy' elements had been discovered in a sample of mica. Its atomic number was believed to be 126. What is the most probable distance of the innermost electrons from the nucleus of an atom of this element? (In such elements, relativistic effects are very important, but ignore them here.)

Theoretical problems

13.9 Is an electron further from the nucleus on average when it is in a $2s$ orbital or a $2p$ orbital?

13.10 What is the most probable point (not radius) at which a $2p$ electron will be found in the hydrogen atom?

13.11 Show by explicit integration that (a) hydrogenic $1s$ and $2s$ orbitals, (b) $2p_x$ and $2p_y$ orbitals are mutually orthogonal.

13.12 Determine whether the p_x and p_y orbitals are eigenfunctions of l_z. If not, does a linear combination exist that is an eigenfunction of l_z?

13.13 Show that l_z and l^2 both commute with the hamiltonian for a hydrogen atom. What is the significance of this result?

13.14 The 'size' of an atom is sometimes considered to be measured by the radius of a sphere that contains 90 per cent of the charge density of the electrons in the outermost occupied orbital. Calculate the 'size' of a hydrogen atom in its ground state according to this definition.

13.15 One of the most famous of the obsolete theories of the hydrogen atom was proposed by Bohr. It has been replaced by quantum mechanics but, by a remarkable coincidence (not the only one where the Coulomb potential is concerned), the energies it predicts agree exactly with those obtained from the Schrödinger equation. In the Bohr atom, an electron travels in a circle around the nucleus. The Coulombic force of attraction ($Ze^2/4\pi\varepsilon_0 r^2$) is balanced by the centrifugal effect of the orbital motion. Bohr proposed that the angular momentum is limited to integral values of $\hbar$. When the two forces are balanced, the atom remains in a stationary state until it makes a spectral transition. Calculate the energies of a hydrogenic atom by using the Bohr model.

13.16 The Bohr model of the atom is specified in Problem 13.15. What features of it are untenable according to quantum mechanics? How does the Bohr ground state differ from the actual ground state? Is there an experimental distinction between the Bohr and quantum mechanical models of the ground state?

13.17 Atomic units of length and energy may be based on the properties of a particular atom. The usual choice is that of a hydrogen atom, with the unit of length being the Bohr radius, a_0, and the unit of energy being the energy of the $1s$ orbital. If the positronium atom (e^+, e^-) were used instead, with analogous definitions of units of length and energy, what would be the relation between these two sets of atomic units?

Additional problems supplied by Carmen Giunta and Charles Trapp

13.18 The diameters of atoms can be estimated from their densities in a condensed state. Calculate the diameters of hydrogen and uranium atoms in this manner from information in the *Data section*. One finds that all atoms are roughly the same size, with $r \approx 0.3 \pm 0.1$ nm. Why is that? In a plot of atomic radius against atomic number some periodicity is evident, but not to the extent seen in a plot of first ionization energies against atomic number. Explain this observation.

13.19 In the Bohr model of the hydrogen atom, the electron orbits the nucleus at a distance of 52.9 pm. Calculate the speed of the electron in the first Bohr orbit. Considering the electron and proton to be classical charges, calculate the electrical field strength at the electron and the magnetic field strength at the proton. Compare to field strengths commonly available in the laboratory.

13.20 Use the radial wave equation for the hydrogen atom to demonstrate that the energies of the $2s$ and $2p$ orbitals are identical.

13.21 Dimensionless ratios that occur in the physical sciences are thought to be of fundamental significance. These ratios tend to be clustered around $(10^{20})^n$, where $n = 0, 1, 2, 3$, and 4. One such ratio in the $n = 0$ group is the mass ratio of the two fundamental particles, the proton and the electron. Scientists are puzzled as to why this ratio should be close to 2000. The precise value of the ratio is determined by comparison of the atomic spectral lines in H and He$^+$. (a) Derive the following relations for the first line in any of the series (Lyman, Balmer, etc.) for H and He$^+$:

$$\gamma = \frac{\frac{1}{4}\tilde{\nu}_{\mathrm{He}} - \tilde{\nu}_{\mathrm{H}}}{\tilde{\nu}_{\mathrm{H}}} = \frac{\mu_{\mathrm{He}} - \mu_{\mathrm{H}}}{\mu_{\mathrm{H}}}$$

where μ is a reduced mass. (b) Calculate m_{H}/m_e from the following data.

	$\lambda(n_2 \rightarrow n_1)/\mathrm{nm}$	$\mathcal{R}_J/\mathrm{cm}^{-1}$
H	121.5664	109 677.7
He$^+$	30.3779	109 722.4

First do the calculation from the wavelength data; then derive a formula for the mass ratio in terms of the Rydberg constants $\mathcal{R}_J$ of the species J and repeat the calculation of the mass ratio from that data.

13.22 Highly excited atoms are said to be in a 'high Rydberg state' and have electrons with large principal quantum numbers. Such 'Rydberg atoms' have several unusual properties and have attracted much attention in recent years, for example, in astrophysics and radioastronomy. For hydrogen atoms with large n, derive a relation for the separation of energy levels. Calculate this separation for $n = 100$; also calculate the average radius, the geometric cross-section, and the ionization energy. Could a thermal collision with another hydrogen atom ionize this Rydberg atom? What minimum velocity of the second atom is required? Could a normal-sized neutral H atom simply pass through the Rydberg atom leaving it undisturbed? What might the radial wavefunction for a $100s$ orbital be like?

13.23 W.P. Wijesundera, S.H. Vosko, and F.A. Parpia (*Phys. Rev.* A 51, 278 (1995)) attempted to determine the electron configuration of the ground state of lawrencium, element 103. The two contending configurations are [Rn]$5f^{14}7s^27p^1$ and [Rn]$5f^{14}6d^7s^2$. Write down the term symbols for each of these configurations, and identify the lowest level within each configuration. Which level would be lowest according to a simple estimate of spin–orbit coupling?

13.24 Stern–Gerlach splittings of atomic beams are small and require either large magnetic field gradients or long magnets for their observation. For a beam of atoms with zero orbital angular momentum, such as H or Ag, the deflection is given by $x = \pm(\mu_B L^2/4E_K)\mathrm{d}\mathcal{B}/\mathrm{d}z$, where L is the length of the magnet, E_K is the average kinetic energy of the atoms in the beam, and $\mathrm{d}\mathcal{B}/\mathrm{d}z$ is the magnetic field gradient. (a) Use the Maxwell–Boltzmann velocity distribution to show that the average translational kinetic energy of atoms emerging as a beam from a pinhole in an oven at temperature T is $2kT$. (b) Calculate the magnetic field gradient required to produce a splitting of 1.00 mm in a beam of Ag atoms from an oven at 1000 K with a magnet of length 50 cm.

14

Molecular structure

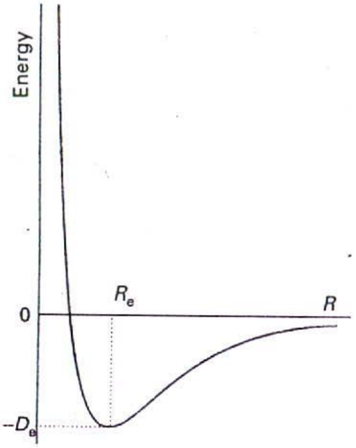
The concepts developed in Chapter 13, particularly those of orbitals, can be extended to a description of the electronic structures of molecules. There are two principal quantum mechanical theories of molecular electronic structure. In valence-bond theory the starting point is the concept of the shared electron pair. We see how to write the wavefunction for such a pair, and how it may be extended to account for the structures of a wide variety of molecules. The theory introduces the concepts of σ and π bonds, promotion, and hybridization that are used widely in chemistry. In molecular orbital theory (with which the bulk of the chapter is concerned), the concept of atomic orbital is extended to that of molecular orbital, which is a wavefunction that spreads over all the atoms in a molecule. This theory may be extended to the description of the electronic properties of solids, and used to account for electrical conduction and semiconduction.

The Born–Oppenheimer approximation

All theories of molecular structure make the same simplification at the outset. Whereas the Schrödinger equation for a hydrogen atom can be solved exactly, an exact solution is not possible for any molecule because the simplest molecule consists of three particles (two nuclei and one electron). The **Born–Oppenheimer approximation** is therefore adopted, in which it is supposed that the nuclei, being so much heavier than an electron, move relatively slowly, and may be treated as stationary while the electrons move relative to them. We can therefore think of the nuclei as being fixed at an arbitrary separation R, and then solve the Schrödinger equation for the wavefunction of the electrons alone.

The approximation is quite good for ground-state molecules, for calculations suggest that the nuclei in H_2 move through only about 1 pm while the electron speeds through 1000 pm, so the error of assuming that the nuclei are stationary is small. Exceptions to the approximation's validity include certain excited states of polyatomic molecules and the ground states of cations; both types of species are important when considering photoelectron spectroscopy (Section 17.8) and mass spectrometry.

The Born–Oppenheimer approximation allows us to select an internuclear separation, and (in principle) to solve the Schrödinger equation for the electrons at that nuclear separation. Then we choose a different separation and repeat the calculation, and so on. In this way we can explore how the energy of the molecule varies with bond length (and, in more complex molecules, with angles too), and obtain a **molecular potential energy curve** (Fig. 14.1).[1] It is called a *potential* energy curve because the kinetic energy of the stationary nuclei is zero. Once the curve has been calculated or determined experimentally (by using the spectroscopic techniques described in Chapters 16 and 17), we can identify the **equilibrium bond length** (the internuclear separation at the minimum of the curve) and the **bond dissociation energy**, D_0, which is closely related to the depth of the minimum below the energy of the infinitely widely separated atoms.[2]



14.1 A molecular potential energy curve. The equilibrium bond length corresponds to the energy minimum.

Valence-bond theory

The **valence-bond theory** (VB theory) of bonding was the first to be developed. The language it introduced, which includes concepts such as spin-pairing, σ and π bonds, and hybridization, is widely used throughout chemistry. It is particularly widespread in the description of the properties and reactions of organic compounds.

14.1 The hydrogen molecule

The simplest molecule with an electron pair bond is H_2. We shall use this molecule to introduce the basic concepts of the theory.

(a) The spatial wavefunction

The wavefunction for an electron on each of two widely separated H atoms is

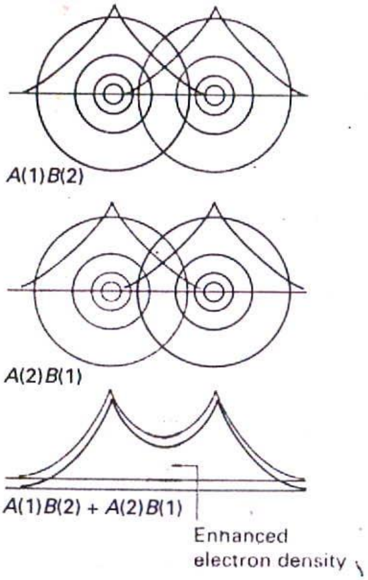
$$\psi = \psi_{\text{H1sA}}(\boldsymbol{r}_1)\psi_{\text{H1sB}}(\boldsymbol{r}_2)$$

if electron 1 is on atom A and electron 2 is on atom B. For simplicity, we shall write this wavefunction as $\psi = A(1)B(2)$. When the atoms are close, it is not possible to know whether it is electron 1 that is on A or electron 2. An equally valid description is therefore $\psi = A(2)B(1)$, in which electron 2 is on A and electron 1 is on B. When two outcomes are equally probable, quantum mechanics instructs us to describe the true state of the system as a superposition of the wavefunctions for each possibility (Section 11.5d), so a better description of the molecule than either wavefunction alone is

$$\psi = A(1)B(2) \pm A(2)B(1) \tag{1}$$

(These linear combinations are not normalized.) It turns out (as shown in the *Justification* below) that the combination with lower energy is the one with a + sign, so the valence-bond wavefunction of the H_2 molecule is

$$\psi = A(1)B(2) + A(2)B(1) \tag{2}$$



14.2 It is very difficult to represent valence-bond wavefunctions because they refer to two electrons simultaneously. However, this illustration is an attempt. The atomic orbital for electron 1 is represented by the black contours, and that of electron 2 is represented by the green contours. The top illustration represents $A(1)B(2)$, and the middle illustration represents the contribution $A(2)B(1)$. When the two contributions are superimposed, there is interference between the black contributions and between the green contributions, resulting in an enhanced (two-electron) density in the internuclear region.

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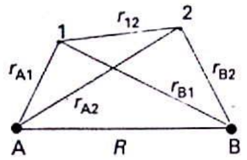
[1] When more than one molecular parameter is changed in a polyatomic molecule, we obtain a potential energy surface.

[2] The dissociation energy differs from the depth of the well by an energy equal to the zero-point vibrational energy of the bonded atoms. If the depth of the well is denoted D_e, then $D_0 = D_e - \frac{1}{2}\hbar\omega$, where ω is the vibrational frequency of the bond.



1

Justification 14.1

The VB wavefunction for H_2 is an approximate solution of the Schrödinger equation in which the potential energy of the two electrons is

$$V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}}+\frac{1}{r_{A2}}+\frac{1}{r_{B1}}+\frac{1}{r_{B2}}\right)+\frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

The coordinates are specified in (1). The four terms in parentheses are the attractive contribution from the interaction between the electrons and the nuclei. The remaining term is the repulsive interaction between the two electrons. The energy of the molecule is calculated by evaluating the expectation value of the hamiltonian

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 + V + \frac{e^2}{4\pi\varepsilon_0 R}$$

with the expression for V given above; the final term is the potential energy of the nucleus–nucleus repulsion. When the wavefunctions in eqn 1 are used, the expectation value turns out to be

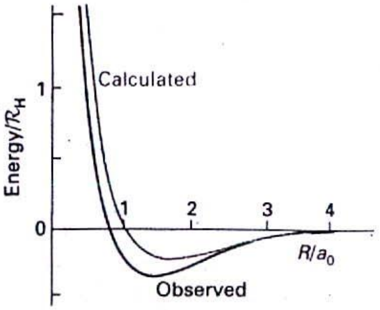
$$E_\pm = 2E_H + \frac{J \pm K}{1 \pm S^2} + \frac{e^2}{4\pi\varepsilon_0 R} \qquad (3)$$

where E_H is the energy of a hydrogen atom and J and K are complicated collections of integrals over the wavefunctions. These integrals represent the interaction of the electrons with the nuclei and the mutual repulsion of the electrons. The integral S is the overlap integral, which is discussed in more detail shortly. The integrals J and K are both negative and the lower energy is achieved with the + sign in eqn 1.

The formation of the bond in H_2 can be pictured as due to the high probability that the two electrons will be found between the two nuclei and hence will bind them together. More formally, the wave pattern represented by the term $A(1)B(2)$ interferes constructively with the wave pattern represented by the contribution $A(2)B(1)$, and there is an enhancement in the value of the wavefunction in the internuclear region (Fig. 14.2).

The electron distribution described by the wavefunction in eqn 2 is called a **σ bond**. A σ bond has cylindrical symmetry around the internuclear axis, and is so called because, when viewed along the internuclear axis, it resembles a pair of electrons in an *s* orbital (and σ is the Greek equivalent of *s*). More precisely, the electrons in a σ bond have zero orbital angular momentum about the internuclear axis.[3]

The molecular potential energy curve for H_2 is calculated by changing the internuclear separation R and evaluating the expectation value of the energy at each selected separation. The resulting graph is shown in Fig. 14.3. The energy falls below that of two separated H atoms as the two atoms are brought within bonding distance and each electron is free to migrate to the other atom. However, the energy reduction that follows from this process is counteracted by an increase in energy from the Coulombic repulsion between the two positively charged nuclei. This positive contribution to the energy becomes large as R becomes small. Consequently, the total potential energy curve passes through a minimum and then climbs to a strongly positive value at small internuclear separations.



14.3 The molecular potential energy curve for the hydrogen molecule showing the variation of the energy of the molecule as the bond length is changed. The calculated curve refers to the valence-bond model.

(b) The role of electron spin

So far, the electron spin has not played a role in the argument, yet a chemist's picture of a covalent bond is one in which the spins of two electrons pair as the atomic orbitals overlap.

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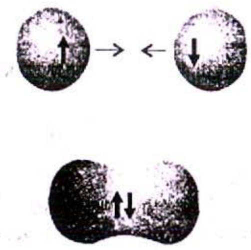
[3] Recall from Section 12.6 that the orbital angular momentum of an electron is related to the number of angular nodes in its wavefunction, but there are no angular nodes in the wavefunction of a σ bond, so it has zero orbital angular momentum.



14.4 The orbital overlap and spin-pairing between electrons in two collinear p orbitals that result in the formation of a σ bond.

The origin of the role of spin is that the wavefunction given in eqn 2 can be formed only by a pair of electrons with opposed spins. Thus, spin-pairing is not an end in itself: it is a means of achieving a spatial wavefunction (and the probability distribution it implies) that corresponds to a low energy.

Justification 14.2

The Pauli principle requires the wavefunction of two electrons to change sign when the labels of the electrons are interchanged (see *Justification 13.7*). The total VB wavefunction for two electrons is

$$\Psi(1,2) = \{A(1)B(2) + A(2)B(1)\}\sigma(1,2)$$

where σ represents the spin component of the wavefunction. When the labels 1 and 2 are interchanged, this wavefunction becomes

$$\begin{aligned}\Psi(2,1) &= \{A(2)B(1) + A(1)B(2)\}\sigma(2,1)\\ &= \{A(1)B(2) + A(2)B(1)\}\sigma(2,1)\end{aligned}$$

The Pauli principle requires that $\Psi(2,1) = -\Psi(1,2)$, which is satisfied only if $\sigma(2,1) = -\sigma(1,2)$. The combination of two spins that has this property is

$$\sigma_-(1,2) = \frac{1}{2^{1/2}}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

which corresponds to paired electron spins (Section 13.7). Therefore, we conclude that the state of lower energy (and hence the formation of a chemical bond) is achieved if the electron spins are paired.

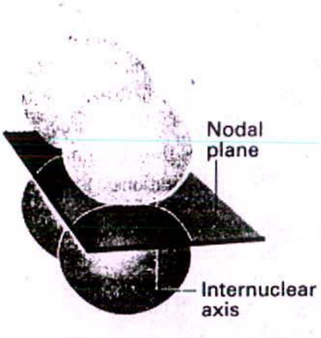
14.2 Homonuclear diatomic molecules

The essential features of valence-bond theory are the pairing of the electrons and the accumulation of electron density in the internuclear region that stems from that pairing. The same description can be applied to more complex molecules, such as **homonuclear diatomic molecules**, which are diatomic molecules in which both atoms belong to the same element. Nitrogen, N_2, is an example. To construct the valence-bond description of N_2, we consider the valence electron configuration of each atom:

N $\quad 2s^2 2p_x^1 2p_y^1 2p_z^1$

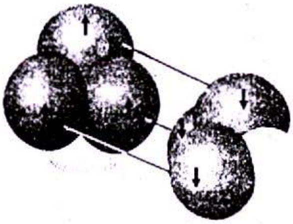
It is conventional to take the z-axis to be the internuclear axis, so we can imagine each atom as having a $2p_z$ orbital pointing towards a $2p_z$ orbital on the other atom (Fig. 14.4), with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis. A σ bond is then formed by spin-pairing between the two electrons in the opposing $2p_z$ orbitals. Its spatial wavefunction is given by eqn 2, but now A and B stand for the two $2p_z$ orbitals.

The remaining $2p$ orbitals cannot merge to give σ bonds as they do not have cylindrical symmetry around the internuclear axis. Instead, the electrons in them merge to form two π bonds (Fig. 14.5). A π bond arises from the spin-pairing of electrons in two p orbitals that approach side-by-side. It is so called because, viewed along the internuclear axis, a π bond resembles a pair of electrons in a p orbital (and π is the Greek equivalent of p). More precisely, an electron in a π bond has one unit of orbital angular momentum about the internuclear axis, for the wavefunction has one angular node.



14.5 A π bond results from spin pairing and orbital overlap of p orbitals that approach side by side.

There are two π bonds in N_2, one formed by spin-pairing in two neighbouring $2p_x$ orbitals and the other by spin-pairing in two neighbouring $2p_y$ orbitals. The overall bonding pattern



14.6 The structure of bonds in a nitrogen molecule which consists of one σ bond and two π bonds. The electron density has cylindrical symmetry around the internuclear axis.

in N_2 is therefore a σ bond plus two π bonds (Fig. 14.6), which is consistent with the Lewis structure :N≡N: for nitrogen.

Illustration

To obtain the VB description of Cl_2, note that the ground-state electron configuration of a Cl atom is $[Ar]3s^2 3p_x^2 3p_y^2 3p_z^1$. A σ bond can be formed between two atoms by spin-pairing of the electrons in the $3p_z$ orbitals. This description is consistent with the Lewis structure $:\ddot{\text{Cl}}\text{—}\ddot{\text{Cl}}:$ for chlorine. The VB wavefunction for the bonding pair is the same as in eqn 2 but with A and B now standing for the two Cl3p_z orbitals.

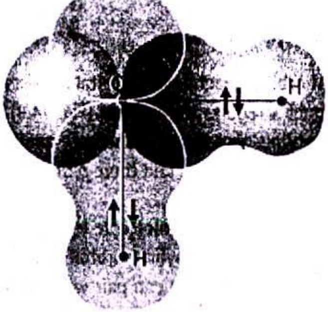
Self-test 14.1 Describe the ground state of HCl in valence-bond terms.

[eqn 2 with $A = \psi_{H1s}$, $B = \psi_{Cl2p_z}$]

14.3 Polyatomic molecules

Each σ bond in a polyatomic molecule is formed by the spin-pairing of electrons in any atomic orbitals with cylindrical symmetry about the relevant internuclear axis. Likewise, π bonds are formed by pairing electrons that occupy atomic orbitals of the appropriate symmetry.

The valence-bond description of H_2O will make this clear. The valence electron configuration of an O atom is $2s^2 2p_x^2 2p_y^1 2p_z^1$. The two unpaired electrons in the O2p orbitals can each pair with an electron in an H1s orbital, and each combination results in the formation of a σ bond (each bond has cylindrical symmetry about the respective O–H internuclear axis). Because the $2p_y$ and $2p_z$ orbitals lie at 90° to each other, the two σ bonds also lie at 90° to each other (Fig. 14.7). We can predict, therefore, that H_2O should be an angular molecule, which it is. However, the theory predicts a bond angle of 90°, whereas the actual bond angle is 104.5°.



14.7 A first approximation to the valence-bond description of bonding in an H_2O molecule. Each σ bond arises from the overlap of an H1s orbital with one of the O2p orbitals. This model suggests that the bond angle should be 90°, which is significantly different from the experimental value.

Example 14.1 Predicting the shape of a molecule by using valence-bond theory

Describe the valence-bond structure of NH_3, and predict the bond angle of the molecule on the basis of this description.

Method Write down the ground-state configuration of an N atom, and decide which electrons and orbitals can be used to form bonds. Then, from the spatial arrangement of those atomic orbitals, infer the shape of the resulting molecule.

Answer The valence electron configuration of an N atom is N $2s^2 2p_x^1 2p_y^1 2p_z^1$. This configuration suggests that three H atoms can form bonds by spin-pairing with the electrons in the three half-filled $2p$ orbitals. The latter are perpendicular to each other, so we predict a trigonal pyramidal molecule with a bond angle of 90°.

Comment The molecule is trigonal pyramidal, but the experimental bond angle is 107°. The origin of this discrepancy is discussed below.

Self-test 14.2 Use valence-bond theory to suggest a shape for the hydrogen peroxide molecule, H_2O_2.

[Each H–O–O bond 90°]

(a) Promotion

An apparent deficiency of valence-bond theory is its inability to account for carbon's tetravalence (its ability to form four bonds). The ground-state configuration of C is $2s^22p_x^12p_y^1$, which suggests that a carbon atom should be capable of forming only two bonds, not four. This deficiency is overcome by allowing for **promotion**, the excitation of an electron to an orbital of higher energy. Although electron promotion requires an investment of energy, it is worthwhile if that energy can be more than recovered from the greater strength or number of bonds that it allows to be formed. Promotion is not a 'real' process in which an atom somehow becomes excited and then forms bonds: it is a contribution to the overall energy change that occurs when bonds form.

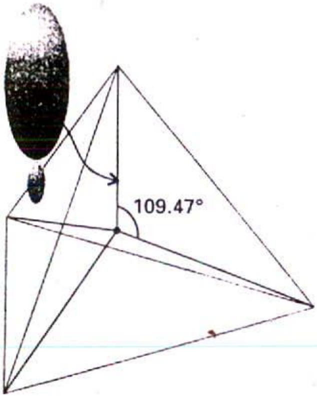
In carbon, for example, the promotion of a $2s$ electron to a $2p$ orbital can be thought of as leading to the configuration $2s^12p_x^12p_y^12p_z^1$, with four unpaired electrons in separate orbitals. These electrons may pair with four electrons in orbitals provided by four other atoms (such as four H1s orbitals if the molecule is CH_4), and hence form four σ bonds. Although energy was required to promote the electron, it is more than recovered by the atom's ability to form four bonds in place of the two bonds of the unpromoted atom. Promotion, and the formation of four bonds, is a characteristic feature of carbon because the promotion energy is quite small: the promoted electron leaves a doubly occupied $2s$ orbital and enters a vacant $2p$ orbital, hence significantly relieving the electron–electron repulsion it experiences in the former.

(b) Hybridization

The description of the bonding in CH_4 (and other alkanes) is still incomplete because it appears to imply the presence of three σ bonds of one type (formed from H1s and C2p orbitals) and a fourth σ bond of a distinctly different character (formed from H1s and C2s). This problem is overcome by realizing that the electron density distribution in the promoted atom is equivalent to the electron density in which each electron occupies a **hybrid orbital** formed by interference between the C2s and C2p orbitals. The origin of the hybridization can be appreciated by thinking of the four atomic orbitals, which are waves centred on a nucleus, as being like ripples spreading from a single point on the surface of a lake:[4] the waves interfere destructively and constructively in different regions, and give rise to four new shapes.

The specific linear combinations that give rise to four equivalent hybrid orbitals are

$$\begin{aligned} h_1 &= s + p_x + p_y + p_z \qquad & h_2 &= s - p_x - p_y + p_z \\ h_3 &= s - p_x + p_y - p_z \qquad & h_4 &= s + p_x - p_y - p_z \end{aligned} \tag{4}$$



14.8 An sp^3 hybrid orbital formed from the superposition of s and p orbitals on the same atom. There are four such hybrids: each one points towards the corner of a regular tetrahedron. The overall electron density remains spherically symmetrical.

As a result of the interference between the component orbitals, each hybrid orbital consists of a large lobe pointing in the direction of one corner of a regular tetrahedron (Fig. 14.8). The angle between the axes of the hybrid orbitals is the tetrahedral angle, $\cos(-1/3) = 109.47°$. Because each hybrid is built from one s orbital and three p orbitals, it is called an **sp^3 hybrid orbital**.

It is now easy to see how the valence-bond description of the CH_4 molecule leads to a tetrahedral molecule containing four equivalent C–H bonds. Each hybrid orbital of the promoted C atom contains a single unpaired electron; an H1s electron can pair with each one, giving rise to a σ bond pointing in a tetrahedral direction. For example, the (un-normalized) wavefunction for the bond formed by the hybrid orbital h_1 and the $1s_A$ orbital (with wavefunction that we shall denote A) is

$$\psi = h_1(1)A(2) + h_1(2)A(1)$$

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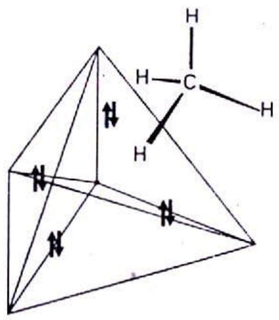
[4] It is admittedly difficult to imagine how a ripple resembling a p orbital could be contrived, but the general idea should be clear.



14.9 Each sp^3 hybrid orbital forms a σ bond by overlap with an H1*s* orbital located at the corner of the tetrahedron. This model accounts for the equivalence of the four bonds in CH_4.

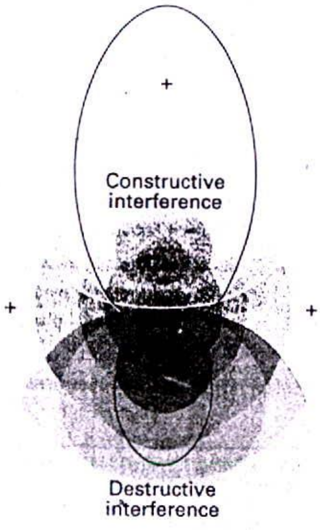
Because each sp^3 hybrid orbital has the same composition, all four σ bonds are identical apart from their orientation in space (Fig. 14.9).

A further feature of hybridization is that a hybrid orbital has pronounced directional character, in the sense that it has an enhanced amplitude in the internuclear region. This directional character arises from the constructive interference between the *s* orbital and the positive lobes of the *p* orbitals (Fig. 14.10). As a result of the enhanced amplitude in the internuclear region, the bond strength is greater than for an *s* or *p* orbital alone. This increased bond strength is another factor that helps to repay the promotion energy.

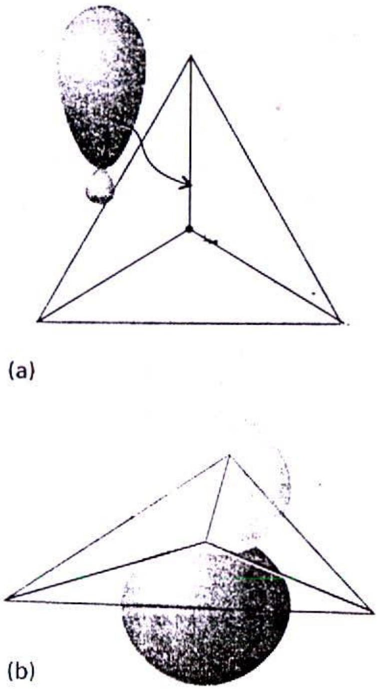
Hybridization can also be used to describe the structure of an ethene molecule, $H_2C{=}CH_2$, and the torsional rigidity of double bonds. An ethene molecule is planar, with HCH and HCC bond angles close to 120°. To reproduce the σ bonding structure, we promote each C atom to a $2s^1 2p^3$ configuration. However, instead of using all four orbitals to form hybrids, we form sp^2 hybrid orbitals by the superposition of an *s* orbital and two *p* orbitals. As shown in Fig. 14.11, the three hybrid orbitals

$$\begin{aligned} h_1 &= s + 2^{1/2} p_y \\ h_2 &= s + \left(\tfrac{3}{2}\right)^{1/2} p_x - \left(\tfrac{1}{2}\right)^{1/2} p_y \\ h_3 &= s - \left(\tfrac{3}{2}\right)^{1/2} p_x - \left(\tfrac{1}{2}\right)^{1/2} p_y \end{aligned} \tag{5}$$

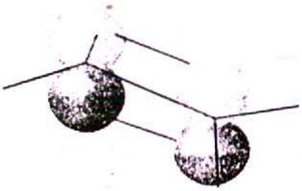
lie in a plane and point towards the corners of an equilateral triangle. The third 2*p* orbital ($2p_z$) is not included in the hybridization, and its axis is perpendicular to the plane in which the hybrids lie.



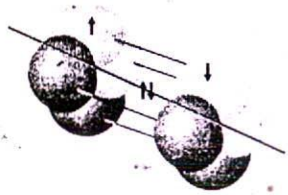
14.10 A more detailed representation of the formation of an sp^3 hybrid by interference between wavefunctions centred on the same atomic nucleus. (To simplify the representation, we have ignored the radial node of the 2*s* orbital.)



14.11 (a) An *s* orbital and two *p* orbitals can be hybridized to form three equivalent orbitals that point towards the corners of an equilateral triangle. (b) The remaining, unhybridized *p* orbital is perpendicular to the plane.



14.12 A representation of the structure of a double bond in ethene; only the π bond is shown explicitly.



14.13 A representation of the structure of a triple bond in ethyne; only the π bonds are shown explicitly. The overall electron density has cylindrical symmetry around the axis of the molecule.

The structure of $CH_2{=}CH_2$ can now be described as follows. The sp^2-hybridized C atoms each form three σ bonds by spin-pairing with either the h_1 hybrid of the other C atom or with H1*s* orbitals. The σ framework therefore consists of C–H and C–C σ bonds at 120° to each other. When the two CH_2 groups lie in the same plane, the two electrons in the unhybridized *p* orbitals can pair and form a π bond (Fig. 14.12). The formation of this π bond locks the framework into the planar arrangement, for any rotation of one CH_2 group relative to the other leads to a weakening of the π bond (and consequently an increase in energy of the molecule).

A similar description applies to ethyne, $HC{\equiv}CH$, a linear molecule. Now the C atoms are *sp* hybridized, and the σ bonds are formed using hybrid atomic orbitals of the form

$$h_1 = s + p_z \qquad h_2 = s - p_z \tag{6}$$

These two orbitals lie along the internuclear axis. The electrons in them pair either with an electron in the corresponding hybrid orbital on the other C atom or with an electron in one of the H1*s* orbitals. Electrons in the two remaining *p* orbitals on each atom, which are perpendicular to the molecular axis, pair to form two perpendicular π bonds (Fig. 14.13).

Other hybridization schemes, particularly those involving *d* orbitals, are often invoked to be consistent with other molecular geometries (Table 14.1). The hybridization of *N* atomic orbitals always results in the formation of *N* hybrid orbitals. For example, sp^3d^2 hybridization results in six equivalent hybrid orbitals pointing towards the corners of a regular octahedron. This octahedral hybridization scheme is sometimes invoked to account for the structure of octahedral molecules, such as SF_6.

Table 14.1[*] Some hybridization schemes

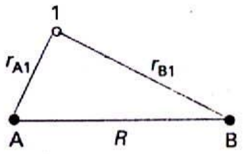
Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, pd^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	$sp^2d^2, sd^4, pd^4, p^3d^2$
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

[*] Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*. Wiley (1944).

Molecular orbital theory

In **molecular orbital theory** (MO theory), it is accepted that electrons should not be regarded as belonging to particular bonds but should be treated as spreading throughout the entire molecule. This theory has been more fully developed than VB theory and provides the language that is widely used in modern discussions of bonding. To introduce it, we follow the same strategy as in Chapter 13, where the one-electron H atom was taken as the fundamental species for discussing atomic structure and then this discussion was developed into a description of many-electron atoms. In this chapter we use the simplest molecular species of all, the hydrogen molecule-ion, H_2^+, to introduce the essential features of bonding, and then use it as a guide to the structures of more complex systems.

14.4 The hydrogen molecule-ion



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The hamiltonian for the single electron in H_2^+ is

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 + V \qquad V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}}+\frac{1}{r_{B1}}-\frac{1}{R}\right) \tag{7}$$

where r_{A1} and r_{B1} are the distances of the electron from the two nuclei (**2**). The one-electron wavefunctions obtained by solving the Schrödinger equation $H\psi = E\psi$ are called **molecular orbitals** (MO). A molecular orbital ψ gives, through the value of $|\psi|^2$, the distribution of the electron in the molecule. A molecular orbital is like an atomic orbital, but spreads throughout the molecule.

The Schrödinger equation can be solved for H_2^+ (within the Born–Oppenheimer approximation), but the wavefunctions are very complicated functions; moreover, the solution cannot be extended to polyatomic systems. Therefore, we shall adopt a simpler procedure that, while more approximate, can be extended readily to other molecules.

(a) Linear combinations of atomic orbitals

If an electron can be found in an atomic orbital belonging to atom A and also in an atomic orbital belonging to atom B, the overall wavefunction is a superposition of the two atomic orbitals:

$$\psi_{\pm} = N(A \pm B) \tag{8}$$

where, for H_2^+, A denotes $\psi_{\mathrm{H}1s\mathrm{A}}$ and B denotes $\psi_{\mathrm{H}1s\mathrm{B}}$ and N is a normalization factor. The technical term for the superposition in eqn 8 is a **linear combination of atomic orbitals** (LCAO). An approximate molecular orbital formed from a linear combination of atomic orbitals is called an LCAO-MO. A molecular orbital that has cylindrical symmetry around the internuclear axis, such as the one we are discussing, is called a **σ orbital** because it resembles an s orbital when viewed along the axis and, more precisely, because it has zero orbital angular momentum around the internuclear axis.

Example 14.2 Normalizing a molecular orbital

Normalize the molecular orbital ψ_+ in eqn 8.

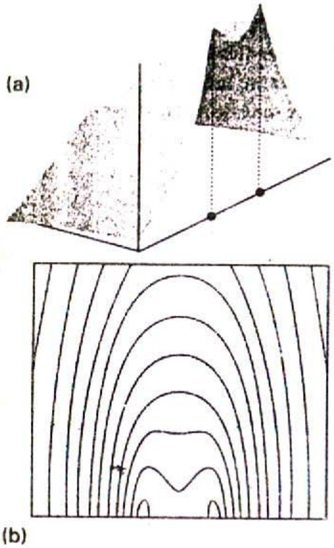
Method We need to find the factor N such that

$$\int \psi^* \psi \, d\tau = 1$$

To proceed, substitute the LCAO into this integral, and make use of the fact that the atomic orbitals are individually normalized.

Answer When we substitute the wavefunction, we find

$$\int \psi^* \psi \, d\tau = N^2 \left\{ \int A^2 \, d\tau + \int B^2 \, d\tau + 2 \int AB \, d\tau \right\}$$
$$= N^2(1 + 1 + 2S)$$



14.14 (a) The amplitude of the bonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude.

where $S = \int AB\,d\tau$. For the integral to be equal to 1, we require

$$N = \frac{1}{\{2(1+S)\}^{1/2}}$$

Comment In H_2^+, $S \approx 0.59$, so $N = 0.56$.

Self-test 14.3 Normalize the orbital ψ_- in eqn 8.

$[N = 1/\{2(1-S)\}^{1/2}$, so $N = 1.10]$

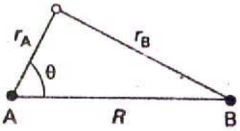
Figure 14.14 shows the contours of constant amplitude for the molecular orbital ψ_+ in eqn 8, and Fig. 14.15 shows its boundary surface. Plots like these are readily obtained using commercially available software. The calculation is quite straightforward, because all we need do is feed in the mathematical forms of the two atomic orbitals, and let the program do the rest. In this case, we use

$$A = \frac{e^{-r_A/a_0}}{(\pi a_0^3)^{1/2}} \qquad B = \frac{e^{-r_B/a_0}}{(\pi a_0^3)^{1/2}} \tag{9}$$

and note that r_A and r_B are not independent (3):

$$r_B = \{r_A^2 + R^2 - 2r_AR\cos\theta\}^{1/2} \tag{10}$$

To make this plot, we have taken $N^2 = 0.31$ (Example 14.2).



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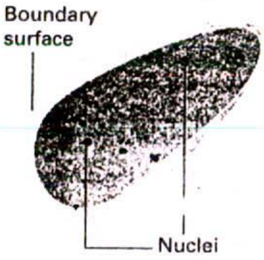
(b) Bonding orbitals

According to the Born interpretation, the probability density of the electron in H_2^+ is proportional to the square modulus of its wavefunction. The probability density corresponding to the (real) wavefunction ψ_+ in eqn 8 is

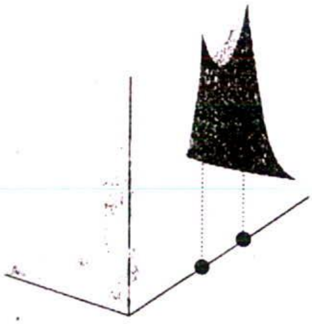
$$\psi_+^2 = N^2(A^2 + B^2 + 2AB) \tag{11}$$

This probability density is plotted in Fig. 14.16.

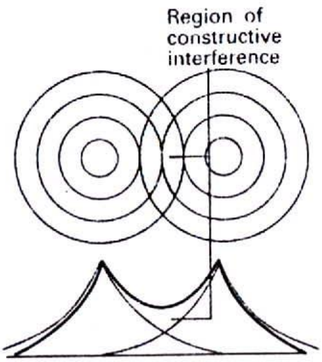
An important feature of the probability density becomes apparent when we examine the internuclear region, where both atomic orbitals have similar amplitudes. According to



14.15 The boundary surface of a σ orbital encloses the region where the electrons that occupy the orbital are most likely to be found. Note that the orbital has cylindrical symmetry.



14.16 The electron density calculated by forming the square of the wavefunction used to construct Fig. 14.14. Note the accumulation of electron density in the internuclear region.



14.17 A representation of the constructive interference that occurs when two H1*s* orbitals overlap and form a bonding σ orbital. Compare this illustration with Fig. 14.14.

eqn 11, the total probability density is proportional to the sum of

1. A^2, the probability density if the electron were confined to the atomic orbital on A.
2. B^2, the probability density if the electron were confined to the atomic orbital on B.
3. $2AB$, an extra contribution to the density.

This last contribution, the **overlap density**, is crucial, because it represents an enhancement of the probability of finding the electron in the internuclear region. The enhancement can be traced to the constructive interference of the two atomic orbitals: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atomic orbital.

We shall frequently use the result that *electrons accumulate in regions where atomic orbitals overlap and interfere constructively*. The accumulation of electron density between the nuclei puts the electron in a position where it interacts strongly with both nuclei. Hence, the energy of the molecule is lower than that of the separate atoms, where each electron can interact strongly with only one nucleus.[5]

The σ orbital we have described is an example of a **bonding orbital**, an orbital which, if occupied, helps to bind two atoms together. Specifically, we label it 1σ as it is the σ orbital of lowest energy. An electron that occupies a σ orbital is called a **σ electron** and, if that is the only electron present in the molecule (as in the ground state of H_2^+), then we report the configuration of the molecule as $1\sigma^1$.

The energy of the 1σ orbital decreases as R decreases from large values because electron density accumulates in the internuclear region as the constructive interference between the atomic orbitals increases (Fig. 14.17). However, at small separations there is too little space between the nuclei for significant accumulation of electron density there. In addition, the nucleus–nucleus repulsion (which is proportional to $1/R$) becomes large. As a result, the energy of the molecule rises at short distances, and there is a minimum in the potential energy curve. Calculations on H_2^+ give $R_e = 130$ pm and $D_e = 1.77$ eV (171 kJ mol^{-1}); the experimental values are 106 pm and 2.6 eV, so this simple LCAO-MO description of the molecule, while inaccurate, is not absurdly wrong.

Justification 14.3

To evaluate the energy of the bonding orbital, we calculate the expectation value of the hamiltonian, just as in VB theory. However, the calculation is much simpler, because there is only one electron, so there are no integrals corresponding to electron–electron repulsions. The expectation value of the hamiltonian in eqn 7 is

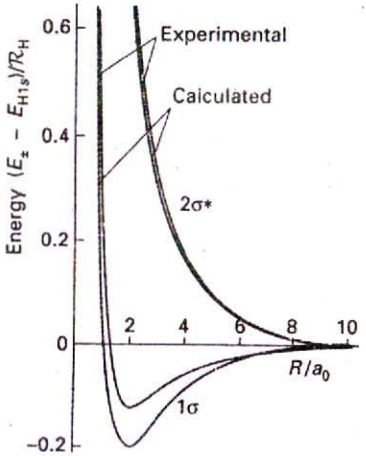
$$E_\pm = E_{\mathrm{H1}s} + \frac{e^2}{4\pi\varepsilon_0 R} - \frac{j \pm k}{1 \pm S} \tag{12}$$

(We have included the energy for both linear combinations in eqn 8 in this expression; for the bonding orbital, use the upper sign throughout.) The integrals that appear in this

---

[5] Unfortunately, this conventional explanation is probably incorrect in the case of H_2^+ (at least), because shifting an electron away from a nucleus into the internuclear region *raises* its potential energy. The modern explanation is more subtle, still controversial, and does not emerge from the simple LCAO treatment given here. It seems that, at the same time as the electron shifts into the internuclear region, the atomic orbitals shrink. This orbital shrinkage improves the electron–nucleus attraction more than it is decreased by the migration to the internuclear region, so there is a net lowering of potential energy. The kinetic energy of the electron is also modified because the curvature of the wavefunction is changed, but the change in kinetic energy is dominated by the change in potential energy.

Throughout the following discussion we ascribe the strength of chemical bonds to the accumulation of electron density in the internuclear region. We leave open the question whether in molecules more complicated than H_2^+ the true source of energy lowering is that accumulation itself or some indirect but related effect.



14.18 The calculated and experimental molecular potential energy curves for a hydrogen molecule-ion.

expression are

$$\begin{aligned} S &= \int AB\,\mathrm{d}\tau = \left\{1 + \frac{R}{a_0} + \tfrac{1}{3}\left(\frac{R}{a_0}\right)^2\right\}\mathrm{e}^{-R/a_0} \\ j &= \frac{e^2}{4\pi\varepsilon_0}\int \frac{A^2}{r_{\mathrm{B}}}\,\mathrm{d}\tau = \frac{e^2}{4\pi\varepsilon_0 R}\left\{1 - \left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-2R/a_0}\right\} \\ k &= \frac{e^2}{4\pi\varepsilon_0}\int \frac{AB}{r_{\mathrm{A}}}\,\mathrm{d}\tau = \frac{e^2}{4\pi\varepsilon_0 a_0}\left(1 + \frac{R}{a_0}\right)\mathrm{e}^{-R/a_0} \end{aligned} \tag{13}$$

All three integrals are positive and decline exponentially towards zero at large internuclear separations. The integral j is a measure of the interaction between a nucleus and electron density centred on the other nucleus; k is a measure of the interaction between a nucleus and the excess probability in the internuclear region arising from overlap. It is easy to use a mathematical software package to plot the energy as a function of R and hence to obtain Fig. 14.18.

(c) Antibonding orbitals

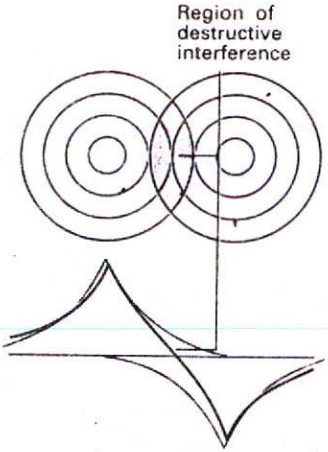
The linear combination ψ_- in eqn 8 corresponds to a higher energy than ψ_+. Because it is also a σ orbital we label it 2σ. This orbital has an internuclear nodal plane where A and B cancel exactly (Fig. 14.19 and Fig. 14.20). The probability density is

$$\psi_-^2 = N^2(A^2 + B^2 - 2AB) \tag{14}$$

There is a reduction in probability density between the nuclei due to the $-2AB$ term (Fig. 14.21); in physical terms, there is destructive interference where the two atomic orbitals overlap. The most significant point of difference between ψ_- and ψ_+ is the existence of a nodal plane in ψ_-, on which the amplitude of one atomic orbital is cancelled by the other. The physical significance of the nodal plane is that an electron that occupies the orbital will not be found anywhere on the plane.

The 2σ orbital is an example of an **antibonding orbital**, an orbital that, if occupied, contributes to a reduction in the cohesion between two atoms and helps to raise the energy of the molecule relative to the separated atoms. Antibonding orbitals are often labelled with an asterisk (*), so this particular orbital could also be denoted $2\sigma^*$ (and read '2 sigma star').

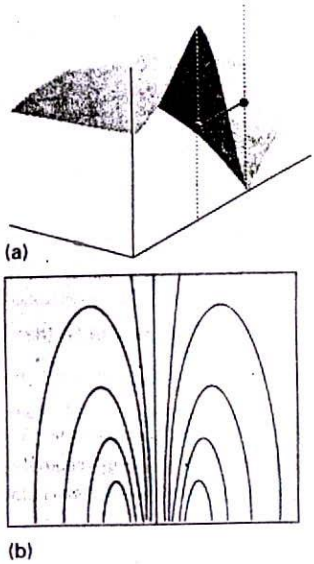
The destabilizing effect of an antibonding electron is partly due to the fact that it is excluded from the internuclear region, and hence is distributed largely outside the bonding region. In effect, whereas a bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart (Fig. 14.22). Figure 14.18 also shows another feature that we draw on later: $|E_- - E_{\mathrm{H1}s}| > |E_+ - E_{\mathrm{H1}s}|$, which indicates that the antibonding orbital is more antibonding than the bonding orbital is bonding. This conclusion stems in part from the presence of the nucleus–nucleus repulsion $(e^2/4\pi\varepsilon_0 R)$, which raises the energy of both molecular orbitals.



14.19 A representation of the destructive interference that occurs when two H1s orbitals overlap and form an antibonding σ^* orbital. Compare this illustration with Fig. 14.20.

14.5 The structures of diatomic molecules

In Chapter 13 we used the hydrogenic atomic orbitals and the building-up principle to deduce the ground electronic configurations of many-electron atoms. We now do the same for many-electron diatomic molecules by using the H_2^+ molecular orbitals. The general procedure is to construct molecular orbitals by combining the available atomic orbitals. The electrons supplied by the atoms are then accommodated in the orbitals so as to achieve the lowest overall energy subject to the constraint of the Pauli exclusion principle, that no more than two electrons may occupy a single orbital (and then must be paired). As in the case of atoms, if several degenerate molecular orbitals are available, we add the electrons singly to each individual orbital before doubly occupying any one orbital (because that minimizes electron–electron repulsions). We also take note of Hund's rule (Section 13.4d) that, if electrons do occupy different degenerate orbitals, then a lower energy is obtained if they do so with parallel spins.



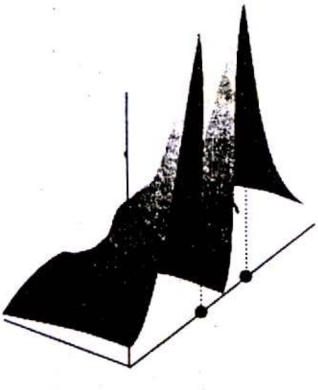
14.20 (a) The amplitude of the antibonding molecular orbital in a hydrogen molecule-ion in a plane containing the two nuclei and (b) a contour representation of the amplitude. Note the internuclear node.

(a) The hydrogen and helium molecules

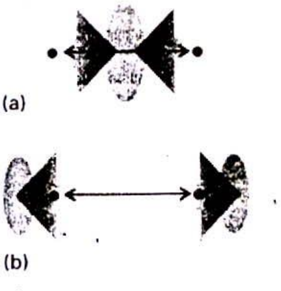
Consider H_2, the simplest many-electron diatomic molecule. Each H atom contributes a $1s$ orbital (as in H_2^+), so we can form the 1σ and $2\sigma^*$ orbitals from them, as we have seen already. At the experimental internuclear separation these orbitals will have the energies shown in Fig. 14.23, which is called a **molecular orbital energy level diagram.** Note that from two atomic orbitals we can build two molecular orbitals. In general, from N atomic orbitals we can build N molecular orbitals.

There are two electrons to accommodate, and both can enter 1σ by pairing their spins. The ground-state configuration is therefore $1\sigma^2$ and the atoms are joined by a bond consisting of an electron pair in a bonding σ orbital. This approach shows that an electron pair, which was the focus of Lewis's account of chemical bonding, represents the maximum number of electrons that can enter a bonding molecular orbital.

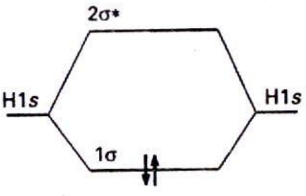
The same argument shows why He does not form diatomic molecules.[6] Each He atom contributes a $1s$ orbital, so 1σ and $2\sigma^*$ molecular orbitals can be constructed. Although these orbitals differ in detail from those in H_2, the general shape is the same, and we can use the same qualitative energy level diagram in the discussion. There are four electrons to accommodate. Two can enter the 1σ orbital, but then it is full, and the next two must enter the $2\sigma^*$ orbital (Fig. 14.24). The ground electronic configuration of He_2 is therefore $1\sigma^2 2\sigma^{*2}$. We see that there is one bond and one antibond. Because an antibond is slightly more antibonding than a bond is bonding, an He_2 molecule has a higher energy than the separated atoms, so it is unstable relative to the individual atoms.



14.21 The electron density calculated by forming the square of the wavefunction used to construct Fig. 14.20. Note the elimination of electron density from the internuclear region.



14.22 A partial explanation of the origin of bonding and antibonding effects. (a) In a bonding orbital, the nuclei are attracted to the accumulation of electron density in the internuclear region. (b) In an antibonding orbital, the nuclei are attracted to an accumulation of electron density outside the internuclear region.



14.23 A molecular orbital energy level diagram for orbitals constructed from the overlap of H1s orbitals; the separation of the levels corresponds to that found at the equilibrium bond length. The ground electronic configuration of H_2 is obtained by accommodating the two electrons in the lowest available orbital (the bonding orbital).

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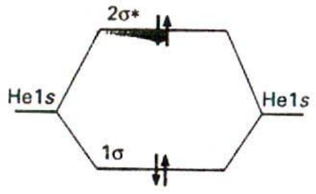
[6] Diatomic helium 'molecules' have been prepared quite recently: they consist of pairs of atoms held together by weak van der Waals forces of the type described in Chapter 22.



14.24 The ground electronic configuration of the hypothetical four-electron molecule He_2 has two bonding electrons and two antibonding electrons. It has a higher energy than the separated atoms, and so is unstable.

(b) Bond order

A measure of the net bonding in a diatomic molecule is its **bond order**, b:

$$b = \tfrac{1}{2}(n - n^*) \qquad [15]$$

where n is the number of electrons in bonding orbitals and n^* is the number of electrons in antibonding orbitals. Thus each electron pair in a bonding orbital increases the bond order by 1 and each pair in an antibonding orbital decreases b by 1. For H_2, $b = 1$, corresponding to a single bond, H–H, between the two atoms. In He_2, $b = 0$, and there is no bond.

As we shall see, the bond order is a useful parameter for discussing the characteristics of bonds, because it correlates with bond length and bond strength:

> **The greater the bond order between atoms of a given pair of elements, the shorter the bond.**
> **The greater the bond order, the greater the bond strength.**

Table 14.2 lists some typical bond lengths in diatomic and polyatomic molecules. The strength of a bond is measured by its **bond dissociation energy**, D_e, the energy required to separate the atoms to infinity.[7] Table 14.3 lists some experimental values of dissociation energies.

Table 14.2* Bond lengths

Bond	Order	R_e/pm
HH	1	74.14
NN	3	109.76
HCl	1	127.45
CH	1	*114*
CC	1	*154*
CC	2	*134*
CC	3	*120*

*More values will be found in the *Data section* at the end of this volume. Numbers in italics are mean values for polyatomic molecules.

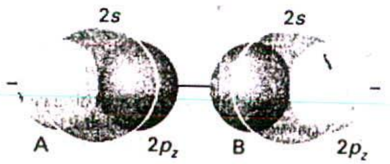
Table 14.3* Bond dissociation energies

Bond	Order	D_e/(kJ mol^{-1})
HH	1	432.1
NN	3	941.7
HCl	1	427.7
CH	1	*435*
CC	1	*368*
CC	2	*720*
CC	3	*962*

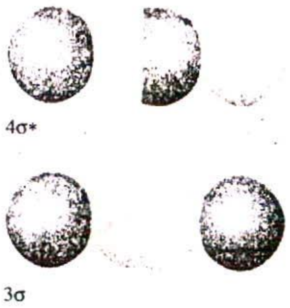
*More values will be found in the *Data section*. Numbers in italics are mean values for polyatomic molecules.

(c) Period 2 diatomic molecules

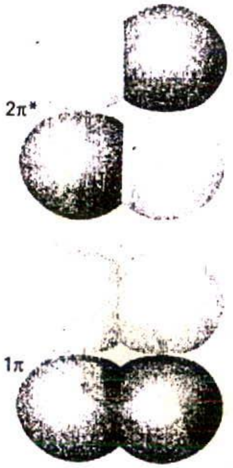
We now see how the concepts we have introduced apply to homonuclear diatomic molecules in general. In elementary treatments, only the orbitals of the valence shell are used to form molecular orbitals.



14.25 According to molecular orbital theory, σ orbitals are built from all orbitals that have the appropriate symmetry. In homonuclear diatomic molecules of Period 2, that means that two 2s and two $2p_z$ orbitals should be used. From these four orbitals, four molecular orbitals can be built.



14.26 A representation of the composition of bonding and antibonding σ orbitals built from the overlap of p orbitals. These illustrations are schematic.



14.27 A schematic representation of the structure of π bonding and antibonding molecular orbitals.

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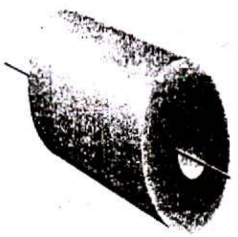
[7] Bond dissociation energies are commonly used in thermodynamic cycles, where bond enthalpies, $\Delta_{\text{bond}}H^{\ominus}$, should be used instead. It follows from the same kind of argument used in *Justification 13.9* concerning ionization enthalpies that

$$X_2(g) \longrightarrow 2X(g) \qquad \Delta_{\text{bond}}H^{\ominus}(T) = D_e + \tfrac{3}{2}RT$$

To derive this relation, we have supposed that the molar constant-pressure heat capacity of X_2 is $\tfrac{7}{2}R$, for there is a contribution from two rotational modes as well as three translational modes.



14.28 In a linear molecule, the electron density in a π orbital has cylindrical symmetry around the internuclear axis.

In Period 2, the valence orbitals are $2s$ and $2p$. A general principle of molecular orbital theory is that *all orbitals of the appropriate symmetry contribute to a molecular orbital*. Thus, to build σ orbitals, we form linear combinations of all atomic orbitals that have cylindrical symmetry about the internuclear axis. These orbitals include the $2s$ orbitals on each atom and the $2p_z$ orbitals on the two atoms (Fig. 14.25). Thus, the general form of the σ orbitals that may be formed is

$$\psi = c_{\mathrm{A}2s}\psi_{\mathrm{A}2s} + c_{\mathrm{B}2s}\psi_{\mathrm{B}2s} + c_{\mathrm{A}2p_z}\psi_{\mathrm{A}2p_z} + c_{\mathrm{B}2p_z}\psi_{\mathrm{B}2p_z} \tag{16}$$

From these four atomic orbitals we can form four molecular orbitals of σ symmetry by an appropriate choice of the coefficients c.

The procedure for calculating the coefficients will be described in Section 14.7. At this stage we adopt a simpler route, and suppose that, because the $2s$ and $2p_z$ orbitals have distinctly different energies, they may be treated separately. That is, the four σ orbitals fall approximately into two sets, one consisting of two molecular orbitals of the form

$$\psi = c_{\mathrm{A}2s}\psi_{\mathrm{A}2s} + c_{\mathrm{B}2s}\psi_{\mathrm{B}2s} \tag{17a}$$

and another consisting of two orbitals of the form

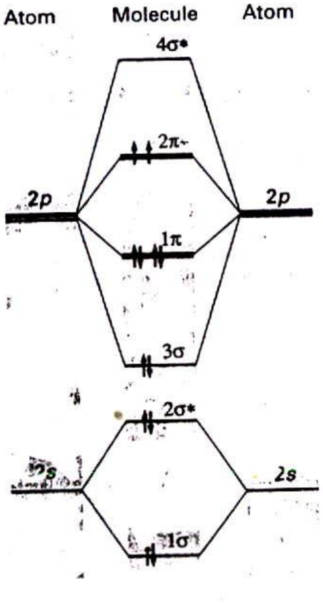
$$\psi = c_{\mathrm{A}2p_z}\psi_{\mathrm{A}2p_z} + c_{\mathrm{B}2p_z}\psi_{\mathrm{B}2p_z} \tag{17b}$$

Because atoms A and B are identical, the energies of their $2s$ orbitals are the same, so the coefficients are equal (apart from a possible difference in sign); the same is true of the $2p_z$ orbitals. Therefore, the two sets of orbitals have the form $\psi_{\mathrm{A}2s} \pm \psi_{\mathrm{B}2s}$ and $\psi_{\mathrm{A}2p_z} \pm \psi_{\mathrm{B}2p_z}$.

The $2s$ orbitals on the two atoms overlap to give a bonding and an antibonding σ orbital (1σ and 2σ, respectively) in exactly the same way as we have already seen for $1s$ orbitals. The two $2p_z$ orbitals directed along the internuclear axis overlap strongly. They may interfere either constructively or destructively, and give a bonding or antibonding σ orbital, respectively (Fig. 14.26). These two σ orbitals are labelled 3σ and $4\sigma^*$, respectively. In general, note how the numbering follows the order of increasing energy.[8]

(d) π orbitals

Now consider the $2p_x$ and $2p_y$ orbitals of each atom. These orbitals are perpendicular to the internuclear axis and may overlap broadside-on. This overlap may be constructive or destructive, and results in a bonding or an antibonding **π orbital** (Fig. 14.27). The notation π is the analogue of p in atoms for, when viewed along the axis of the molecule, a π orbital looks like a p orbital, and has one unit of orbital angular momentum around the internuclear axis. The two $2p_x$ orbitals overlap to give a bonding and antibonding π_x orbital, and the two $2p_y$ orbitals overlap to give two π_y orbitals. The π_x and π_y bonding orbitals are degenerate; so too are their antibonding partners. Strictly, because we are dealing with molecules with cylindrical symmetry, we should consider the complex forms of the p orbitals, one corresponding to circulation about the internuclear axis clockwise and the other anticlockwise. That is, we form $\pi_{\pm} \propto p_x \pm ip_y$, corresponding to angular momenta $\lambda\hbar$ with $\lambda = \pm 1$. Each complex orbital is like a cylindrical torus (Fig. 14.28). Although it is conventional to draw the real forms, it should not be forgotten that each π orbital in a linear molecule corresponds to a cylindrical distribution of charge.



14.29 The molecular orbital energy level diagram for homonuclear diatomic molecules. As remarked in the text, this diagram should be used for O_2 and F_2.

In some cases, π orbitals are less strongly bonding than σ orbitals because their maximum overlap occurs off-axis. This relative weakness suggests that the molecular orbital energy level diagram ought to be as shown in Fig. 14.29. However, we must remember that we have constructed the diagram on the assumption that the $2s$ and $2p_z$ orbitals contribute to different sets of molecular orbitals, whereas in fact all four atomic orbitals contribute jointly

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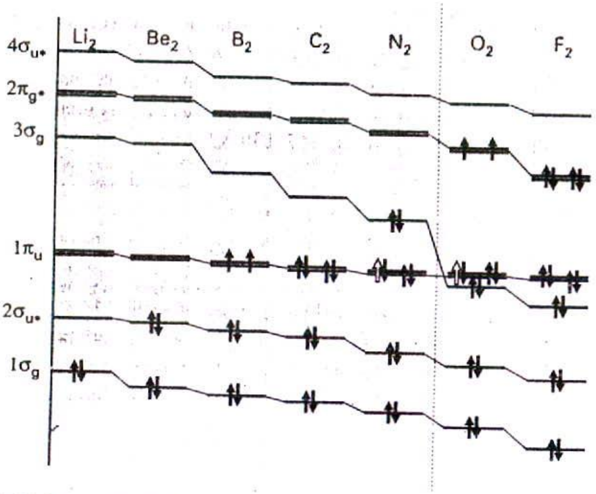
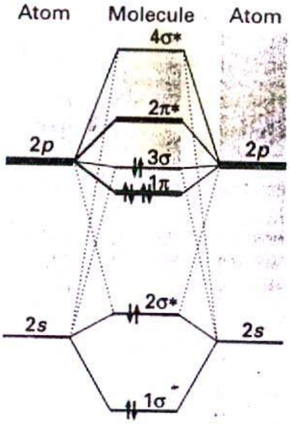
[8] In an alternative system of notation, 1σ and 2σ are used to designate the molecular orbitals formed from the core $1s$ orbitals of the atoms; the orbitals we are considering would then be labelled from 3 to 6. We are ignoring orbitals formed from core orbitals.



14.30 The variation of the orbital energies of Period 2 homonuclear diatomics. The g and u labels are explained later (Section 14.6a).



14.31 An alternative molecular orbital energy level diagram for homonuclear diatomic molecules. As remarked in the text, this diagram should be used for diatomics up to and including N_2.

to the four σ orbitals. Hence, there is no guarantee that this order of energies should prevail, and it is found experimentally (by spectroscopy) and by detailed calculation that the order varies along Period 2 (Fig. 14.30). The order shown in Fig. 14.31 is appropriate as far as N_2, and Fig. 14.29 applies for O_2 and F_2. The relative order is controlled by the separation of the 2*s* and 2*p* orbitals in the atoms, which increases across the group. The consequent switch in order occurs at about N_2.

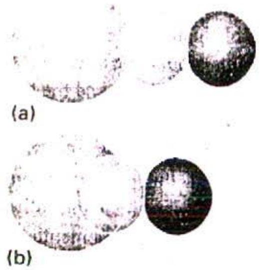
(e) The overlap integral

The extent to which two atomic orbitals on different atoms overlap is measured by the **overlap integral**, S:

$$S = \int \psi_A^* \psi_B \, d\tau \qquad [18]$$

If the atomic orbital ψ_A on A is small wherever the orbital ψ_B on B is large, or vice versa, then the product of their amplitudes is everywhere small and the integral—the sum of these products—is small (Fig. 14.32). If ψ_A and ψ_B are simultaneously large in some region of space, then S may be large. If the two normalized atomic orbitals are identical (for example, 1*s* orbitals on the same nucleus), then $S = 1$. In some cases, simple formulas can be given for overlap integrals and the variation of S with bond length plotted (Fig. 14.33). It follows that $S = 0.59$ for two H1*s* orbitals at the equilibrium bond length in H_2^+, which is an unusually large value. Typical values for orbitals with $n = 2$ are in the range 0.2 to 0.3.

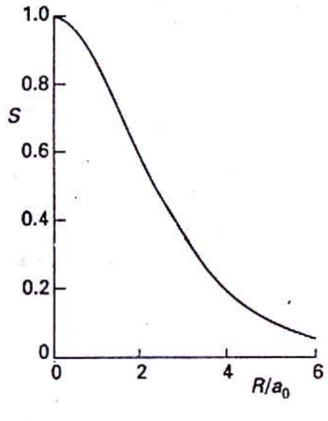
Now consider the arrangement in which an *s* orbital is superimposed on a p_x orbital of a different atom (Fig. 14.34). The integral over the region where the product of orbitals is positive exactly cancels the integral over the region where the product of orbitals is negative, so overall $S = 0$ exactly. Therefore, there is no net overlap between the *s* and *p* orbitals in this arrangement.



14.32 (a) When two orbitals are on atoms that are far apart, the wavefunctions are small where they overlap, so S is small. (b) When the atoms are closer, both orbitals have significant amplitudes where they overlap, and S may approach 1. Note that S will decrease again as the two atoms approach more closely than shown here, because the region of negative amplitude of the *p* orbital starts to overlap the positive overlap of the *s* orbital. When the centres of the atoms coincide, $S = 0$.

(f) The structures of homonuclear diatomic molecules

We show the general layout of the valence-shell atomic orbitals of Period 2 atoms on the left and right of the molecular orbital energy level diagrams in Figs. 14.29 and 14.31. The lines in



14.33 The overlap integral, S, between two H1s orbitals as a function of their separation R.

the middle are an indication of the energies of the molecular orbitals that can be formed by overlap of atomic orbitals: from the eight valence shell orbitals (four from each atom), we can form eight molecular orbitals. With the orbitals established, we can deduce the ground configurations of the molecules by adding the appropriate number of electrons to the orbitals and following the building-up rules. Anionic species (such as the peroxide ion, O_2^{2-}) need more electrons than the parent neutral molecules; cationic species (such as O_2^+) need fewer.

Consider N_2, which has 10 valence electrons. For this molecule, we use Fig. 14.31. Two electrons pair, occupy, and fill the 1σ orbital; the next two occupy and fill the $2\sigma^*$ orbital. Six electrons remain. There are two 1π orbitals, so four electrons can be accommodated in them. The last two enter the 3σ orbital. The ground-state configuration of N_2 is therefore $1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2$ and the bond order is $\frac{1}{2}(8-2) = 3$. This bond order accords with the Lewis structure of the molecule (:N≡N:) and is consistent with its high dissociation energy ($942\ \mathrm{kJ\,mol^{-1}}$).

The ground-state electron configuration of O_2, with 12 valence electrons, is based on Fig. 14.29, and is $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*2}$. Its bond order is 2. According to the building-up principle, however, the two $2\pi^*$ electrons occupy different orbitals: one will enter $2\pi_x^*$ and the other will enter $2\pi_y^*$. Because the electrons are in different orbitals, they will have parallel spins. Therefore, we can predict that an O_2 molecule will have a net spin angular momentum $S = 1$ and, in the language introduced in Section 13.7, be in a triplet state. Because electron spin is the source of a magnetic moment, we can go on to predict that oxygen should be paramagnetic.[9] This prediction, which valence-bond theory does not make, is confirmed by experiment.

An F_2 molecule has two more electrons than an O_2 molecule. Its configuration is therefore $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4}$ and $b = 1$. We conclude that F_2 is a singly bonded molecule, in agreement with its Lewis structure. The low bond order is consistent with its low dissociation energy ($154\ \mathrm{kJ\,mol^{-1}}$). The hypothetical molecule dineon, Ne_2, has two further electrons: its configuration is $1\sigma^2 2\sigma^{*2} 3\sigma^2 1\pi^4 2\pi^{*4} 4\sigma^{*2}$ and $b = 0$. The zero bond order is consistent with the monatomic nature of Ne.

Example 14.3 Judging the relative bond strengths of molecules and ions

Judge whether N_2^+ is likely to have a larger or smaller dissociation energy than N_2.

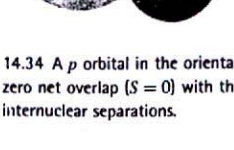
Method Because the molecule with the larger bond order is likely to have the larger dissociation energy, compare their electronic configurations and assess their bond orders.

Answer From Fig. 14.31, the electron configurations and bond orders are

$$\begin{array}{lll} N_2 & 1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^2 & b = 3 \\ N_2^+ & 1\sigma^2 2\sigma^{*2} 1\pi^4 3\sigma^1 & b = 2\frac{1}{2} \end{array}$$

Because the cation has the smaller bond order, we expect it to have the smaller dissociation energy.

Comment The experimental dissociation energies are $945\ \mathrm{kJ\,mol^{-1}}$ for N_2 and $842\ \mathrm{kJ\,mol^{-1}}$ for N_2^+.



14.34 A p orbital in the orientation shown here has zero net overlap ($S = 0$) with the s orbital at all internuclear separations.

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[9] A paramagnetic substance tends to move into a magnetic field; a diamagnetic substance tends to move out of one. Paramagnetism, the rarer property, arises when the molecules have unpaired electron spins. Both properties are discussed in more detail in Section 22.6.

Self-test 14.4 Which can be expected to have the higher dissociation energy, F_2 or F_2^+?

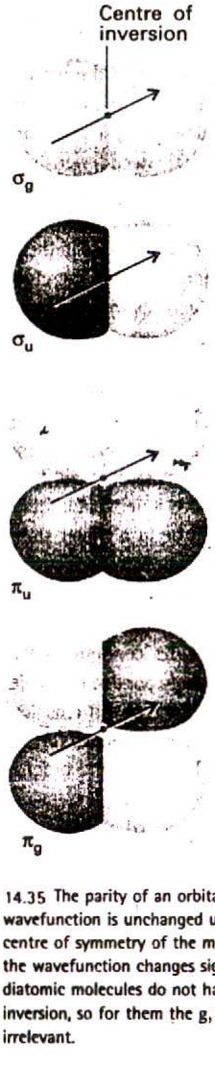
[F_2^+]

14.6 More about notation

We have seen how to label molecular orbitals by taking note of their symmetries with respect to rotation around the internuclear axis. Certain other features of their symmetry can also be used. As we shall see in later chapters, these symmetry designations are used to formulate selection rules in molecular spectroscopy. Symmetry designations are described in detail in Chapter 15, and the following remarks are expanded there.

(a) Parity

The molecular orbitals of homonuclear diatomic molecules are labelled with a subscript g or u which specifies their parity, their behaviour under inversion. To decide on the parity, consider any point in a homonuclear diatomic molecule, and note the sign of the orbital. Then imagine travelling on a straight line through the centre of the molecule to a point the same distance out on the other side; this process is called **inversion** and the central point is the **centre of inversion** (Fig. 14.35). If the orbital has the same sign, it has even parity and is denoted g (from *gerade*, the German word for even). If the orbital has opposite sign, then it has odd parity and is denoted u (from *ungerade*, uneven). The parity designation applies only to homonuclear diatomic molecules, because heteronuclear diatomic molecules (such as HCl) do not have a centre of inversion.



14.35 The parity of an orbital is even (g) if its wavefunction is unchanged under inversion in the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign. Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g, u classification is irrelevant.

We see from Fig. 14.35 that a bonding σ orbital has even parity; so we write it σ_g; an antibonding σ orbital has odd parity and is written σ_u. A bonding π orbital has odd parity and is denoted π_u and an antibonding π orbital has even parity, denoted π_g.[10]

(b) Term symbols

The term symbols of linear molecules (the analogues of the symbols ^{2}P, etc. for atoms) are constructed in a similar way to those for atoms, but now we must pay attention to the component of total orbital angular momentum about the internuclear axis, $\Lambda\hbar$. The value of $|\Lambda|$ is denoted by the symbols $\Sigma, \Pi, \Delta, \ldots$ for $|\Lambda| = 0, 1, 2\ldots$, respectively. These labels are the analogues of $\mathrm{S}, \mathrm{P}, \mathrm{D}, \ldots$ for atoms.

The value of Λ is the sum of the values of λ for the individual electrons in a molecule.[11] A single electron in a σ orbital has $\lambda = 0$: the orbital is cylindrically symmetrical and has no angular nodes when viewed along the internuclear axis. Therefore, if that is the only electron present, $\Lambda = 0$. The term symbol for H_2^+ is therefore Σ. As in atoms, we use a superscript with the value of $2S + 1$ to denote the multiplicity of the term. In this case, because there is only one electron, $S = s = \frac{1}{2}$ and the term symbol is $^2\Sigma$, a doublet term. The overall parity of the term is added as a right subscript, and (if there are several electrons) is calculated by using

$$\mathrm{g} \times \mathrm{g} = \mathrm{g} \qquad \mathrm{u} \times \mathrm{u} = \mathrm{g} \qquad \mathrm{u} \times \mathrm{g} = \mathrm{u} \tag{19}$$

(The rules can be generated by interpreting g as $+1$ and u as -1.) For H_2^+, the parity of the only occupied orbital is g, so the term itself is also g, and in full dress is $^2\Sigma_g$. The term symbol for any closed-shell homonuclear diatomic molecule is $^1\Sigma_g$ because the spin is zero (all electrons paired), there is no orbital angular momentum from a closed shell, and the overall parity is g.

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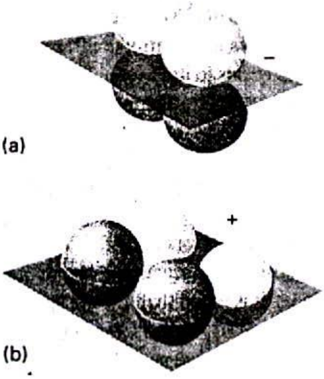
[10] For simplicity in comparing homonuclear and heteronuclear molecules, we ignore the parity subscripts when numbering orbitals; however, a more formal convention is to number the g and u orbitals separately.

[11] Recall from Section 14.5d that $\lambda\hbar$ is the component of orbital angular momentum on the internuclear axis.



14.36 The ± in a term symbol refers to the symmetry of an orbital when it is reflected in a plane containing the two nuclei.

A π electron in a diatomic molecule has one unit of orbital angular momentum about the internuclear axis ($\lambda = \pm 1$) and, if it is the only electron outside a closed shell, gives rise to a Π term. If there are two π electrons (as in O_2) then the term symbol may be either Σ (if the electrons are travelling in opposite directions, which is the case if they occupy different π orbitals, one with $\lambda = +1$ and the other with $\lambda = -1$) or Δ (if they are travelling in the same direction, which is the case if they occupy the same π orbital, both $\lambda = +1$, for instance). For O_2, the two π electrons occupy different orbitals with parallel spins, so the ground term is $^3\Sigma$. The overall parity of the molecule is

$$(\text{closed shell}) \times g \times g = g$$

The term symbol is therefore $^3\Sigma_g$.

For Σ terms, a $\pm$ superscript denotes the behaviour of the molecular wavefunction under reflection in a plane containing the nuclei (Fig. 14.36). If, for convenience, we think of O_2 as having one electron in $2\pi_x$, which changes sign under reflection in the xz-plane, and the other electron in $2\pi_y$, which does not change sign under reflection in the same plane, the overall reflection symmetry is

$$(\text{closed shell}) \times (+) \times (-) = (-)$$

and the full term symbol is $^3\Sigma_g^-$. The need for all this dressing of a basic symbol will become apparent when we deal with the spectroscopic selection rules in Chapter 17.

14.7 Heteronuclear diatomic molecules

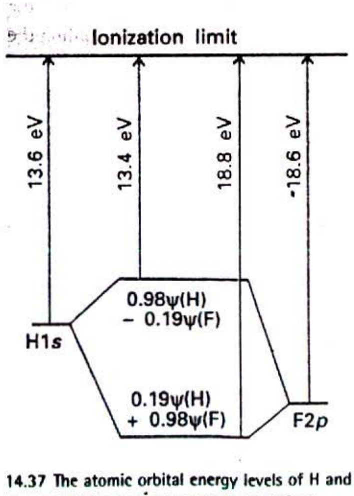
A heteronuclear diatomic molecule is a diatomic molecule formed from atoms of two different elements, such as CO and HCl. The electron distribution in the covalent bond between the atoms is not evenly shared because it is energetically favourable for the electron pair to be found closer to one atom than the other. This imbalance results in a **polar bond**, a covalent bond in which the electron pair is shared unequally by the two atoms. The bond in HF, for instance, is polar, with the electron pair closer to the F atom. The accumulation of the electron pair near the F atom results in that atom having a net negative charge, which is called a **partial negative charge** and denoted $\delta-$. There is a matching **partial positive charge**, $\delta+$, on the H atom.

(a) Polar bonds

A polar bond consists of two electrons in an orbital of the form

$$\psi = c_A A + c_B B \tag{20}$$

with unequal coefficients. The proportion of the atomic orbital A in the bond is $|c_A|^2$ and that of B is $|c_B|^2$. A nonpolar bond has $|c_A|^2 = |c_B|^2$ and a pure ionic bond has one coefficient zero (so the species A^+B^- would have $c_A = 0$ and $c_B = 1$). The atomic orbital with the lower energy makes the larger contribution to the bonding molecular orbital. The opposite is true of the antibonding orbital, for which the dominant component comes from the atomic orbital with higher energy.



14.37 The atomic orbital energy levels of H and F atoms and the molecular orbitals they form.

These points can be illustrated by considering HF, and judging the energies of the atomic orbitals from the ionization energies of the atoms. The general form of the molecular orbitals is

$$\psi = c_H \psi_H + c_F \psi_F \tag{21}$$

where ψ_H is an H1s orbital and ψ_F is an F2p orbital. The H1s orbital lies at 13.6 eV below the zero of energy (the separated proton and electron) and the F2p orbital lies at 18.6 eV below the zero of energy (Fig. 14.37). Hence, the bonding σ orbital in HF is mainly F2p and the antibonding σ orbital is mainly H1s orbital in character. The two electrons in the bonding orbital are most likely to be found in the F2p orbital, so there is a partial negative charge on the F atom and a partial positive charge on the H atom.

Table 14.4* Pauling electronegativities

Element	χ_P
H	2.2
C	2.6
N	3.0
O	3.4
F	4.0
Cl	3.2
Cs	0.79

*More values will be found in the *Data section.*

(b) Electronegativity

The charge distribution in bonds is commonly discussed in terms of the **electronegativity**, χ (chi), of the elements involved. The electronegativity is a parameter introduced by Linus Pauling as a measure of the power of an atom to attract electrons to itself when it is part of a compound. Pauling used valence-bond arguments to suggest that an appropriate numerical scale of electronegativities could be defined in terms of bond dissociation energies, D, and proposed that the difference in electronegativities could be expressed as

$$|\chi_A - \chi_B| = 0.102\{D(\text{A—B}) - \tfrac{1}{2}[D(\text{A—A}) + D(\text{B—B})]\}^{1/2} \qquad [22]$$

Electronegativities based on this definition are called **Pauling electronegativities.** A list of Pauling electronegativities is given in Table 14.4. The most electronegative elements are those close to fluorine; the least are those close to caesium. It is found that, the greater the difference in electronegativities, the greater the polar character of the bond. The difference for HF, for instance, is 1.78; a C–H bond, which is commonly regarded as almost-nonpolar, has an electronegativity difference of 0.51.

The American spectroscopist R.S. Mulliken proposed an alternative definition of electronegativity. He argued that an element is likely to be highly electronegative if it has a high ionization energy (so it will not release electrons readily) and a high electron affinity (so it is energetically favorable to acquire electrons). The **Mulliken electronegativity scale** is therefore based on the definition

$$\chi_M = \tfrac{1}{2}(I + E_{ea}) \qquad [23]$$

where I is the ionization energy of the element and E_{ea} is its electron affinity, both in electronvolts (Section 13.4f).[12] The Mulliken and Pauling scales are approximately in line with one another.[13]

(c) The variation principle

A more systematic way of discussing bond polarity and finding the coefficients in the linear combinations used to build molecular orbitals is provided by the **variation principle:**

> **If an arbitrary wavefunction is used to calculate the energy, the value calculated is never less than the true energy.**

This principle is the basis of all modern molecular structure calculations. The arbitrary wavefunction is called the **trial wavefunction.** The principle implies that, if we vary the coefficients in the trial wavefunction until the lowest energy is achieved (by evaluating the expectation value of the hamiltonian for each wavefunction), then those coefficients will be the best. We might get a lower energy if we use a more complicated wavefunction (for example, by taking a linear combination of several atomic orbitals on each atom), but we shall have the optimum (minimum energy) molecular orbital that can be built from the chosen **basis set,** the given set of atomic orbitals.

The method can be illustrated by the trial wavefunction in eqn 20. We show in the *Justification* below that the coefficients are given by the solutions of the two **secular equations**[14]

$$\begin{aligned}(\alpha_A - E)c_A + (\beta - ES)c_B &= 0\\ (\beta - ES)c_A + (\alpha_B - E)c_B &= 0\end{aligned} \qquad (24)$$

---

[12] There are certain technical difficulties with this definition in connection with the electronic state chosen to represent the state of the atom in a compound.

[13] A reasonably reliable conversion between the two is $\chi_P = 1.35\chi_M^{1/2} - 1.37$.

[14] The name 'secular' is derived from the Latin word for age or generation. The term comes via astronomy, where the same equations appear in connection with slowly accumulating modifications of planetary orbits.

The parameter α is called a **Coulomb integral**. It can be interpreted as the energy of the electron when it occupies A (for α_A) or B (for α_B), and is negative. In a homonuclear diatomic molecule, $\alpha_A = \alpha_B$. The parameter β is called a **resonance integral** (for classical reasons). It vanishes when the orbitals do not overlap, and at equilibrium bond lengths it is normally negative.

Justification 14.4

The trial wavefunction in eqn 20 is real but not normalized because at this stage the coefficients can take arbitrary values. Therefore, we can write $\psi^* = \psi$ but do not assume that $\int \psi^2\, d\tau = 1$. The energy of the trial wavefunction is the expectation value of the energy operator (the hamiltonian, H, Section 11.5):

$$E = \frac{\int \psi^* H \psi\, d\tau}{\int \psi^* \psi\, d\tau} \tag{25}$$

We must search for values of the coefficients in the trial function that minimize the value of E. This is a standard problem in calculus, and is solved by finding the coefficients for which

$$\frac{\partial E}{\partial c_A} = 0 \qquad \frac{\partial E}{\partial c_B} = 0$$

The first step is to express the two integrals in terms of the coefficients. The denominator is

$$\begin{aligned}\int \psi^2\, d\tau &= \int (c_A A + c_B B)^2\, d\tau \\ &= c_A^2 \int A^2\, d\tau + c_B^2 \int B^2\, d\tau + 2c_A c_B \int AB\, d\tau \\ &= c_A^2 + c_B^2 + 2c_A c_B S\end{aligned}$$

because the individual atomic orbitals are normalized and the third integral is the overlap integral S (eqn 18). The numerator is

$$\begin{aligned}\int \psi H \psi\, d\tau &= \int (c_A A + c_B B) H (c_A A + c_B B)\, d\tau \\ &= c_A^2 \int AHA\, d\tau + c_B^2 \int BHB\, d\tau + c_A c_B \int AHB\, d\tau \\ &\quad + c_A c_B \int BHA\, d\tau\end{aligned}$$

There are some complicated integrals in this expression, but we can combine them all into the parameters

$$\alpha_A = \int AHA\, d\tau \qquad \alpha_B = \int BHB\, d\tau \qquad \beta = \int AHB\, d\tau = \int BHA\, d\tau \tag*{[26]}$$

Then

$$\int \psi H \psi\, d\tau = c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta$$

The complete expression for E is

$$E = \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2c_A c_B \beta}{c_A^2 + c_B^2 + 2c_A c_B S} \tag{27}$$

Its minimum is found by differentiation with respect to the two coefficients and setting the results equal to 0. This involves elementary but slightly tedious work, and the end result is eqn 24.

To solve the secular equations for the coefficients we need to know the energy E of the orbital. As for any set of simultaneous equations, the secular equations have a solution if the **secular determinant**, the determinant of the coefficients, is zero, that is, if

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0 \qquad (28)$$

This determinant expands to a quadratic equation in E (see Example 14.4). Its two roots give the energies of the bonding and antibonding molecular orbitals formed from the atomic orbitals and, according to the variation principle, these roots are the best energies for the given basis set.

Example 14.4 Finding the roots of a secular determinant

Find the energies E of the bonding and antibonding orbitals of a homonuclear diatomic molecule by solving eqn 28.

Method We need to know that a 2 × 2 determinant expands as follows:

$$\begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc$$

Answer When we apply the determinant expansion rule to eqn 28 with $\alpha_A = \alpha_B = \alpha$, we get

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

The solutions of this equation are

$$E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$$

Self-test 14.5 Find the coefficients corresponding to these two energies.

[See below; eqn 30]

The values of the coefficients in the linear combination are obtained by solving the secular equations using the two energies obtained from the secular determinant. The lower energy gives the coefficients for the bonding molecular orbital, the upper energy the coefficients for the antibonding molecular orbital. The secular equations give expressions for the ratio of the coefficients in each case, so we need a further equation in order to find their individual values. This equation is obtained by demanding that the best wavefunction should also be normalized. This condition means that, at this final stage, we must also ensure that

$$\int \psi^2 d\tau = c_A^2 + c_B^2 + 2c_A c_B S = 1 \qquad (29)$$

(d) Two simple cases

The complete solutions of the secular equations are very cumbersome, even for 2 × 2 determinants, but there are two cases where the roots can be written down very simply.

We saw in Example 14.4 and its Self-test that, when the two atoms are the same, and we can write $\alpha_A = \alpha_B = \alpha$, the solutions are

$$\begin{aligned} E_+ &= \frac{\alpha+\beta}{1+S} & c_A &= \frac{1}{\{2(1+S)\}^{1/2}} & c_B &= c_A \\ E_- &= \frac{\alpha-\beta}{1-S} & c_A &= \frac{1}{\{2(1-S)\}^{1/2}} & c_B &= -c_A \end{aligned} \qquad (30)$$

In this case, the bonding orbital has the form

$$\psi_+ = \frac{A+B}{\{2(1+S)\}^{1/2}} \qquad (31a)$$

and the corresponding antibonding orbital is

$$\psi_- = \frac{A-B}{\{2(1-S)\}^{1/2}} \qquad (31b)$$

in agreement with the discussion of homonuclear diatomics we have already given, but now with the normalization constant in place.

The second simple case is for a heteronuclear diatomic molecule but with $S = 0$ (a common approximation in elementary work). The secular determinant is then

$$\begin{vmatrix} \alpha_A - E & \beta \\ \beta & \alpha_B - E \end{vmatrix} = (\alpha_A - E)(\alpha_B - E) - \beta^2 = 0$$

The solutions can be expressed in terms of the parameter ζ (zeta), with[15]

$$\zeta = \tfrac{1}{2}\arctan\frac{2|\beta|}{\alpha_B - \alpha_A} \qquad (32)$$

and are

$$\begin{aligned} E_- &= \alpha_A - \beta\cot\zeta & \psi_- &= -A\sin\zeta + B\cos\zeta \\ E_+ &= \alpha_B + \beta\cot\zeta & \psi_+ &= A\cos\zeta + B\sin\zeta \end{aligned} \qquad (33)$$

An important feature revealed by these solutions is that, as the difference $|\alpha_A - \alpha_B|$ increases, the value of ζ decreases.[16] When the energy difference is large the energies of the molecular orbitals differ only slightly from those of the atomic orbitals, which implies in turn that the bonding and antibonding effects are small. That is, *the strongest bonding and antibonding effects are obtained when the two contributing orbitals have closely similar energies.* The difference in energy between core and valence orbitals is the justification for neglecting the contribution of core orbitals to bonding. The core orbitals of one atom have a similar energy to the core orbitals of the other atom; but core–core interaction is largely negligible because the overlap between them (and hence the value of β) is so small.

Example 14.5 Calculating the molecular orbitals of HF

Calculate the wavefunctions and energies of the σ orbitals in the HF molecule, taking $\beta = -1.0$ eV and the following ionization energies: H1*s*: 13.6 eV, F2*s*: 40.2 eV, F2*p*: 18.6 eV.

---

[15] $\arctan x$ is the same as $\tan^{-1} x$.

[16] Because $\tan x \approx x$ and $\cot x \approx 1/x$ when $x \ll 1$, when $|\alpha_A - \alpha_B| \gg 2|\beta|$ we can write $\zeta \approx |\beta|/(\alpha_B - \alpha_A)$, which implies that $\tan\zeta \approx |\beta|/(\alpha_B - \alpha_A)$, and hence that $\cot\zeta \approx (\alpha_B - \alpha_A)/|\beta|$. Then (noting that $\beta/|\beta| = -1$) the energies of the two molecular orbitals are

$$E_- \approx \alpha_B \qquad E_+ \approx \alpha_A$$

Because $\sin\zeta \approx \zeta$ and $\cos\zeta \approx 1$ when $\zeta \ll 1$, the orbitals are respectively almost pure *B* and almost pure *A*.

Method Because the F2p and H1s orbitals are much closer in energy than the F2s and H1s orbitals, to a first approximation neglect the contribution of the F2s orbital. To use eqn 33, we need to know the values of the Coulomb integrals α_H and α_F. Because these integrals represent the energies of the H1s and F2p electrons, respectively, they are approximately equal to (the negative of) the ionization energies of the atoms. Calculate ζ from eqn 32 (with A identified as F and B as H), and then write the wavefunctions by using eqn 33.

Answer Refer to Fig. 14.37. Setting $\alpha_H = -13.6\text{eV}$ and $\alpha_F = -18.6\text{ eV}$ gives $\tan 2\zeta = 0.40$; so $\zeta = 10.9°$. Then

$$E_- = -13.4\text{ eV} \qquad \psi = 0.98\psi_H - 0.19\psi_F$$
$$E_+ = -18.8\text{ eV} \qquad \psi_+ = 0.19\psi_H + 0.98\psi_F$$

Comment Notice how the lower energy orbital (the one with energy -18.8 eV) has a composition that is more F2p orbital than H1s, and that the opposite is true of the higher energy, antibonding orbital.

Self-test 14.6 The ionization energy of Cl is 13.1 eV; find the form and energies of the σ orbitals in the HCl molecule using $\beta = -1.0$ eV.

[$E_- = -12.3$ eV, $\psi_- = -0.62\psi_H + 0.79\psi_{Cl}$;
$E_+ = -14.4$ eV, $\psi_+ = 0.79\psi_H + 0.62\psi_{Cl}$]

Molecular orbitals for polyatomic systems

The molecular orbitals of polyatomic molecules are built in the same way as in diatomic molecules, the only difference being that we use more atomic orbitals to construct the molecular orbitals. As for diatomic molecules, polyatomic molecular orbitals spread over the entire molecule. A molecular orbital has the general form

$$\psi = \sum_i c_i\psi_i \tag{34}$$

where ψ_i is an atomic orbital and the sum extends over all the valence orbitals of all the atoms in the molecule. To find the coefficients, we set up the secular equations and the secular determinant, just as for diatomic molecules, solve the latter for the energies, and then use these energies in the secular equations to find the coefficients of the atomic orbitals for each molecular orbital.

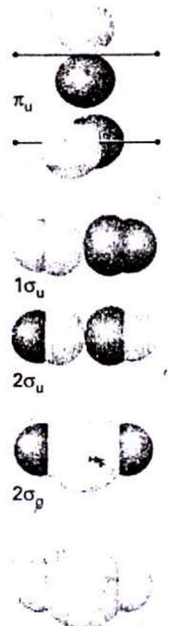
The principal difference between diatomic and polyatomic molecules lies in the greater range of shapes that are possible: a diatomic molecule is necessarily linear, but a triatomic molecule, for instance, may be either linear or angular with a characteristic bond angle. The shape of a polyatomic molecule—the specification of its bond lengths and its bond angles—can be predicted by calculating the total energy of the molecule for a variety of nuclear positions, and then identifying the conformation that corresponds to the lowest energy. However, more insight into the features that control molecular geometry can be obtained by analysing the orbitals and their energies in a more pictorial fashion. We shall illustrate what is involved by considering H_2O, which has an experimental bond angle of 104°.

14.8 Walsh diagrams

The molecular orbitals of H_2O (and of H_2X molecules in general) have the form

$$\psi = c_1\psi_{H_A1s} + c_2\psi_{H_B1s} + c_3\psi_{O2s} + c_4\psi_{O2p_x} + c_5\psi_{O2p_y} + c_6\psi_{O2p_z}$$

There are six such orbitals (because they are built from six atomic orbitals) and eight valence electrons to accommodate in them. We shall consider two hypothetical conformations of the molecule, the linear 180° molecule and the angular 90° molecule, and then decide how the molecular orbitals of one shape turn into the molecular orbitals of the other as the bond angle changes from 180° to 90°. The procedure results in the construction of a **Walsh diagram**, a diagram showing the variation of orbital energy with molecular geometry.



14.38 The molecular orbitals that can be constructed from the H1*s*, O2*s*, and O2*p* atomic orbitals in a hypothetical linear H_2O molecule.

(a) The Walsh diagram for H_2X molecules

The molecular orbitals of a hypothetical linear HOH molecule are classified as either σ or π (Fig. 14.38):

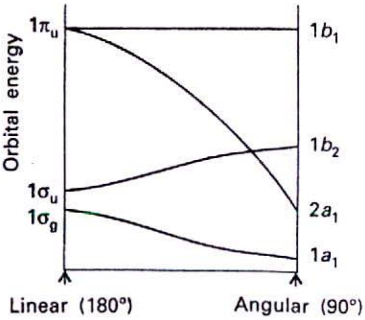
$$\begin{aligned} \psi_{\sigma_g} &= c_1\psi_{\mathrm{O}2s} + c_2(\psi_{\mathrm{H_A}1s} + \psi_{\mathrm{H_B}1s}) && \text{(two orbitals)} \\ \psi_{\pi_u} &= \psi_{\mathrm{O}2p_x},\ \psi_{\mathrm{O}2p_z} && \text{(one orbital each)} \qquad (35) \\ \psi_{\sigma_u} &= c_3\psi_{\mathrm{O}2p_y} + c_4(\psi_{\mathrm{H_A}1s} - \psi_{\mathrm{H_B}1s}) && \text{(two orbitals)} \end{aligned}$$

We have added the parity labels, but they no longer tell us which is bonding and antibonding. Thus, there are two σ_g orbitals, one bonding (with the two coefficients the same sign) and the other antibonding (with the coefficients of opposite sign). There are no orbitals of π symmetry on the H atoms, so the O2p_x and O2p_z orbitals do not form bonding and antibonding molecular orbitals. They are examples of **nonbonding orbitals**, orbitals that do not contribute directly to the bonding between atoms. The coefficients in the molecular orbitals may be found in the normal way, by setting up and solving the secular determinants using estimates of the Coulomb and resonance integrals, and the energies of the orbitals are shown on the left of the diagram in Fig. 14.39.

The molecular orbitals of a hypothetical 90° molecule are formed from the following groupings of atomic orbitals (Fig. 14.40):

$$\begin{aligned} \psi_{a_1} &= c_1\psi_{\mathrm{O}2s} + c_2\psi_{\mathrm{O}2p_z} + c_3(\psi_{\mathrm{H_A}1s} + \psi_{\mathrm{H_B}1s}) && \text{(three orbitals)} \\ \psi_{b_1} &= \psi_{\mathrm{O}2p_x} && \qquad (36) \\ \psi_{b_2} &= c_4\psi_{\mathrm{O}2p_y} + c_5(\psi_{\mathrm{H_A}1s} - \psi_{\mathrm{H_B}1s}) && \text{(two orbitals)} \end{aligned}$$

(The coefficients are different from those in eqn 35.) We can no longer classify the orbitals as σ and π because those labels apply only when there is an axis of symmetry; the labels used here will be explained in Chapter 15 (as will be the choice of the orbitals from which each molecular orbital is built).[17]



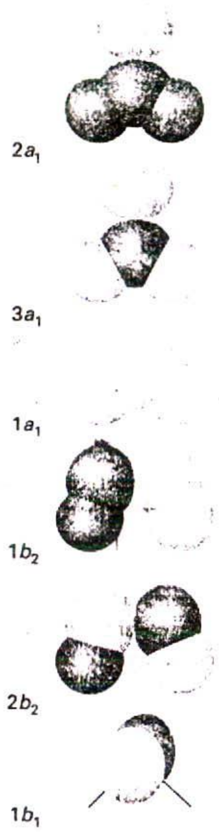
14.39 The Walsh diagram for H_2O. The energies of the linear molecule are shown on the left (see Fig. 14.38 for their compositions) and those of the 90° molecule are shown on the right (see Fig. 14.40). The actual molecule has a bond angle of 104°.

The lowest energy orbital in 90° H_2O is the one labelled $1a_1$, which is built from the overlap of the O2*s* and O2p_z orbitals with the $\psi_{\mathrm{H_A}1s} + \psi_{\mathrm{H_B}1s}$ combination of H1*s* orbitals. The energy of the $1a_1$ orbital rises as the bond angle increases, in part because the weakly bonding H–H overlap decreases and in part because the loss of p_z character diminishes the overlap with the H–H combination. The energy of the $1b_2$ orbital is lowered because the H1*s* orbitals move into a better position for overlap with the O2p_y orbital; their weakly *anti*bonding H–H overlap is also reduced. The biggest change occurs for the $2a_1$ orbital. This molecular orbital is principally an O2*s* orbital in the 90° molecule, but correlates with a pure O2p_z orbital in the 180° molecule. Hence, it shows a steep rise in energy as the bond angle increases. The $1b_1$ orbital is a nonbonding O2*p* orbital perpendicular to the molecular plane in the 90° molecule and remains nonbonding in the linear molecule. Hence, its energy barely changes with angle.

---

[17] As remarked earlier, the central feature of molecular orbital theory is the formation of molecular orbitals from all the atomic orbitals available that have the appropriate symmetry, and the linear combinations listed above can be regarded as a grouping of the atomic orbitals into different symmetry classes. This grouping is the subject of Chapter 15.

The principal feature that determines whether or not the H_2O molecule is bent is whether the $2a_1$ orbital is occupied. This orbital has considerable O2*s* character in the bent molecule but not in the linear molecule. Therefore, a lower total energy is achieved if, when it is occupied, the molecule is bent. The shape adopted by an H_2O molecule therefore depends on the number of electrons that occupy the orbitals.



14.40 The molecular orbitals that can be constructed from the H1*s*, O2*s*, and O2*p* atomic orbitals in a hypothetical 90° H_2O molecule.

Example 14.6 Using a Walsh diagram to predict a shape

Predict the shape of the H_2O molecule from the Walsh diagram.

Method Choose an intermediate bond angle along the horizontal axis of the H_2O diagram in Fig. 14.39, and accommodate eight electrons. Then consider whether the energy can be reduced by a modification of the bond angle. To do so, look at the effect on the energies of the occupied orbitals of a change in bond angle.

Answer The resulting configuration is $1a_1^2 2a_1^2 1b_2^2 1b_1^2$. The $2a_1$ orbital is occupied, so we expect the nonlinear molecule to have a lower energy than the linear molecule.

Self-test 14.7 Predict the shape of the BeH_2 molecule.

[Linear]

14.9 The Hückel approximation

Molecular orbital theory takes large molecules and extended aggregates of atoms, such as solid materials, into its stride. First we shall consider **conjugated molecules**, in which there is an alternation of single and double bonds along a chain of carbon atoms.

Although the classification of an orbital as σ or π is strictly valid only in linear molecules, it is also used to denote the *local* symmetry with respect to a given A–B bond axis. Moreover, in nonlinear molecules, there is no orbital angular momentum around the bond axis: the π orbital is a (real) standing wave with electron density on each side of the local molecular plane.

The π molecular orbital energy level diagrams of conjugated molecules can be constructed using a set of approximations suggested by Erich Hückel in 1931. In his approach, the π orbitals are treated separately from the σ orbitals, and the latter form a rigid framework that determines the general shape of the molecule. All the C atoms are treated identically, so all the Coulomb integrals α for the atomic orbitals that contribute to the π orbitals are set equal. For example, in ethene, we take the σ bonds as fixed, and concentrate on finding the energies of the single π bond and its companion antibond. In butadiene (**4**), the σ framework is taken as fixed, and we concentrate on finding the π orbitals spreading across the four C atoms.

4

(a) The secular determinant

We express the π orbitals as LCAOs of the C2*p* orbitals that lie perpendicular to the molecular plane. In ethene we would write

$$\psi = c_A A + c_B B \tag{37}$$

and in butadiene

$$\psi = c_A A + c_B B + c_C C + c_D D \tag{38}$$

where the *A* is a C2*p* orbital on atom A, and so on. Next, the optimum coefficients and energies are found by the variation principle as explained in Section 14.7c. That is, we have to solve the secular determinant, which in the case of ethene is eqn 28 with $\alpha_A = \alpha_B = \alpha$.

The determinant for butadiene is similar, but more atoms contribute and, being at various distances from each other, they have different overlap and resonance integrals:

Ethene:

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \tag{39}$$

Butadiene:

$$\begin{vmatrix} \alpha - E & \beta_{\mathrm{AB}} - ES_{\mathrm{AB}} & \beta_{\mathrm{AC}} - ES_{\mathrm{AC}} & \beta_{\mathrm{AD}} - ES_{\mathrm{AD}} \\ \beta_{\mathrm{BA}} - ES_{\mathrm{BA}} & \alpha - E & \beta_{\mathrm{BC}} - ES_{\mathrm{BC}} & \beta_{\mathrm{BD}} - ES_{\mathrm{BD}} \\ \beta_{\mathrm{CA}} - ES_{\mathrm{CA}} & \beta_{\mathrm{CB}} - ES_{\mathrm{CB}} & \alpha - E & \beta_{\mathrm{CD}} - ES_{\mathrm{CD}} \\ \beta_{\mathrm{DA}} - ES_{\mathrm{DA}} & \beta_{\mathrm{DB}} - ES_{\mathrm{DB}} & \beta_{\mathrm{DC}} - ES_{\mathrm{DC}} & \alpha - E \end{vmatrix} = 0 \tag{40}$$

The roots of the ethene determinant can be found very easily (they are the same as those in Example 14.4). However, for elementary calculations, the roots of the butadiene determinant are obviously going to prove difficult to find. In a modern computation all the resonance integrals and overlap integrals would be included, but an indication of the molecular orbital energy level diagram can be obtained very readily if we make the following additional **Hückel approximations**:

1. All overlap integrals are set equal to zero.
2. All resonance integrals between non-neighbours are set equal to zero.
3. All remaining resonance integrals are set equal (to β).

These approximations are obviously very severe, but they let us calculate at least a general picture of the molecular orbital energy levels with very little work. The assumptions result in the following structure of the secular determinant:

1. All diagonal elements: $\alpha - E$.
2. Off-diagonal elements between neighbouring atoms: β.
3. All other elements: 0.

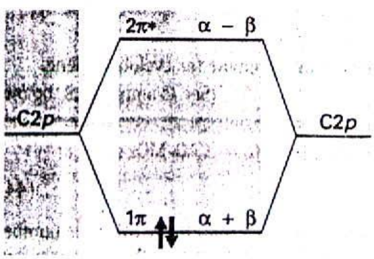
(b) Ethene and frontier orbitals

For ethene, the Hückel approximations lead to

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = (\alpha - E)^2 - \beta^2 = 0 \tag{41}$$

The roots of the equation are

$$E_{\pm} = \alpha \pm \beta \tag{42}$$



14.41 The Hückel molecular orbital energy levels of ethene. Two electrons occupy the lower π orbital.

The + sign corresponds to the bonding combination (β is negative) and the − sign corresponds to the antibonding combination (Fig. 14.41).[18] The building-up principle then leads to the configuration $1\pi^2$, because each carbon atom supplies one electron to the π system. We can also estimate the $\pi^* \leftarrow \pi$ excitation energy (2|β|). The constant β is often left as an adjustable parameter; an approximate value for (C2p,C2p)-overlap π-bonds is about $-75\ \mathrm{kJ\,mol^{-1}}$, corresponding to -0.8 eV.

The **highest occupied molecular orbital** in ethene, its HOMO, is the 1π orbital; the **lowest unfilled molecular orbital**, its LUMO, is the $2\pi^*$ orbital. These two orbitals jointly form the **frontier orbitals** of the molecule. The frontier orbitals are important because they are largely responsible for many of the chemical and spectroscopic properties of the molecule.

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[18] To see the effect of neglecting overlap, compare the result obtained here with eqn 30.

(c) Butadiene and π-electron binding energy

For butadiene, the approximations result in the determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \qquad (43)$$

Example 14.7 Finding the roots of a determinant

Find the roots of the butadiene secular determinant.

Method A 4 × 4 determinant is expanded in a series of steps like the 2 × 2 determinant treated in Example 14.4. After expansion, the terms are grouped to give a polynomial in E, which is set equal to 0 and then solved for E. A 4 × 4 determinant expands into a quartic equation, but we shall see that it may be expressed as a quadratic equation that can be solved by elementary methods.

Answer

$$\begin{aligned} &\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} \\ &= (\alpha - E)\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} - \beta \begin{vmatrix} \beta & \beta & 0 \\ 0 & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} \\ &= (\alpha - E)^2 \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} - \beta(\alpha - E)\begin{vmatrix} \beta & \beta \\ 0 & \alpha - E \end{vmatrix} \\ &\quad - \beta^2 \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} + \beta^2 \begin{vmatrix} 0 & \beta \\ 0 & \alpha - E \end{vmatrix} \\ &= (\alpha - E)^4 - (\alpha - E)^2\beta^2 - (\alpha - E)^2\beta^2 - (\alpha - E)^2\beta^2 + \beta^4 \\ &= (\alpha - E)^4 - 3(\alpha - E)^2\beta^2 + \beta^4 = 0 \end{aligned}$$

With $x = (\alpha - E)^2/\beta^2$, the expanded determinant has the form of a quadratic equation

$$x^2 - 3x + 1 = 0$$

The roots are $x = 2.62$ and 0.38. Therefore, the energies of the four LCAO-MOs are

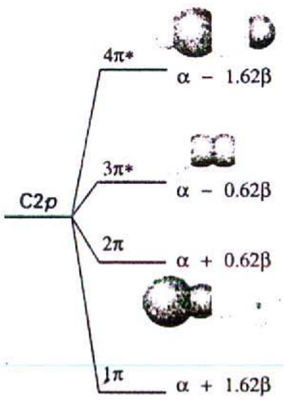
$$E = \alpha \pm 1.62\beta, \qquad \alpha \pm 0.62\beta$$

Self-test 14.8 Write down and expand the secular determinant for cyclobutadiene.
[See Example 14.8, below]

We have seen in Example 14.7 that the energies of the four LCAO-MOs are

$$E = \alpha \pm 1.62\beta, \qquad \alpha \pm 0.62\beta \qquad (44)$$

These orbitals and their energies are drawn in Fig. 14.42. Note that, the greater the number of internuclear nodes, the higher the energy of the orbital. There are four electrons to accommodate, so the ground-state configuration is $1\pi^2 2\pi^2$. The frontier orbitals of butadiene are the 2π orbital (the HOMO, which is largely bonding) and the 3π orbital (the



14.42 The Hückel molecular orbital energy levels of butadiene and the top view of the corresponding π orbitals. The four p electrons (one supplied by each C) occupy the two lower π orbitals. Note that the orbitals are delocalized.

LUMO, which is largely antibonding). 'Largely' bonding means that an orbital has both bonding and antibonding interactions between various neighbours, but the bonding effects dominate. 'Largely antibonding' indicates that the antibonding effects dominate.

An important point emerges when we calculate the total **π-electron binding energy, E_π**, the sum of the energies of each π electron, and compare it with what we find in ethene. In ethene the total energy is

$$E_\pi = 2(\alpha + \beta) = 2\alpha + 2\beta$$

In butadiene it is

$$E_\pi = 2(\alpha + 1.62\beta) + 2(\alpha + 0.62\beta) = 4\alpha + 4.48\beta$$

Therefore, the energy of the butadiene molecule lies lower by 0.48β (about -36 kJ mol^{-1}) than the sum of two individual π bonds. This extra stabilization of a conjugated system is called the **delocalization energy.**

Example 14.8 Estimating the delocalization energy

Use the Hückel approximation to find the energies of the π orbitals of cyclobutadiene, and estimate the delocalization energy.

Method Set up the secular determinant using the same basis as for butadiene, but note that atoms A and D are also now neighbours. Then solve for the roots of the secular equation and assess the total π-bond energy. For the delocalization energy, subtract from the total π-bond energy the energy of two π bonds.

Answer The secular determinant is

$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

This determinant expands to

$$x(x-4) = 0 \qquad x = \left(\frac{\alpha - E}{\beta}\right)^2$$

The solutions are $x = 0$ and $x = 4$, so the energies of the orbitals are

$$E = \alpha + 2\beta, \qquad \alpha, \qquad \alpha, \qquad \alpha - 2\beta$$

Four electrons must be accommodated. Two occupy the lowest orbital (of energy $\alpha + 2\beta$), and two occupy the doubly degenerate orbitals (of energy α). The total energy is therefore $4\alpha + 4\beta$. Two isolated π bonds would have an energy $4\alpha + 4\beta$; therefore, in this case, the delocalization energy is zero.

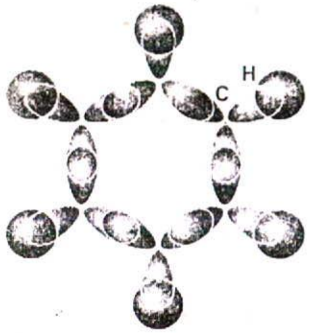
Self-test 14.9 Repeat the calculation for benzene.

[Next subsection]

(d) Benzene and aromatic stability

The most notable example of delocalization conferring extra stability is benzene and the aromatic molecules based on its structure. Benzene is often expressed in a mixture of valence-bond and molecular orbital terms with, typically, valence-bond language used for its σ framework and molecular orbital language used to describe its π electrons.

First, the valence-bond component. The six C atoms are regarded as sp^2 hybridized, with a single unhybridized perpendicular $2p$ orbital. One H atom is bonded by $(Csp^2,H1s)$ overlap to each C carbon, and the remaining hybrids overlap to give a regular hexagon of atoms (Fig. 14.43). The internal angle of a regular hexagon is 120°, so sp^2 hybridization is ideally suited for forming σ bonds. We see that benzene's hexagonal shape permits strain-free σ bonding.



14.43 The σ framework of benzene is formed by the overlap of Csp^2 hybrids, which fit without strain into a hexagonal arrangement.

Now consider the molecular orbital component of the description. The six C2p orbitals overlap to give six π orbitals that spread all round the ring. Their energies are calculated within the Hückel approximation by solving the secular determinant

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha-E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha-E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha-E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha-E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha-E \end{vmatrix} = 0 \tag{45}$$

When this determinant is expanded in the same way as in Example 14.7, the roots are found to be simply

$$E = \alpha \pm 2\beta, \qquad \alpha \pm \beta, \qquad \alpha \pm \beta \tag{46}$$

as shown in Fig. 14.44. The orbitals there have been given symmetry labels which we explain in Chapter 15. Note that the lowest energy orbital is bonding between all neighbouring atoms, the highest energy orbital is antibonding between each pair of neighbours, and the intermediate orbitals are a mixture of bonding, nonbonding, and antibonding character between adjacent atoms.

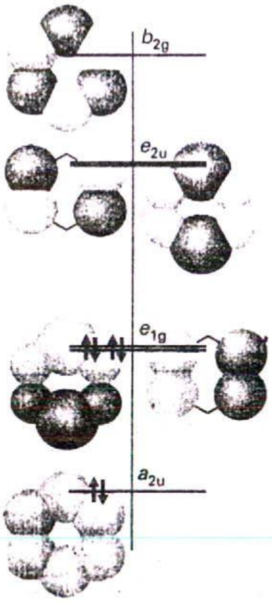
We now apply the building-up principle to the π system. There are six electrons to accommodate (one from each C atom), so the three lowest orbitals (a_{2u} and the doubly degenerate pair e_{1g}) are fully occupied, giving the ground-state configuration $a_{2u}^2 e_{1g}^4$. A significant point is that the only molecular orbitals occupied are those with net bonding character.

The π-electron energy of benzene is

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$$

If we ignored delocalization and thought of the molecule as having three isolated π bonds, it would be ascribed a π-electron energy of only $3(2\alpha + 2\beta) = 6\alpha + 6\beta$. The delocalization energy is therefore $2\beta \approx -150\ \text{kJ mol}^{-1}$, which is considerably more than for butadiene.

This discussion suggests that aromatic stability can be traced to two main contributions. First, the shape of the regular hexagon is ideal for the formation of strong σ bonds: the σ framework is relaxed and without strain. Second, the π orbitals are such as to be able to accommodate all the electrons in bonding orbitals, and the delocalization energy is large.



14.44 The Hückel orbitals of benzene and the corresponding energy levels. The symmetry labels are explained in Chapter 15. The bonding and antibonding character of the delocalized orbitals reflects the numbers of nodes between the atoms. In the ground state, only the net bonding orbitals are occupied.

(e) Semi-empirical and ab initio methods

Modern techniques of molecular electronic structure calculation have moved on considerably from the techniques we have been describing, but they are clear descendants of these more elementary methods. They still involve expressing molecular orbitals as linear combinations of atomic orbitals, setting up secular determinants in which various integrals appear, finding their roots, and then solving secular equations for the coefficients. However, the principal difference is the inclusion of electron–electron repulsion into the energy calculation and looking for self-consistent solutions, in much the same way as for atoms

(Section 13.5). There are two main strategies of calculation. In semi-empirical methods many of the integrals are estimated by appealing to spectroscopic data or physical properties such as ionization energies, and using a series of rules to set certain integrals equal to zero. In the ***ab initio* methods**, an attempt is made to calculate all the integrals that appear in the secular determinant. Both procedures employ a great deal of computational effort and, along with cryptanalysts and meteorologists, theoretical chemists are among the heaviest users of the fastest computers.

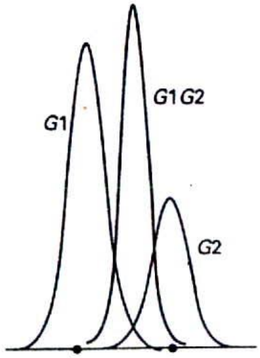
The Hückel method is a primitive example of a semi-empirical procedure: all the properties of the π system are expressed in terms of the two parameters α and β and all overlap integrals are set equal to zero. In a more sophisticated procedure, we write the π orbitals as linear combination of atomic orbitals, but use the full hamiltonian, including the electron–electron repulsions proportional to $1/r_{ij}$. Moreover, we also make sure that the many-electron wavefunction (the product of the individual occupied molecular orbitals) satisfies the Pauli principle. When all this is worked through, it turns out that the secular determinant includes integrals of the form

$$(AB|CD) = \int A(1)B(1)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)C(2)D(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{47}$$

where A, B, C, and D are atomic orbitals which in general may be centred on different nuclei. It can be appreciated that, if there are several dozen atomic orbitals used to build the molecular orbitals, then there will be tens of thousands of integrals of this form to evaluate.

One severe approximation is called **complete neglect of differential overlap** (CNDO), in which all integrals are set to zero unless A and B are the same orbitals centred on the same nucleus, and likewise for C and D. The surviving integrals are then adjusted until the energy levels are in good agreement with experiment. The more recent semi-empirical methods make less draconian decisions about which integrals are to be ignored, but they are all descendants of the early CNDO technique. These procedures are now readily available in commercial software packages and can be used with very little detailed knowledge of their mode of calculation. The packages also have sophisticated graphical output procedures, which enable one to analyse the shapes of orbitals and the distribution of electric charge in molecules. The latter is important when assessing, for instance, the likelihood that a given molecule will bind to an active site in an enzyme. Such studies can greatly reduce the time and cost of screening compounds for potential pharmacological activity.

Commercial packages are also available for *ab initio* calculations. Here the problem is to evaluate as efficiently as possible thousands of integrals. This task is greatly facilitated by expressing the atomic orbitals used in the LCAOs as linear combinations of Gaussian orbitals. A **Gaussian type orbital** (GTO) is a function of the form e^{-ar^2}. The advantage of GTOs over the correct orbitals (which are proportional to e^{-r}) is that the product of two Gaussian functions is itself a Gaussian function that lies between the centres of the two contributing functions (Fig. 14.45). In this way, the four-centre integrals like that in eqn 47 become two-centre integrals of the form



14.45 The product of two Gaussian functions (the green curves) is itself a Gaussian function located between the two contributing Gaussians.

$$(AB|CD) = \int X(1)\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)Y(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{48}$$

where X is the Gaussian corresponding to the product AB and Y is the corresponding Gaussian from BD. Integrals of this form are much easier and faster to evaluate numerically than the original four-centre integrals. Although more GTOs have to be used to simulate the atomic orbitals, there is an overall increase in speed of computation.

14.10 The band theory of solids

The extreme case of delocalization is a solid, in which atom after atom lies in a three-dimensional array and takes part in bonding spreading throughout the crystal. Two types of solid are distinguished by the temperature dependence of their electrical conductivity:

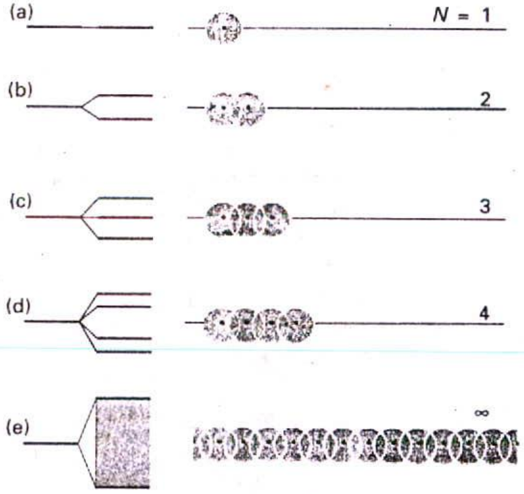
> A **metallic conductor** is a substance with a conductivity that decreases as the temperature is raised.
>
> A **semiconductor** is a substance with a conductivity that increases as the temperature is raised.

A semiconductor generally has a lower conductivity than that typical of metals, but the magnitude of the conductivity is not the criterion of the distinction. It is conventional to classify semiconductors with very low electrical conductivities as **insulators**. We shall use this term, but it should be appreciated that it is one of convenience rather than one of fundamental significance.

We shall consider a one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one *s* orbital available for forming molecular orbitals. We can construct the LCAO-MOs of the solid by adding *N* atoms in succession to a line, and then find the electronic structure using the building-up principle.

(a) The formation of bands

One atom contributes one *s* orbital at a certain energy (Fig. 14.46). When a second atom is brought up it overlaps the first, and forms a bonding and antibonding orbital. The third atom overlaps its nearest neighbour (and only slightly the next-nearest), and from these three atomic orbitals three molecular orbitals are formed: one is fully bonding, one fully antibonding, and the intermediate orbital is nonbonding between neighbours. The fourth atom leads to the formation of a fourth molecular orbital. At this stage, we can begin to see that the general effect of bringing up successive atoms is to spread the range of energies covered by the molecular orbitals, and also to fill in the range of energies with more and more orbitals (one more for each atom). When *N* atoms have been added to the line, there



14.46 The formation of a band of N molecular orbitals by successive addition of N atoms to a line. Note that the band remains of finite width as $N \rightarrow \infty$ and, although it looks continuous, it consists of N different orbitals.

are N molecular orbitals covering a band of energies of finite width, and the Hückel secular determinant is

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \cdots & 0 \\ \beta & \alpha - E & \beta & 0 & 0 & \cdots & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & \cdots & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & \cdots & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \cdots & \alpha - E \end{vmatrix} = 0 \qquad (49)$$

where β is now the (s, s) resonance integral. The theory of determinants applied to such a symmetrical example as this (technically a 'tridiagonal determinant') leads to the following expression for the roots:

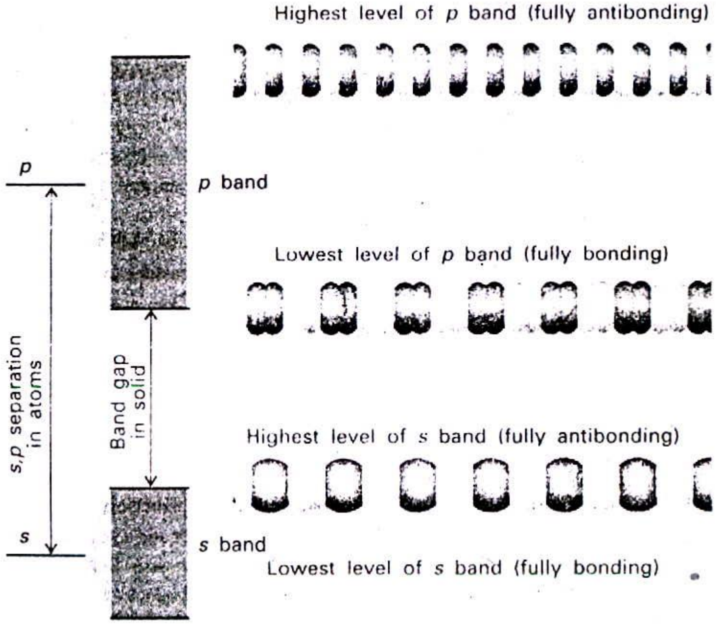
$$E_k = \alpha + 2\beta \cos\left(\frac{k\pi}{N+1}\right) \qquad k = 1, 2, \ldots, N \qquad (50)$$

When N is infinitely large, the difference between neighbouring energy levels (the energies corresponding to k and $k + 1$) is infinitely small, but the band still has finite width overall:

$$E_N - E_1 \rightarrow 4\beta \text{ as } N \rightarrow \infty \qquad (51)$$

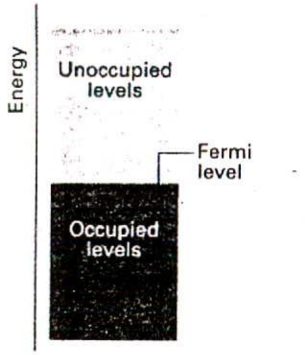
We can think of this band as consisting of N different molecular orbitals, the lowest-energy orbital ($k = 1$) being fully bonding, and the highest-energy orbital ($k = N$) being fully antibonding between adjacent atoms (Fig. 14.47). Similar bands form in three-dimensional solids.

The band formed from overlap of s orbitals is called the **s band**. If the atoms have p orbitals available, the same procedure leads to a **p band** (as shown in the upper half of Fig. 14.47). If the atomic p orbitals lie higher in energy than the s orbitals, then the p band



14.47 The overlap of s orbitals gives rise to an s band, and the overlap of p orbitals gives rise to a p band. In this case, the s and p orbitals of the atoms are so widely spaced that there is a band gap. In many cases the separation is less, and the bands overlap.

lies higher than the s band, and there may be a **band gap**, a range of energies to which no orbital corresponds.



14.48 When N electrons occupy a band of N orbitals, it is only half full and the electrons near the Fermi level (the top of the filled levels) are mobile.

(b) The occupation of orbitals at $T = 0$

Now consider the electronic structure of a solid formed from atoms each able to contribute one electron (for example, the alkali metals). There are N atomic orbitals and therefore N molecular orbitals squashed into an apparently continuous band. There are N electrons to accommodate.

At $T = 0$, only the lowest $\frac{1}{2}N$ molecular orbitals are occupied (Fig. 14.48), and the HOMO is called the **Fermi level**. However, unlike in the discrete molecules we have considered so far, there are empty orbitals very close in energy to the Fermi level, so it requires hardly any energy to excite the uppermost electrons. Some of the electrons are therefore very mobile, and give rise to electrical conductivity.

(c) The occupation of orbitals at $T > 0$

At temperatures above absolute zero, electrons can be excited by the thermal motion of the atoms. The population, P, of the orbitals is given by the **Fermi–Dirac distribution**, a version of the Boltzmann distribution that takes into account the effect of the Pauli principle:

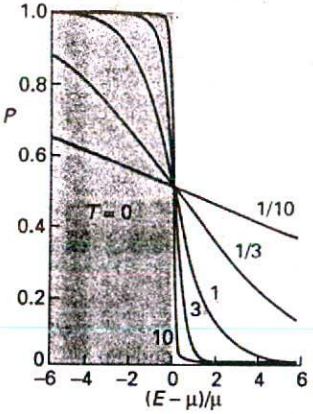
$$P = \frac{1}{e^{(E-\mu)/kT} + 1} \tag{52}$$

The quantity μ is the **chemical potential**,[19] which in this context is the energy of the level for which $P = \frac{1}{2}$ (note that the chemical potential changes as the temperature changes). The shape of the Fermi–Dirac distribution is shown in Fig. 14.49. For energies well above μ, the 1 in the denominator can be neglected, and then

$$P \approx e^{-(E-\mu)/kT} \tag{53}$$

The population now resembles a Boltzmann distribution, decaying exponentially with increasing energy. The higher the temperature, the longer the exponential tail.

The electrical conductivity of a metallic solid decreases with increasing temperature even though more electrons are excited into empty orbitals. This apparent paradox is resolved by noting that the increase in temperature causes more vigorous thermal motion of the atoms, so collisions between the moving electrons and an atom are more likely. That is, the electrons are scattered out of their paths through the solid, and are less efficient at transporting charge.



14.49 The Fermi–Dirac distribution, which gives the population of the levels at a temperature T. The high-energy tail decays exponentially towards zero. The curves are labelled with the value of μ/kT. The tinted grey region shows the occupation of levels at $T = 0$.

(d) Insulators and semiconductors

When each atom provides two electrons, the $2N$ electrons fill the N orbitals of the s band. The Fermi level now lies at the top of the band (at $T = 0$), and there is a gap before the next band begins (Fig. 14.50). As the temperature is increased, the tail of the Fermi–Dirac distribution extends across the gap, and electrons populate the empty orbitals of the upper band. They are now mobile, and the solid is an electric conductor. In fact, the solid is a semiconductor, because the electrical conductivity depends on the number of electrons that are promoted across the gap, and that number increases as the temperature is raised. If the gap is large, though, very few electrons will be promoted at ordinary temperatures, and the conductivity will remain close to zero, giving an insulator. Thus, the conventional distinction between an insulator and a semiconductor is related to the size of the band gap and is not an absolute distinction like that between a metal (incomplete bands at $T = 0$) and a semiconductor (full bands at $T = 0$).

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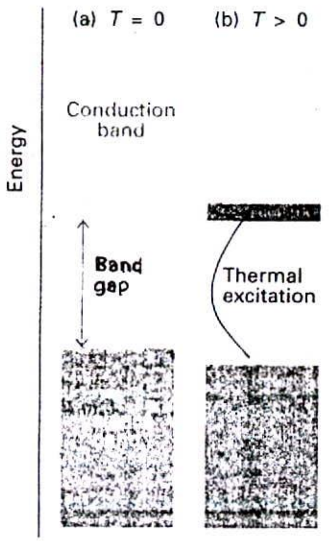
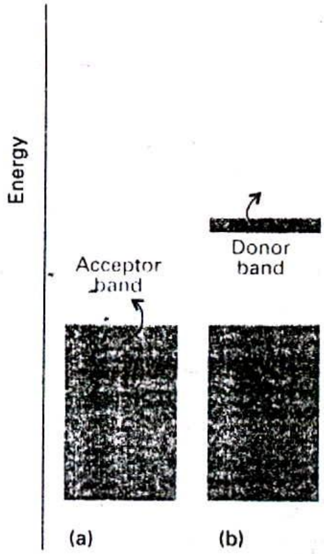
[19] Note that the 'chemical potential' in eqn 52 is an energy, not a molar Gibbs energy, as in the thermodynamic use of the term.



14.50 (a) When $2N$ electrons are present, the band is full and the material is an insulator at $T = 0$. (b) At temperatures above $T = 0$, electrons populate the levels of the upper 'conduction' band at the expense of the filled 'valence' band and the solid is a semiconductor.



14.51 (a) A dopant with fewer electrons than its host can form a narrow band that accepts electrons from the valence band. The holes in the band are mobile, and the substance is a p-type semiconductor. (b) A dopant with more electrons than its host forms a narrow band that can supply electrons to the conduction band. The electrons it supplies are mobile, and the substance is an n-type semiconductor.

Another method of increasing the number of charge carriers and enhancing the semiconductivity of a solid is to implant foreign atoms into an otherwise pure material. If these **dopants** can trap electrons, they withdraw electrons from the filled band, leaving holes which allow the remaining electrons to move (Fig. 14.51). This procedure gives rise to **p-type semiconductivity**, the p indicating that the holes are positive relative to the electrons in the band. Alternatively, a dopant might carry excess electrons (for example, phosphorus atoms introduced into germanium), and these additional electrons occupy otherwise empty bands, giving **n-type semiconductivity**, where n denotes the negative charge of the carriers. The preparation of doped but otherwise ultrapure materials was described in Section 8.7.

Checklist of key ideas

The Born–Oppenheimer approximation

- ☐ Born–Oppenheimer approximation
- ☐ molecular potential energy curve
- ☐ bond dissociation energy

Valence-bond theory

- ☐ valence-bond theory (VB theory)

14.1 The hydrogen molecule

- ☐ σ bond

14.2 Homonuclear diatomic molecules

- ☐ homonuclear diatomic molecules
- ☐ π bond

14.3 Polyatomic molecules

- ☐ promotion
- ☐ hybrid orbital
- ☐ sp^3 hybrid orbital
- ☐ sp^2 hybrid orbital
- ☐ sp hybrid orbital

Molecular orbital theory

- ☐ molecular orbital theory (MO theory)

14.4 The hydrogen molecule-ion

- ☐ molecular orbital (MO)
- ☐ linear combination of atomic orbitals (LCAO)
- ☐ LCAO-MO
- ☐ σ orbital
- ☐ overlap density
- ☐ bonding orbital
- ☐ σ electron
- ☐ antibonding orbital

14.5 The structures of diatomic molecules

- ☐ molecular orbital energy level diagram
- ☐ bond order (15)
- ☐ bond dissociation energy
- ☐ π orbital
- ☐ overlap integral (18)

14.6 More about notation

- ☐ parity
- ☐ centre of inversion

14.7 Heteronuclear diatomic molecules

- ☐ polar bond
- ☐ partial negative charge
- ☐ partial positive charge
- ☐ electronegativity
- ☐ Pauling electronegativity
- ☐ Mulliken electronegativity
- ☐ variation principle
- ☐ trial wavefunction
- ☐ basis set
- ☐ secular equations
- ☐ Coulomb integral
- ☐ resonance integral
- ☐ secular determinant

Molecular orbitals for polyatomic systems

14.8 Walsh diagrams

- ☐ Walsh diagram
- ☐ nonbonding orbital

14.9 The Hückel approximation

- ☐ conjugated molecule
- ☐ Hückel approximations
- ☐ ~~highest~~ occupied molecular orbital (HOMO)
- ☐ lowest unoccupied molecular orbital (LUMO)
- ☐ frontier orbital
- ☐ π-electron binding energy
- ☐ delocalization energy
- ☐ semi-empirical methods
- ☐ *ab initio* methods
- ☐ complete neglect of differential overlap (CNDO)
- ☐ Gaussian type orbital (GTO)

14.10 The band theory of solids

- ☐ metallic conductor
- ☐ semiconductor
- ☐ insulator
- ☐ *s* band
- ☐ *p* band
- ☐ band gap
- ☐ Fermi level
- ☐ Fermi–Dirac distribution
- ☐ chemical potential
- ☐ dopant
- ☐ p-type semiconductivity
- ☐ n-type semiconductivity

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Exercises

14.1 (a) Give the ground-state electron configurations and bond orders of (a) Li_2, (b) Be_2, and (c) C_2.

14.1 (b) Give the ground-state electron configurations of (a) H_2^-, (b) N_2, and (c) O_2.

14.2 (a) Give the ground-state electron configurations of (a) CO, (b) NO, and (c) CN^-.

14.2 (b) Give the ground-state electron configurations of (a) ClF, (b) CS, and (c) O_2^-.

14.3 (a) From the ground-state electron configurations of B_2 and C_2, predict which molecule should have the greater bond dissociation energy.

14.3 (b) Which of the molecules N_2, NO, O_2, C_2, F_2, and CN would you expect to be stabilized by (a) the addition of an electron to form AB^-, (b) the removal of an electron to form AB^+?

14.4 (a) Sketch the molecular orbital energy level diagram for XeF and deduce its ground-state electron configurations. Is XeF likely to have a shorter bond length than XeF^+?

14.4 (b) Sketch the molecular orbital energy level diagrams for BrCl and deduce its ground-state electron configurations. Is BrCl likely to have a shorter bond length than $BrCl^-$?

14.5 (a) Where appropriate, give the parity of (a) π^* in F_2, (b) σ^* in NO, (c) δ in Tl_2, (d) δ^* in Fe_2.

14.5 (b) Give the parities of the six π molecular orbitals of benzene.

14.6 (a) The term symbol for the ground state of N_2^+ is ${}^2\Sigma_g^+$. What is the total spin and total orbital angular momentum of the molecule? Show that the term symbol agrees with the electron configuration that would be predicted using the building-up principle.

14.6 (b) One of the excited states of the C_2 molecule has the valence electron configuration $1\sigma_g^2 2\sigma_u^{*2} 1\pi_u^3 2\pi_g^1$. Give the multiplicity and parity of the term.

14.7 (a) Use the electron configurations of NO and N_2 to predict which is likely to have the shorter bond length.

14.7 (b) Arrange the species O_2^+, O_2, O_2^-, O_2^{2-} in order of increasing bond length.

14.8 (a) Show that the sp^2 hybrid orbital $(s + 2^{1/2}p)/3^{1/2}$ is normalized to 1 if the s and p orbitals are normalized to 1.

14.8 (b) Normalize the molecular orbital $\psi_s(\mathrm{A}) + \lambda\psi_s(\mathrm{B})$ in terms of the parameter λ and the overlap integral S.

14.9 (a) Confirm that the bonding and antibonding combinations $\psi_s(\mathrm{A}) \pm \psi_s(\mathrm{B})$ are mutually orthogonal in the sense that their mutual overlap is zero.

14.9 (b) Suppose that a molecular orbital has the form $N(0.145A + 0.844B)$. Find a linear combination of the orbitals A and B that is orthogonal to this combination.

14.10 (a) Which of the following triatomic molecules and ions are expected to be linear: (a) CO_2, (b) NO_2, (c) NO_2^+? Give reasons in each case.

14.10 (b) Which of the following triatomic molecules and ions are expected to be linear: (a) NO_2^-, (b) SO_2, (c) H_2O, (d) H_2O^{2+}? Give reasons in each case.

14.11 (a) Construct the molecular orbital energy level diagrams of ethene (ethylene) on the basis that the molecule is formed from the appropriately hybridized CH_2 or CH fragments.

14.11 (b) Construct the molecular orbital energy level diagrams of ethyne (acetylene) on the basis that the molecule is formed from the appropriately hybridized CH_2 or CH fragments.

14.12 (a) Write down the secular determinants for (a) linear H_3, (b) cyclic H_3 within the Hückel approximation.

14.12 (b) Predict the electronic configurations of (a) the benzene anion, (b) the benzene cation. Estimate the π-bond energy in each case.

Problems

Numerical problems

14.1 Show that, if a wave $\cos kx$ centred on A (so that x is measured from A) interferes with a similar wave $\cos k'x$ centred on B (with x measured from B) a distance R away, then constructive interference occurs in the intermediate region when $k = k' = \pi/2R$ and destructive interference if $kR = \frac{3}{2}\pi$ and $k'R = \frac{3}{2}\pi$.

14.2 The overlap integral between two H1s orbitals on nuclei separated by a distance R is $S = \{1 + (R/a_0) + \frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$. Plot this function for $0 \geq R < \infty$.

14.3 Before doing the calculation below, sketch how the overlap between an s orbital and a σp orbital can be expected to depend on their separation. The overlap integral between an H1s orbital and an H2p orbital on nuclei separated by a distance R is $S = (R/a_0)\{1 + (R/a_0) + \frac{1}{3}(R/a_0)^2\}e^{-R/a_0}$. Plot this function, and find the separation for which the overlap is a maximum.

14.4 Calculate the total amplitude of the normalized bonding and antibonding LCAO-MOs that may be formed from two H1s orbitals at a separation of 106 pm. Plot the two amplitudes for positions along the molecular axis both inside and outside the internuclear region.

14.5 Repeat the calculation in Problem 14.4, but plot the probability densities of the two orbitals. Then form the difference density, the difference between ψ^2 and $\frac{1}{2}\{\psi_s(\mathrm{A})^2 + \psi_s(\mathrm{B})^2\}$.

14.6 Imagine a small electron-sensitive probe of volume 1.00 pm^3 inserted into an H_2^+ molecule ion in its ground state. Calculate the probability that it will register the presence of an electron at the following positions: (a) at nucleus A, (b) at nucleus B, (c) halfway between A and B, (d) at a point 20 pm along the bond from A and 10 pm perpendicularly. Do the same for the molecule-ion the instant after the electron has been excited into the antibonding LCAO-MO.

14.7 The energy of H_2^+ with internuclear separation R is given by the expression

$$E = E_{\mathrm{H}} - \frac{V_1 + V_2}{1 + S} + \frac{e^2}{4\pi\varepsilon_0 R}$$

where E_{H} is the energy of an isolated H atom, V_1 is the attractive potential energy between the electron centred on one nucleus and the charge of the other nucleus, V_2 is the attraction between the overlap density and one of the nuclei, S is the overlap integral. The values are given below. Plot the molecular potential energy curve and find the bond dissociation energy (in electronvolts) and the equilibrium bond length.

R/a_0	0	1	2	3	4
V_1/E_{h}	1.000	0.729	0.473	0.330	0.250
V_2/E_{h}	1.000	0.736	0.406	0.199	0.092
S	1.000	0.858	0.587	0.349	0.189

where $E_{\mathrm{h}} = 27.3$ eV, $a_0 = 52.9$ pm, and $E_{\mathrm{H}} = -\frac{1}{2}E_{\mathrm{h}}$.

14.8 The same data as in Problem 14.7 may be used to calculate the molecular potential energy curve for the antibonding orbital, which is given by

$$E = E_{\mathrm{H}} - \frac{V_1 - V_2}{1 - S} + \frac{e^2}{4\pi\varepsilon_0 R}$$

Plot the curve.

14.9 In the 'free electron molecular orbital' (FEMO) theory, the electrons in a conjugated molecule are treated as independent particles in a box of length L. Sketch the form of the two occupied orbitals in butadiene predicted by this model and predict the minium excitation energy of the molecule. The tetraene $CH_2{=}CHCH{=}CHCH{=}CHCH{=}CH_2$ can be treated as a box of length $8R$, where $R \approx 140$ pm (as in this case, an extra half bond-length is often added at each end of the box). Calculate the minimum excitation energy of the molecule and sketch the HOMO and LUMO. Estimate the colour a sample of the compound is likely to appear in white light.

Theoretical problems

14.10 An sp^2 hybrid orbital that lies in the xy plane and makes an angle of 120° to the x-axis has the form

$$\psi = \frac{1}{3^{1/2}}\left(s - \frac{1}{2^{1/2}}p_x + \frac{3^{1/2}}{2^{1/2}}p_y\right)$$

Use hydrogenic atomic orbitals to write the explicit form of the hybrid orbital. Show that it has its maximum amplitude in the direction specified.

14.11 Use the expressions in Problems 14.7 and 14.8 to show that the antibonding orbital is more antibonding than the bonding orbital is bonding at most internuclear separations.

14.12 Derive the expressions used in Problems 14.7 and 14.8 using the normalized LCAO-MOs for the H_2^+ molecule-ion. Proceed by evaluating the expectation value of the hamiltonian for the ion. Make use of the fact that $\psi_s(\mathrm{A})$ and $\psi_s(\mathrm{B})$ each individually satisfy the Schrödinger equation for an isolated H atom.

14.13 Construct the Walsh diagram for an AH_3 molecule, and use it to predict the shapes of (a) NH_3, (b) CH_3^+.

14.14 Take as a trial function for the ground state of the hydrogen atom (a) e^{-kr}, (b) e^{-kr^2} and use the variation principle to find the optimum value of k in each case. Identify the better wavefunction. The only part of the laplacian that need be considered is the part that involves radial derivatives (eqn 12.63).

Additional problems supplied by Carmen Giunta and Charles Trapp

14.15 J.G. Dojahn, E.C.M. Chen, and W.E. Wentworth (*J. Phys. Chem.* **100**, 9649 (1996)) characterized the potential energy curves of homonuclear diatomic halogen molecules and molecular anions. Among the properties they report are the the equilibrium internuclear distance R_e, the vibrational wavenumber, $\tilde{\nu}$, and the dissociation energy, D_e.

Species	r_e/pm	$\tilde{\nu}$/cm^{-1}	D_e/eV
F_2	1.411	916.6	1.60
F_2^-	1.900	450.0	1.31

Rationalize these data by using qualitative molecular orbital configurations.

14.16 Rydberg molecules can be thought of as molecular analogues of Rydberg atoms. However Rydberg molecules do not involve atomic orbitals with analogously large quantum numbers ($n = 100$), but rather atomic orbitals with n one higher than the n values of the valence shells of the constituent atoms. Nevertheless speculate about the existence of Rydberg H_2 as formed from two H atoms with $100s$ electrons. Make reasonable guesses about the binding energy, the equilibrium internuclear separation, the vibrational force constant, and the rotational constant. Is such a molecule likely to exist under any circumstances?

14.17 Set up and solve the Hückel secular equations for the π electrons in NO_3^-. Express the energies in terms of the Coulomb integrals, α_O and α_N, and the resonance integral β. Determine the delocalization energy of the nitrate ion.

14.18 In Exercise 14.12a, you were invited to set up the Hückel secular determinants for linear and cyclic H_3. The same secular determinant applies to the molecular ions H_3^+ and D_3^+. The molecular ion H_3^+ was discovered as long ago as 1912 by J.J. Thomson, but only more recently has the equilateral-triangular structure been confirmed by M.J. Gaillard, *et al.* (*Phys. Rev.* A17, 1797 (1978)). The molecular ion H_3^+ is the simplest polyatomic species with a confirmed existence and plays an important role in interstellar chemistry. (a) Solve the Hückel secular equations for the energies of the H_3 system in terms of the parameters α and β, draw an energy level diagram for the orbitals, and determine the binding energies of the molecules H_3^{2+}, H_3^+, H_3, and H_3^-. (b) Accurate quantum mechanical calculations by G.D. Carney and R.N. Porter (*J. Chem. Phys.* **65**, 3547 (1976)) give the dissociation energy for the process $H_3^+(g) \rightarrow 2H(g) + H^+(g)$ as 849 kJ mol^{-1}. From this information and data in Table 2.6, calculate the enthalpy of the reaction $H^+(g) + H_2(g) \rightarrow H_3^+(g)$. Compare to the binding energy of $H_2(g)$. (c) From your equations and the information given, calculate a value for the the resonance integral, β, in H_3^+; then go on to calculate the binding energies for the other H_3 species in (a).

14.19 There is some indication that other hydrogen ring compounds and ions in addition to H_3 and D_3 species may play a role in interstellar chemistry. According to J.S. Wright and G.A. DiLabio (*J. Phys. Chem.* **96**, 10793 (1992)), H_5^-, H_6, and H_7^+ are particularly stable, whereas H_4 and H_5^+ are not. Confirm these statements by Hückel calculations.

15

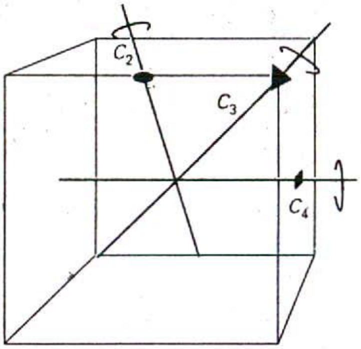
Molecular symmetry

In this chapter we sharpen the concept of 'shape' into a precise definition of 'symmetry', and show that symmetry may be discussed systematically. We see how to classify any molecule according to its symmetry, and how to use this classification to discuss molecular properties. After describing the symmetry properties of molecules themselves, we turn to a consideration of the effect of symmetry transformations on orbitals, and see that their transformation properties can be used to set up a labelling scheme. These symmetry labels are used to identify what integrals necessarily vanish. One important integral is the overlap integral between two orbitals. By knowing which atomic orbitals may have nonzero overlap, we can decide which ones can contribute to the formation of molecular orbitals. We also see how to select linear combinations of atomic orbitals that match the symmetry of the nuclear framework. Finally, by considering the symmetry properties of integrals, we see that it is possible to derive the selection rules that govern spectroscopic transitions.

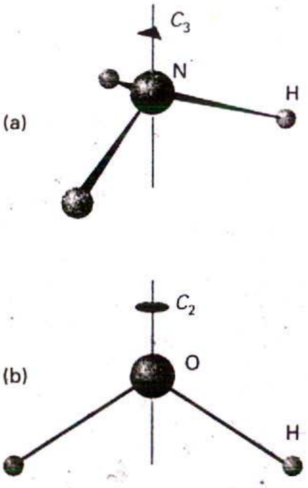
The systematic discussion of symmetry is called **group theory**. Much of group theory is a summary of common sense about the symmetries of objects. However, because group theory is systematic, its rules can be applied in a straightforward, mechanical way, and in some cases it gives unexpected results. In most cases the theory gives a simple, direct method for arriving at useful conclusions with the minimum of calculation, and this is the aspect we stress here.

The symmetry elements of objects

Some objects are 'more symmetrical' than others. A sphere is more symmetrical than a cube because it looks the same after it has been rotated through any angle about any diameter. A cube looks the same only if it is rotated through certain angles about specific axes, such as 90°, 180°, or 270° about an axis passing through the centres of any of its opposite faces (Fig. 14.1), or by 120° or 240° about an axis passing through any of its opposite corners. Similarly, an NH_3 molecule is 'more symmetrical' than an H_2O molecule because NH_3 looks the same after rotations of 120° or 240° about the axis shown in Fig. 14.2, whereas H_2O looks the same only after a rotation of 180°.



15.1 Some of the symmetry elements of a cube. The twofold, threefold, and fourfold axes are labelled with the conventional symbols.



15.2 (a) An NH_3 molecule has a threefold (C_3) axis and (b) an H_2O molecule has a twofold (C_2) axis. Both have other symmetry elements too.

An action that leaves an object looking the same after it has been carried out is called a **symmetry operation**. Typical symmetry operations include rotations, reflections, and inversions. There is a corresponding **symmetry element** for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed. For instance, a rotation (a symmetry operation) is carried out around an axis (the corresponding symmetry element). We shall see that we can classify molecules by identifying all their symmetry elements, and grouping together molecules that possess the same set of symmetry elements. This procedure, for example, puts the trigonal pyramidal species NH_3 and SO_3^{2-} into one group and the angular species H_2O and SO_2 into another group.

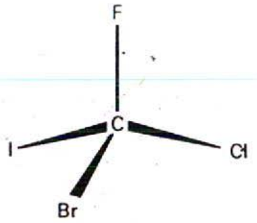
15.1 Operations and symmetry elements

The classification of objects according to symmetry elements corresponding to operations that leave at least one common point unchanged gives rise to the **point groups**. There are five kinds of symmetry operation (and five kinds of symmetry element) of this kind. When we consider crystals (Chapter 21), we shall meet symmetries arising from translation through space. These more extensive groups are called **space groups**.

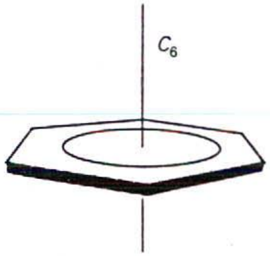
The **identity**, E, consists of doing nothing; the corresponding symmetry element is the entire object. Because every object is indistinguishable from itself if nothing is done to it, every object possesses at least the identity element. One reason for including the identity is that some molecules have only this symmetry element (**1**); another reason is technical and connected with the detailed formulation of group theory.

An n**-fold rotation** (the operation) about an n**-fold axis of symmetry**, C_n (the corresponding element), is a rotation through $360°/n$. The operation C_1 is a rotation through 360°, and is equivalent to the identity operation E. An H_2O molecule has one twofold axis, C_2. An NH_3 molecule has one threefold axis, C_3, with which is associated two symmetry operations, one being 120° rotation in a clockwise sense and the other 120° rotation in a counter-clockwise sense.[1] A pentagon has a C_5 axis, with two (clockwise and counter-clockwise) rotations through 72° associated with it. It also has an axis denoted C_5^2, corresponding to two successive C_5 rotations; there are two such operations, one through 144° in a clockwise sense and the other through 144° in a counter-clockwise sense. A cube has three C_4 axes, four C_3 axes, and six C_2 axes. However, even this high symmetry is exceeded by a sphere, which possesses an infinite number of symmetry axes (along any diameter) of all possible integral values of n. If a molecule possesses several rotation axes, then the one (or more) with the greatest value of n is called the **principal axis**. The principal axis of a benzene molecule is the sixfold axis perpendicular to the hexagonal ring (**2**).

A **reflection** (the operation) in a **mirror plane**, σ (the element), may contain the principal axis of a molecule or be perpendicular to it. If the plane is parallel to the principal axis, it is called 'vertical' and denoted σ_v. An H_2O molecule has two vertical planes of symmetry



1 CBrClFI



2 Benzene

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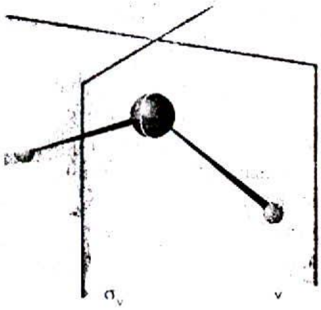
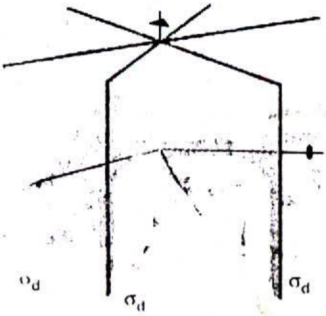
[1] There is only one twofold rotation associated with a C_2 axis because clockwise and counter-clockwise 180° rotations are identical.

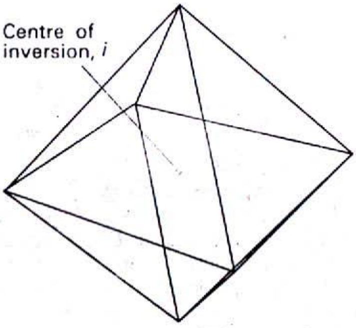


15.3 An H_2O molecule has two mirror planes. They are both vertical (that is, contain the principal axis) and so are denoted σ_v and σ'_v.



15.4 Dihedral mirror planes (σ_d) bisect the C_2 axes perpendicular to the principal axis.

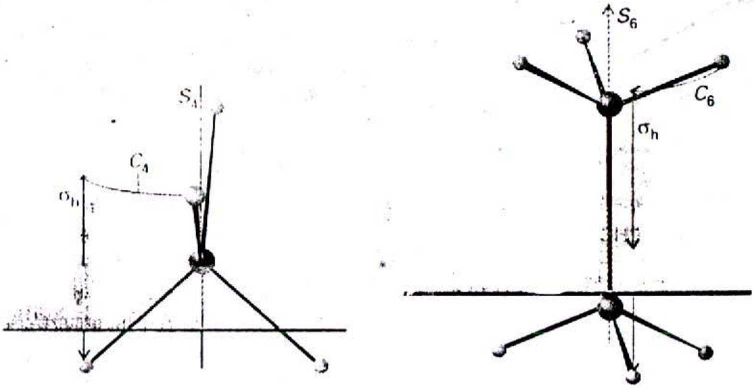
(Fig. 15.3) and an NH_3 molecule has three. A vertical mirror plane that bisects the angle between two C_2 axes is called a 'dihedral plane' and is denoted σ_d (Fig. 15.4). When the plane of symmetry is perpendicular to the principal axis it is called 'horizontal' and denoted σ_h. A C_6H_6 molecule has a C_6 principal axis and a horizontal mirror plane (as well as several other symmetry elements).



15.5 A regular octahedron has a centre of inversion (i).

In an inversion (the operation) through a **centre of symmetry**, i (the element), we imagine taking each point in a molecule, moving it to the centre of the molecule, and then moving it out the same distance on the other side,[2] that is, the point (x, y, z) is taken into the point $(-x, -y, -z)$. Neither an H_2O molecule nor an NH_3 molecule has a centre of inversion, but a sphere and a cube do have one. A C_6H_6 molecule does have a centre of inversion, as does a regular octahedron (Fig. 15.5); a regular tetrahedron and a CH_4 molecule do not.

An ***n*-fold improper rotation** (the operation) about an n-fold axis of improper rotation or an ***n*-fold improper rotation axis**, S_n (the symmetry element), is composed of two successive transformations. The first component is a rotation through $360°/n$, and the second is a reflection through a plane perpendicular to the axis of that rotation; neither operation alone needs to be a symmetry operation. A CH_4 molecule has three S_4 axes (Fig. 15.6).



(a) (b)

15.6 (a). A CH_4 molecule has a fourfold improper rotation axis (S_4): the molecule is indistinguishable after a 90° rotation followed by a reflection across the horizontal plane, but neither operation alone is a symmetry operation. (b) The staggered form of ethane has an S_6 axis composed of a 60° rotation followed by a reflection.

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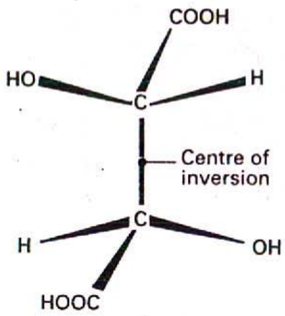
[2] This operation was first encountered in Section 14.6a in connection with the parity classification of orbitals.

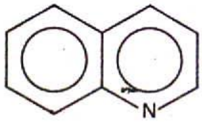
15.2 The symmetry classification of molecules

To classify molecules according to their symmetries, we list their symmetry elements and collect together molecules with the same list of elements. This procedure puts CH_4 and CCl_4, which both possess the same symmetry elements as a regular tetrahedron, into the same group, and H_2O into another group.

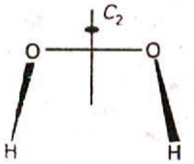
The name of the group to which a molecule belongs is determined by the symmetry elements it possesses. There are two systems of notation (Table 15.1). The **Schoenflies system** is more common for the discussion of individual molecules, and the **Hermann–Mauguin system**, or **International system**, is used almost exclusively in the discussion of crystal symmetry.



3 Meso-tartaric acid



4 Quinoline



5 H_2O_2

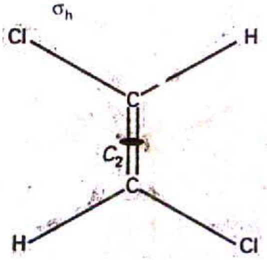
Table 15.1 The notation for point groups•

C_i	$\bar{1}$								
C_s	m								
C_1	1	C_2	2	C_3	3	C_4	4	C_6	6
		C_{2v}	$2mm$	C_{3v}	$3m$	C_{4v}	$4mm$	C_{6v}	$6mm$
		C_{2h}	$2/m$	C_{3h}	$\bar{6}$	C_{4h}	$4/m$	C_{6h}	$6/m$
		D_2	222	D_3	32	D_4	422	D_6	622
		D_{2h}	mmm	D_{3h}	$\bar{6}2m$	D_{4h}	$4/mmm$	D_{6h}	$6/mmm$
		D_{2d}	$\bar{4}2m$	D_{3d}	$\bar{3}m$	S_4	$\bar{4}/m$	S_6	$\bar{3}$
T	23	T_d	$\bar{4}3m$	T_h	$m3$				
O	432	O_h	$m3m$						

•In the International system (or Hermann–Mauguin system) for point groups, a number n denotes the presence of an n-fold axis and m denotes a mirror plane. A diagonal line / indicates that the mirror plane is perpendicular to the symmetry axis. It is important to distinguish symmetry elements of the same type but of different classes, as in $4/mmm$, in which there are three classes of mirror plane (σ_v, σ_h, and σ_d). A bar over a number indicates that the element is combined with an inversion. The only groups listed in this table are the so-called crystallographic point groups (Section 21.1).

(a) The groups C_1, C_i, and C_s

A molecule belongs to the group C_1 if it has no element other than the identity (as in (1)). It belongs to C_i if it has the identity and the inversion alone (3), and to C_s if it has the identity and a mirror plane alone (4).

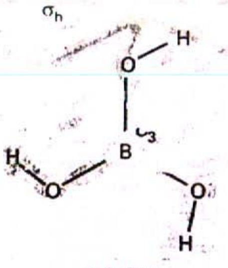


6 *trans*-CHCl=CHCl

(b) The groups C_n, C_{nv}, and C_{nh}

A molecule belongs to the group C_n if it possesses an n-fold axis.[3] An H_2O_2 molecule has the elements E and C_2 (5), so it belongs to the group C_2.

If in addition to the identity and a C_n axis a molecule has n vertical mirror planes σ_v, then it belongs to the group C_{nv}. An H_2O molecule, for example, has the symmetry elements E, C_2, and $2\sigma_v$, so it belongs to the group C_{2v}. An NH_3 molecule has the elements E, C_3, and $3\sigma_v$, so it belongs to the group C_{3v}. A heteronuclear diatomic molecule such as HCl belongs to the group $C_{\infty v}$ because all rotations around the axis and reflections across the axis are symmetry operations. Other members of the group $C_{\infty v}$ include the linear OCS molecule and a cone.



7 $B(OH)_3$

Objects that in addition to the identity and an n-fold principal axis also have a horizontal mirror plane σ_h belong to the groups C_{nh}. An example is *trans*-CHCl=CHCl (6), which has the elements E, C_2, and σ_h, and so belongs to the group C_{2h}; the molecule $B(OH)_3$ in the conformation shown in (7) belongs to the group C_{3h}. The presence of certain symmetry

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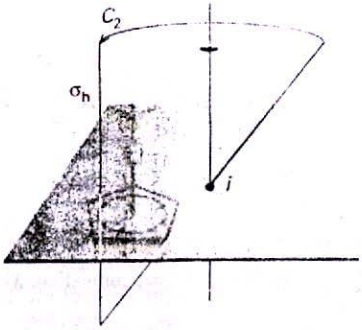
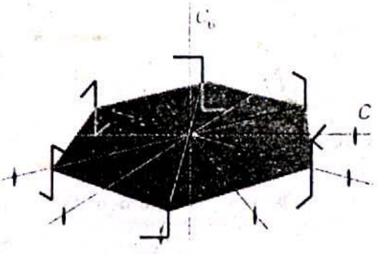
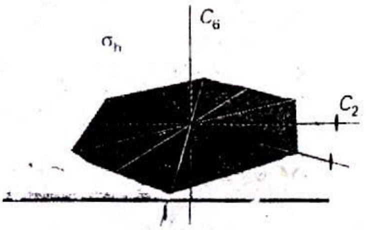
[3] Note that symbol C_n is now playing a triple role: as the label of a symmetry element, a symmetry operation, and a group.



15.7 The presence of a twofold axis and a horizontal mirror plane jointly imply the presence of a centre of inversion in the molecule.



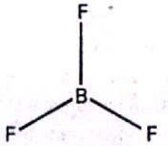
15.8 A molecule with n twofold rotation axes perpendicular to an n-fold rotation axis belongs to the group D_n.



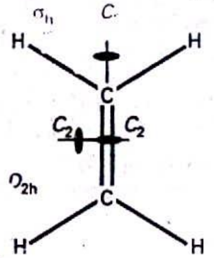
15.9 A molecule with a mirror plane perpendicular to a C_n axis, and with n twofold axes in the plane, belongs to the group D_{nh}.

elements may be implied by the presence of others: thus, in C_{2h} the operations C_2 and σ_h jointly imply the presence of a centre of inversion (Fig. 15.7).

(c) The groups D_n, D_{nh}, and D_{nd}



8 BF_3



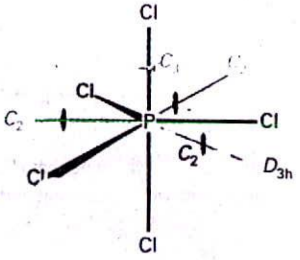
9 $H_2C{=}CH_2$

A molecule that has an n-fold principal axis and n twofold axes perpendicular to C_n belongs to the group D_n (Fig. 15.8). A molecule belongs to D_{nh} if it also possesses a horizontal mirror plane (Fig. 15.9). The planar trigonal BF_3 molecule has the elements E, C_3, $3C_2$, and σ_h (with one C_2 axis along each B–F bond), and so belongs to D_{3h} (8). The C_6H_6 molecule has the elements E, C_6, $3C_2$, $3C_2'$, and σ_h together with some others that these elements imply,[4] so it belongs to D_{6h}. All homonuclear diatomic molecules, such as N_2, belong to the group $D_{\infty h}$ because all rotations around the axis are symmetry operations, as are end-to-end rotation and end-to-end reflection; $D_{\infty h}$ is also the group of the linear OCO and HCCH molecules and of a uniform cylinder. Other examples of D_{nh} molecules are shown in (9), (10), and (11).

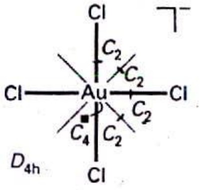
A molecule belongs to the group D_{nd} if in addition to the elements of D_n it possesses n dihedral mirror planes σ_d. The twisted, 90° allene (12) belongs to D_{2d}, and the staggered conformation of ethane (13) belongs to D_{3d}.

(d) The groups S_n

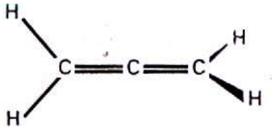
Molecules that have not been classified into one of the groups mentioned so far, but which possess one S_n axis, belong to the group S_n. An example is tetraphenylmethane, which



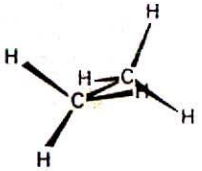
10 PCl_5



11 $[AuCl_4]^-$



12 $H_2C{=}C{=}CH_2$



13 C_2H_6

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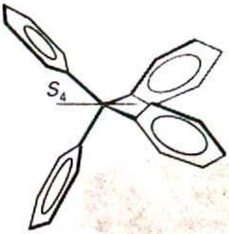
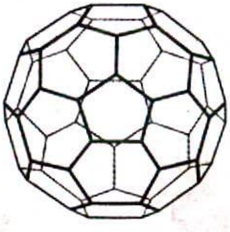
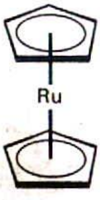
[4] The prime on $3C_2'$ indicates that the three C_2 axes are different from the other three C_2 axes.



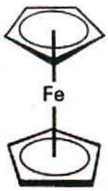
14 $C(C_6H_5)_4$



15 Buckminsterfullerene, C_{60}

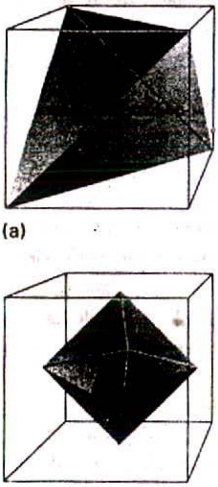


16 Ruthenocene, $Ru(C_6H_5)_2$



17 Excited ferrocene, $Fe(C_6H_5)_2^*$

belongs to the point group S_4 (**14**). Molecules belonging to S_n with $n > 4$ are rare. Note that the group S_2 is the same as C_i, so such a molecule will already have been classified as C_i.



15.10 (a) Tetrahedral and (b) octahedral molecules are drawn in a way that shows their relation to a cube: they belong to the cubic groups T_d and O_h, respectively.

(e) The cubic groups

A number of very important molecules (for example, CH_4 and SF_6) possess more than one principal axis. Most belong to the **cubic groups**, and in particular to the tetrahedral groups T, T_d, and T_h or to the octahedral groups O, O_h (Fig. 15.10). A few icosahedral (20-faced) molecules, belonging to the **icosahedral group**, I (Fig. 15.11), are also known: they include some of the boranes and buckminsterfullerene, C_{60} (**15**). The groups T_d and O_h are the groups of the regular tetrahedron (for example, CH_4) and the regular octahedron (for example, SF_6), respectively. If the object possesses the rotational symmetry of the tetrahedron or the octahedron, but none of their planes of reflection, then it belongs to the simpler groups T or O (Fig. 15.12). The group T_h is based on T but also contains a centre of inversion (Fig. 15.13).

(f) The full rotation group

The **full rotation group**, R_3 (the 3 refers to rotation in three dimensions), consists of an infinite number of rotation axes with all possible values of n. A sphere and an atom belong to R_3, but no molecule does. Exploring the consequences of R_3 is a very important way of applying symmetry arguments to atoms, and is an alternative approach to the theory of orbital angular momentum.

Example 15.1 Identifying a point group of a molecule

Identify the point group to which a ruthenocene molecule (**16**) belongs.

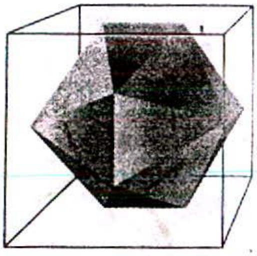
Method The identification of a molecule's point group is simplified by referring to the flow diagram in Fig. 15.14 and the shapes shown in Fig. 15.15.

Answer The path to trace through the flow diagram in Fig. 15.14 is shown by a green line; it ends at D_{nh}. Because the molecule has a fivefold axis, it belongs to the group D_{5h}.

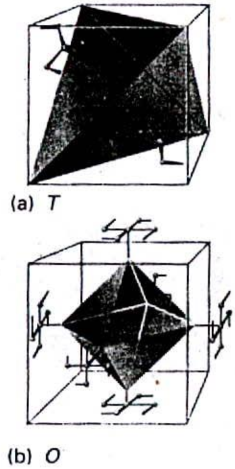
Comment If the rings were staggered, as they are in an excited state of ferrocene that lies 4 kJ mol^{-1} above the ground state (**17**), the horizontal reflection plane would be absent, but dihedral planes would be present.

Self-test 15.1 Classify the pentagonal antiprismatic excited state of ferrocene.

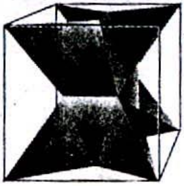
$[D_{5d}]$



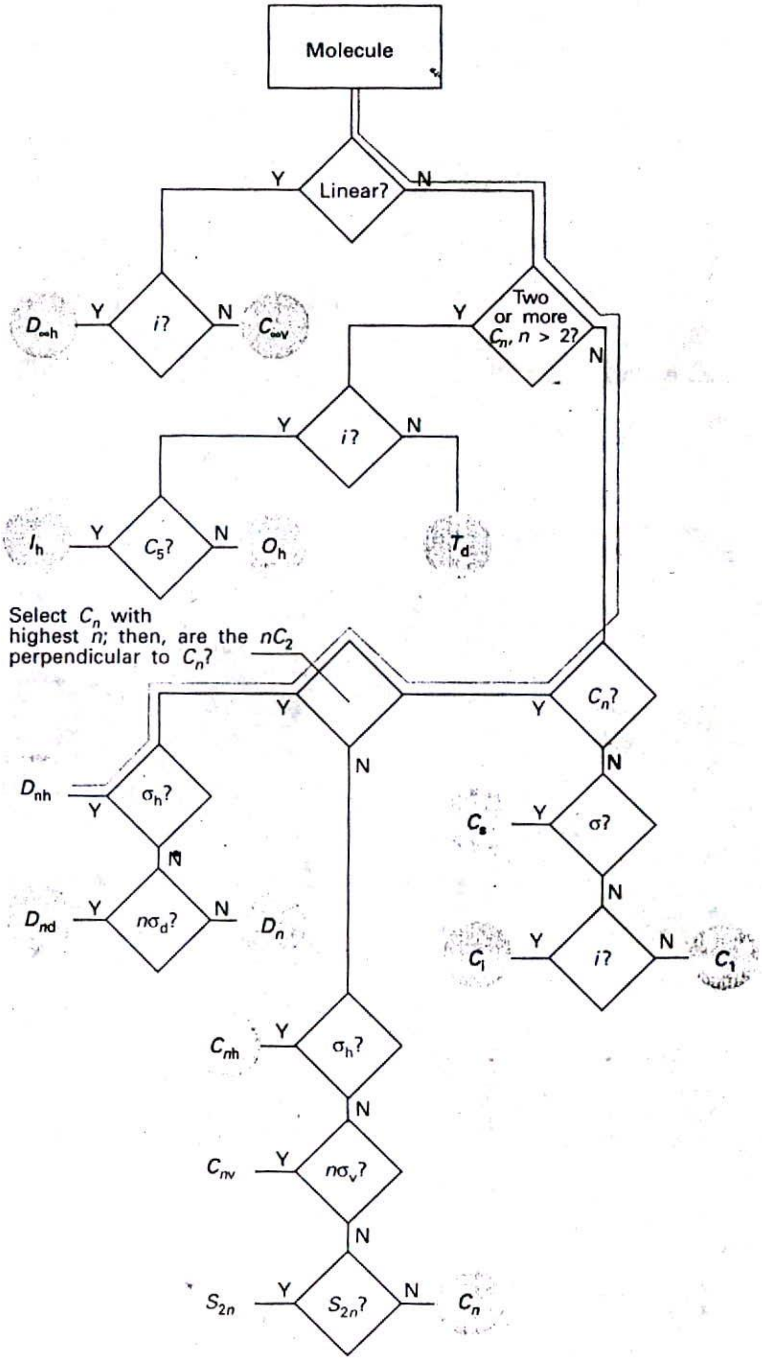
15.11 The relation of an icosahedron to a cube. The buckminsterfullerene molecule (**15**) is related to this object by cutting off each apex to form a regular pentagon.



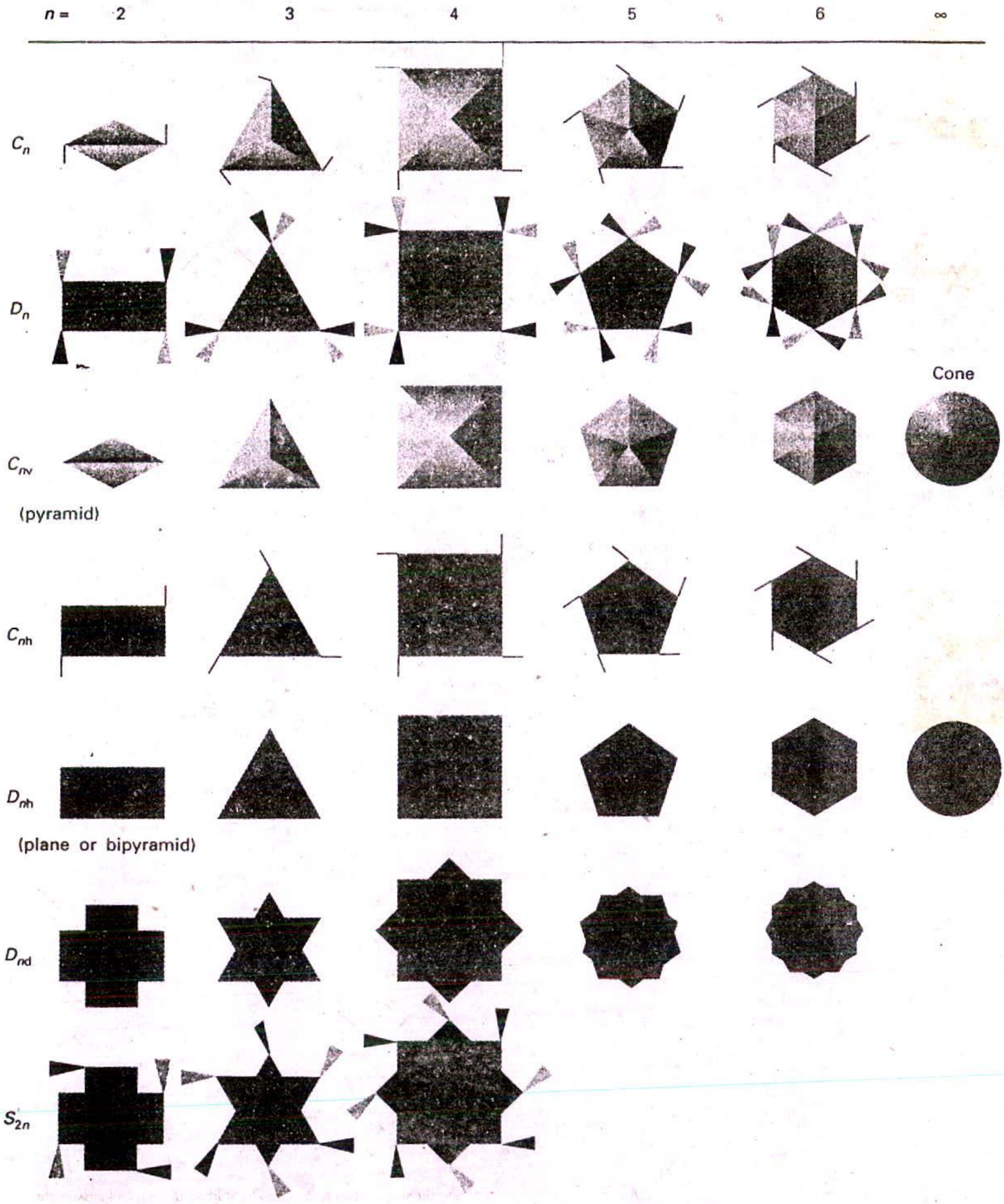
15.12 Shapes corresponding to the point groups (a) T and (b) O. The presence of the windmill-like structures reduces the symmetry of the object from T_d and O_h, respectively.



15.13 The shape of an object belonging to the group T_h.



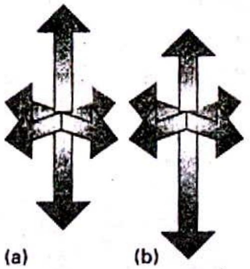
15.14 A flow diagram for determining the point group of a molecule. Start at the top and answer the question posed in each diamond (Y = yes, N = no).



15.15 A summary of the shapes corresponding to different point groups. The group to which a molecule belongs can often be identified from this diagram without going through the formal procedure in Fig. 15.14.

15.3 Some immediate consequences of symmetry

Some statements about the properties of a molecule can be made as soon as its point group has been identified.

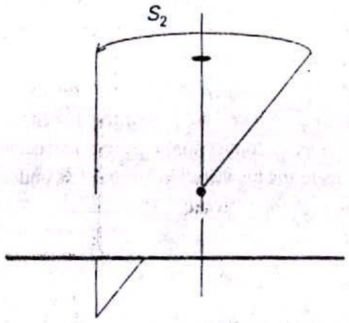


15.16 (a) A molecule with a C_n axis cannot have a dipole perpendicular to the axis, but (b) it may have one parallel to the axis. The arrows represent local contributions to the overall electric dipole, such as may arise from bonds between pairs of neighbouring atoms with different electronegativities.

(a) Polarity

A **polar molecule** is one with a permanent electric dipole moment (HCl, O_3, and NH_3 are examples). If the molecule belongs to the group C_n with $n > 1$, it cannot possess a charge distribution with a dipole moment perpendicular to the symmetry axis because the symmetry of the molecule implies that any dipole that exists in one direction perpendicular to the axis is cancelled by an opposing dipole (Fig. 15.16a). For example, the perpendicular component of the dipole associated with one OH bond in H_2O is cancelled by an equal but opposite component of the dipole of the second OH bond, so any dipole that the molecule has must be parallel to the twofold symmetry axis. However, as the group makes no reference to operations relating the two ends of the molecule, a charge distribution may exist that results in a dipole along the axis (Fig. 15.16b), and H_2O has a dipole moment parallel to its twofold symmetry axis. The same remarks apply to the group C_{nv}, so molecules belonging to any of the C_{nv} groups may be polar. In all the other groups, such as C_{3h}, D, etc., there are symmetry operations that take one end of the molecule into the other. Therefore, as well as having no dipole perpendicular to the axis, such molecules can have none along the axis, for otherwise these additional operations would not be symmetry operations.

We can conclude that only molecules belonging to the groups C_n, C_{nv}, and C_s may have a permanent electric dipole moment. For C_n and C_{nv}, that dipole moment must lie along the symmetry axis. Thus ozone, O_3, which is angular and belongs to the group C_{2v}, may be polar (and is), but carbon dioxide, CO_2, which is linear and belongs to the group $D_{\infty h}$, is not.



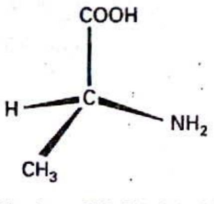
15.17 Some symmetry elements are implied by the other symmetry elements in a group. Any molecule containing an inversion also possesses at least an S_2 element because i and S_2 are equivalent.

(b) Chirality

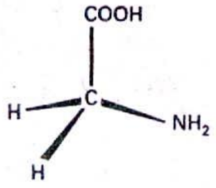
A **chiral molecule** (from the Greek word for 'hand') is a molecule that cannot be superimposed on its mirror image. Chiral molecules are optically active in the sense that they rotate the plane of polarized light (a property discussed in more detail in Section 22.2). A chiral molecule and its mirror-image partner constitute an **enantiomeric pair** of isomers and rotate the plane of polarization in equal but opposite directions.

It follows from the theory of optical activity that a molecule may be chiral only if it does not possess an axis of improper rotation, S_n. However, we need to be aware that such an axis may be present under a different name, and be implied by other symmetry elements that are present. For example, molecules belonging to the groups C_{nh} possess an S_n axis implicitly because they possess both C_n and σ_h, which are the two components of an improper rotation axis. Any molecule containing a centre of inversion, i, also possesses an S_2 axis, because i is equivalent to C_2 in conjunction with σ_h, and that combination of elements is S_2 (Fig. 15.17). It follows that all molecules with centres of inversion are achiral (that is, not chiral) and hence optically inactive. Similarly, because $S_1 = \sigma$, it follows that any molecule with a mirror plane is achiral.

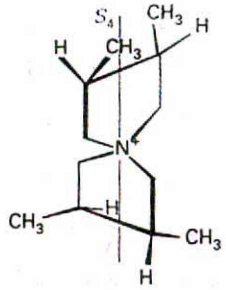
A molecule may be chiral if it does not have a centre of inversion or a mirror plane, which is the case with the amino acid alanine (**18**), but not with glycine (**19**). However, a molecule may be achiral even though it does not have a centre of inversion. For example, the S_4 species (**20**) is achiral and optically inactive: though it lacks i, it does have an S_4 axis.



18 L-Alanine, $NH_2CH(CH_3)COOH$



19 Glycine, NH_2CH_2COOH



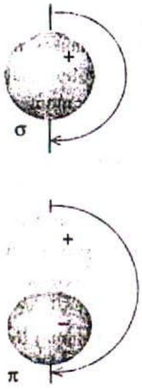
20 $N(CH_2CH(CH_3)CH(CH_3)CH_2)_2^+$

Character tables

We shall now turn our attention away from the symmetries of molecules themselves and direct it towards the symmetry characteristics of orbitals that belong to the various atoms in a molecule. This material will enable us to discuss the formulation and labelling of molecular orbitals and selection rules in spectroscopy.

15.4 Character tables and symmetry labels

We saw in Chapter 14 that molecular orbitals of diatomic and linear polyatomic molecules are labelled σ, π, etc. These labels refer to the symmetries of the orbitals with respect to rotations around the principal symmetry axis of the molecule. Thus, a σ orbital does not change sign under a rotation through any angle, a π orbital changes sign when rotated by 180°, and so on (Fig. 15.18). The symmetry classifications σ and π can also be assigned to individual atomic orbitals in a linear molecule. For example, we can speak of an individual p_z orbital as having σ symmetry if the z-axis lies along the bond, because p_z is cylindrically symmetrical about the bond. This labelling of orbitals according to their behaviour under rotations can be generalized and extended to nonlinear polyatomic molecules, where there may be reflections and inversions to take into account as well as rotations.



15.18 A rotation through 180° about the internuclear axis leaves the sign of a σ orbital unchanged but the sign of a π orbital is changed. In the language introduced in this chapter, the characters of the C_2 rotation are +1 and −1 for the σ and π orbitals, respectively.

Labels analogous to σ and π are also used to denote the symmetries of orbitals in polyatomic molecules. These labels look like a, a_1, e, e_g, and we first encountered them in Section 14.8a in connection with H_2O and in Fig. 14.44 in connection with the molecular orbitals of benzene. As we shall see, these labels indicate the behaviour of the orbitals under the symmetry operations of the relevant point group of the molecule.

(a) The structure of character tables

A label is assigned to an orbital by referring to the **character table** of the group, a table that characterizes the different symmetry types possible in the point group. Thus, to assign the labels σ and π, we use the table shown in the margin. This table is a fragment of the full character table for a linear molecule. The entry +1 shows that the orbital remains the same and the entry −1 shows that the orbital changes sign under the operation C_2 at the head of the column (as illustrated in Fig. 15.18). So, to assign the label σ or π to a particular orbital, we compare the orbital's behaviour with the information in the character table.

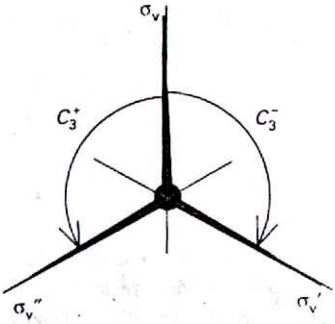
	C_2	(i.e. rotation by 180°)
σ	+1	(i.e. no change of sign)
π	−1	(i.e. change of sign)

The entries in a complete character table are derived using the formal techniques of group theory, and are called **characters**, χ. These numbers characterize the essential features of each symmetry type in a way that we can illustrate by using the C_{3v} character table (Table 15.2). Character tables for other groups are given at the end of the *Data section* and are used in exactly the same way.

Table 15.2* The C_{3v} character table

C_{3v}, $3m$	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	$z^2, x^2 + y^2$
A_2	1	1	−1		
E	2	−1	0	(x, y)	$(xy, x^2 - y^2), (xz, yz)$

*More character tables are given at the end of the *Data section* at the end of this volume.



15.19 Symmetry operations in the same class are related to one another by the symmetry operations of the group. Thus, the three mirror planes shown here are related by threefold rotations, and the two rotations shown here are related by reflection in σ_v.

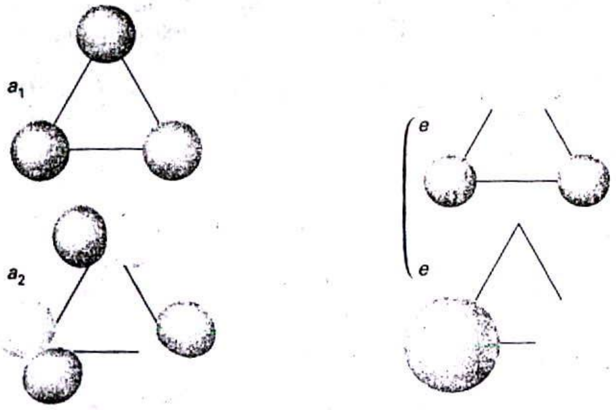
The columns in a character table are labelled with the symmetry operations of the group, which in C_{3v} are E, C_3, and σ_v. The numbers multiplying each operation are the numbers of members of each class. Symmetry operations fall into the same class if they are of the same type (for example, rotations) *and* can be transformed into one another by a symmetry operation of the group. From the C_{3v} character table we see that the two threefold rotations (clockwise and counter-clockwise rotations by 120°) belong to the same class: they are related by a reflection (Fig. 15.19). The three reflections (one through each of the three vertical mirror planes) also lie in the same class: they are related by the threefold rotations. The two reflections of the group C_{2v} fall into *different* classes: although they are both reflections, one cannot be transformed into the other by any symmetry operation of the group.

The total number of operations in a group is called the **order**, h, of the group. The order of C_{3v}, for instance, is 6.

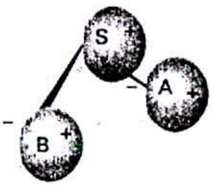
The rows under the labels for the operations summarize the symmetry properties of the orbitals. They are labelled with the **symmetry species** (the analogues of the labels σ and π). More formally, the symmetry species label the **irreducible representations** of the group, which (as explained in the *Justification* below) are the basic types of behaviour that orbitals may show when subjected to the symmetry operations of the group. They are the analogues of the -1 and $+1$ given earlier, and which showed, respectively, whether an orbital changed sign or did not change sign when the molecule was subjected to a rotation of 180° about its internuclear axis. By convention, irreducible representations are labelled with upper-case Roman letters (such as A_1 and E) but the orbitals to which they apply are labelled with the lower-case italic equivalents (so an orbital of symmetry species A_1 is called an a_1 orbital).[5] Examples of each type of orbital are shown in Fig. 15.20.

Justification 15.1

Character tables are derived from the representation of the effects of symmetry operations by matrices. As an illustration, consider the C_{2v} molecule SO_2 and the valence p_x orbitals on each atom, which we shall denote p_S, p_A, and p_B (Fig. 15.21). Under σ_v, the change



15.20 Typical symmetry-adapted linear combinations of orbitals in a C_{3v} molecule.



15.21 The three p_x orbitals that are used to illustrate the construction of a matrix representation in a C_{2v} molecule (SO_2).

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[5] Note that care must be taken to distinguish the identity element E (italic, a column heading) from the symmetry label E (Roman, a row label).

$(p_S, p_B, p_A) \leftarrow (p_S, p_A, p_B)$ takes place. We can express this transformation by using matrix multiplication:

$$(p_S, p_B, p_A) = (p_S, p_A, p_B)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{1a}$$

This relation can be expressed more succinctly as

$$(p_S, p_B, p_A) = (p_S, p_A, p_B)\mathbf{D}(\sigma_v) \tag{1b}$$

The matrix $\mathbf{D}(\sigma_v)$ is called a **representative** of the operation σ_v. Representatives take different forms according to the **basis**, the set of orbitals, that has been adopted.

We can use the same technique to find matrices that reproduce the other symmetry operations. For instance, C_2 has the effect $(-p_S, -p_B, -p_A) \leftarrow (p_S, p_A, p_B)$, and its representative is

$$\mathbf{D}(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \tag{2}$$

The effect of σ'_v is $(-p_S, -p_A, -p_B) \leftarrow (p_S, p_A, p_B)$, and its representative is

$$\mathbf{D}(\sigma'_v) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{3}$$

The identity operation has no effect on the basis, so its representative is the unit matrix:

$$\mathbf{D}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4}$$

The set of matrices that represents all the operations of the group is called a **matrix representation**, Γ, of the group for the particular basis we have chosen. We denote this three-dimensional representation by the symbol $\Gamma^{(3)}$. The discovery of a matrix representation of the group means that we have found a link between the symbolic manipulations of the operations and algebraic manipulations involving numbers.

The character of an operation in a particular matrix representation is the sum of the diagonal elements of the representative of that operation. Thus, in the basis we are illustrating, the characters of the representatives are

$\mathbf{D}(E)$	$\mathbf{D}(C_2)$	$\mathbf{D}(\sigma_v)$	$\mathbf{D}(\sigma'_v)$
3	−1	1	−3

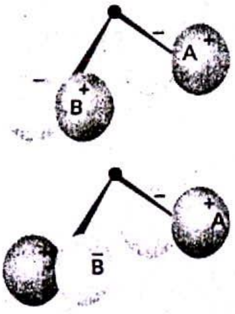
The character of an operation depends on the basis.

Inspection of the representatives shows that they are all of **block-diagonal form:**

$$\mathbf{D} = \begin{pmatrix} \blacksquare & 0 & 0 \\ 0 & \blacksquare & \blacksquare \\ 0 & \blacksquare & \blacksquare \end{pmatrix}$$

The symmetry operations of C_{2v} never mix p_S with the other two functions. Consequently, the basis can be cut into two parts, one consisting of p_S alone and the other of (p_A, p_B). It is readily verified that the p_S orbital itself is a basis for the one-dimensional representation

$$\mathbf{D}(E) = 1 \qquad \mathbf{D}(C_2) = -1 \qquad \mathbf{D}(\sigma_v) = 1 \qquad \mathbf{D}(\sigma'_v) = -1$$



15.22 Two symmetry-adapted linear combinations of the basis orbitals shown in Fig. 15.21. The two combinations each span a one-dimensional irreducible representation, and their symmetry species are different.

which we shall call $\Gamma^{(1)}$. The remaining two basis functions are a basis for the two-dimensional representation $\Gamma^{(2)}$:

$$\mathbf{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \mathbf{D}(C_2) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

$$\mathbf{D}(\sigma_v) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \mathbf{D}(\sigma_v') = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

These matrices are the same as those of the original three-dimensional representation, except for the loss of the first row and column. We say that the original three-dimensional representation has been **reduced** to the **direct sum** of a one-dimensional representation spanned by p_S, and a two-dimensional representation spanned by (p_A, p_B). This reduction is consistent with the common sense view that the central orbital plays a role different from the other two. The reduction is denoted symbolically by writing

$$\Gamma^{(3)} = \Gamma^{(1)} + \Gamma^{(2)} \qquad (5)$$

The one-dimensional representation cannot be reduced any further, and is called an **irreducible representation** of the group (an 'irrep'). We can demonstrate that the two-dimensional representation is reducible (for this basis in this group) by switching attention to the linear combinations $p_1 = p_A + p_B$ and $p_2 = p_A - p_B$. These combinations are sketched in Fig. 15.22. The representatives in the new basis can be constructed from the old by noting, for example, that under σ_v, $(p_B, p_A) \leftarrow (p_A, p_B)$. In this way we find the following representation in the new basis:

$$\mathbf{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \mathbf{D}(C_2) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\mathbf{D}(\sigma_v) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \mathbf{D}(\sigma_v') = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

The new representatives are all in block-diagonal form, and the two combinations are not mixed with each other by any operation of the group. We have therefore achieved the reduction of $\Gamma^{(2)}$ to the sum of two one-dimensional representations. Thus, p_1 spans

$$\mathbf{D}(E) = 1 \qquad \mathbf{D}(C_2) = -1 \qquad \mathbf{D}(\sigma_v) = 1 \qquad \mathbf{D}(\sigma_v') = -1$$

which is the same one-dimensional representation as that spanned by p_S, and p_2 spans

$$\mathbf{D}(E) = 1 \qquad \mathbf{D}(C_2) = 1 \qquad \mathbf{D}(\sigma_v) = -1 \qquad \mathbf{D}(\sigma_v') = -1$$

which is a different one-dimensional representation; we shall denote it $\Gamma^{(1)\prime}$.

Now we can make the final link to the material in the text. *The character table of a group is the list of the characters of all its irreducible representations.* At this point we have found two irreducible representations of the group C_{2v} (Table 15.3). The two

Table 15.3* The C_{2v} character table

C_{2v}, $2mm$	E	C_2	σ_v	σ_v'	$h = 4$	
A_1	1	1	1	1	z	z^2, y^2, x^2
A_2	1	1	−1	−1		xy
B_1	1	−1	1	−1	x	xz
B_2	1	−1	−1	1	y	yx

* More character tables are given at the end of the *Data section*.

irreducible representations are normally labelled B_1 and A_2, respectively. An A or a B is used to denote a one-dimensional representation; A is used if the character under the principal rotation is $+1$, and B is used if the character is -1. Subscripts are used to distinguish the irreducible representations if there is more than one of the same type: A_1 is reserved for the representation with character 1 for all operations. When higher dimensional irreducible representations are permitted, E denotes a two-dimensional irreducible representation and T a three-dimensional irreducible representation; all the irreducible representations of C_{2v} are one-dimensional.

There are in fact only two more species of irreducible representations of this group, for a surprising theorem of group theory states that

$$\text{Number of symmetry species} = \text{number of classes} \qquad (6)$$

In C_{2v} (Table 15.3), for instance, there are four classes (four columns in the character table), so there are only four species of irreducible representation. The character table in Table 15.3 therefore shows the characters of *all* the irreducible representations of this group.

(b) Character tables and orbital degeneracy

The characters of the identity operation, E, reveal the degeneracy of the orbitals. Thus, in a C_{3v} molecule, any orbital with a symmetry label a_1 or a_2 is non-degenerate. Any doubly degenerate pair of orbitals in C_{3v} must be labelled e because only E symmetry species have characters greater than 1.

Because there are no characters greater than 2 in the column headed E in C_{3v}, we know that there can be no triply degenerate orbitals in a C_{3v} molecule. This last point is a powerful result of group theory, for it means that, with a glance at the character table of a molecule, we can state the maximum possible degeneracy of its orbitals.

Example 15.2 Using a character table to judge degeneracy

Can a trigonal planar molecule such as BF_3 have triply degenerate orbitals? What is the minimum number of atoms from which a molecule can be built that does display triple degeneracy?

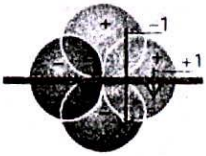
Method First, identify the point group, and then refer to the corresponding character table in the *Data section*. The maximum number in the column headed by the identity E is the maximum orbital degeneracy possible in a molecule of that point group. For the second part, consider the shapes that can be built from two, three, etc. atoms, and decide which number can be used to form a molecule that can have orbitals of symmetry species T.

Answer Trigonal planar molecules belong to the point group D_{3h}. Reference to the character table for this group shows that the maximum degeneracy is 2, as no character exceeds 2 in the column headed E. Therefore, the orbitals cannot be triply degenerate. A tetrahedral molecule (symmetry group T) has an irreducible representation with a T symmetry species. The minimum number of atoms needed to build such a molecule is four (as in P_4, for instance).

Self-test 15.2 A buckminsterfullerene molecule, C_{60}, belongs to the icosahedral point group. What is the maximum possible degree of degeneracy of its orbitals?

[5]

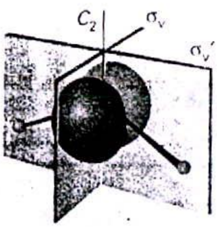
(c) Characters and operations



15.23 The two orbitals shown here have different properties under reflection through the mirror plane: one changes sign (character −1), the other does not (character +1).

The characters in the rows labelled A and B and in the columns headed by symmetry operations other than the identity E indicate the behaviour of an orbital under the corresponding operations: a +1 indicates that an orbital is unchanged, and a −1 indicates that it changes sign. It follows that we can identify the symmetry label of the orbital by comparing the changes that occur to an orbital under each operation, and then comparing the resulting +1 or −1 with the entries in a row of the character table for the point group concerned.

For the rows labelled E or T (which refer to the behaviour of sets of doubly and triply degenerate orbitals, respectively), the characters in a row of the table are the *sums* of the characters summarizing the behaviour of the individual orbitals in the basis. Thus, if one member of a doubly degenerate pair remains unchanged under a symmetry operation but the other changes sign (Fig. 15.23), then the entry is reported as $\chi = 1 - 1 = 0$. Care must be exercised with these characters because the transformations of orbitals can be quite complicated; nevertheless, the sums of the individual characters are commonly integers.



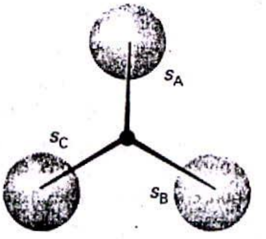
15.24 A p_x orbital on the central atom of a C_{2v} molecule and the symmetry elements of the group.

As an example, consider the O2p_x orbital in H_2O. Because H_2O belongs to the point group C_{2v}, we know by referring to the C_{2v} character table (Table 15.3) that the labels available for the orbitals are A_1, A_2, B_1, and B_2. We can decide the appropriate label for O2p_x by noting that under a 180° rotation (C_2) the orbital changes sign (Fig. 15.24), so it must be either B_1 or B_2, as only these two symmetry types have character −1 under C_2. The O2p_x orbital also changes sign under the reflection σ_v', which identifies it as B_1. As we shall see, any molecular orbital built from this atomic orbital will also be a b_1 orbital. Similarly, O2p_y changes sign under C_2 but not under σ_v'; therefore, it can contribute to b_2 orbitals.

The behaviour of s, p, and d orbitals on a central atom under the symmetry operations of the molecule is so important that the symmetry species of these orbitals are generally indicated in a character table. To make these allocations, we look at the symmetry species of x, y, and z, which appear on the right-hand side of the character table. Thus, the position of z in Table 15.2 shows that p_z (which is proportional to $zf(r)$), has symmetry species A_1 in C_{3v}, whereas p_x and p_y (which are proportional to $xf(r)$ and $yf(r)$, respectively) are jointly of E symmetry. In technical terms, we say that p_x and p_y jointly span an irreducible representation of symmetry species E. An s orbital on the central atom always spans the fully symmetrical irreducible representation (typically labelled A_1) of a group as it is unchanged under all symmetry operations.

The five d orbitals of a shell are represented by xy for d_{xy}, etc., and are also listed on the right of the character table. We can see at a glance that in C_{3v}, d_{xy} and $d_{x^2-y^2}$ on a central atom jointly belong to E and hence form a doubly degenerate pair.

(d) The classification of linear combinations of orbitals

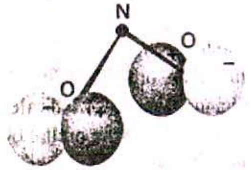


15.25 The three H1s orbitals used to construct symmetry-adapted linear combinations in a C_{3v} molecule such as NH_3.

So far, we have dealt with the symmetry classification of individual orbitals. The same technique may be applied to linear combinations of orbitals on atoms that are related by symmetry transformations of the molecule, such as the combination $\psi_1 = \psi_A + \psi_B + \psi_C$ of the three H1s orbitals in the C_{3v} molecule NH_3 (Fig. 15.25). This combination remains unchanged under a C_3 rotation and under any of the three vertical reflections of the group, so its characters are

$$\chi(E) = 1 \qquad \chi(C_3) = 1 \qquad \chi(\sigma_v) = 1$$

Comparison with the C_{3v} character table shows that ψ_1 is of symmetry species A_1, and therefore that it contributes to a_1 molecular orbitals in NH_3.



15.26 One symmetry-adapted linear combination of $O2p_x$ orbitals in the C_{2v} NO_2 molecule.

Example 15.3 Identifying the symmetry species of orbitals

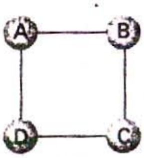
Identify the symmetry species of the orbital $\psi = \psi_A - \psi_B$ in a C_{2v} NO_2 molecule, where ψ_A is an $O2p_x$ orbital on one O atom and ψ_B that on the other O atom.

Method The negative sign in ψ indicates that the sign of ψ_B is opposite to that of ψ_A. We need to consider how the combination changes under each operation of the group, and then write the character as $+1$, -1, or 0 as specified above. Then we compare the resulting characters with each row in the character table for the point group, and hence identify the symmetry species.

Answer The combination is shown in Fig. 15.26. Under C_2, ψ changes into itself, implying a character of $+1$. Under the reflection σ_v, both orbitals change sign, so $\psi \rightarrow -\psi$, implying a character of -1. Under σ'_v, $\psi \rightarrow -\psi$, so the character for this operation is also -1. The characters are therefore

$$\chi(E) = 1 \qquad \chi(C_2) = 1 \qquad \chi(\sigma_v) = -1 \qquad \chi(\sigma'_v) = -1$$

These values match the characters of the A_2 symmetry species, so ψ can contribute to an a_2 orbital.



21

Self-test 15.3 Identify the symmetry type of the combination $\psi_A - \psi_B + \psi_C - \psi_D$ in a square planar array of H atoms of point group D_{4h} (21).

$[B_{2g}]$

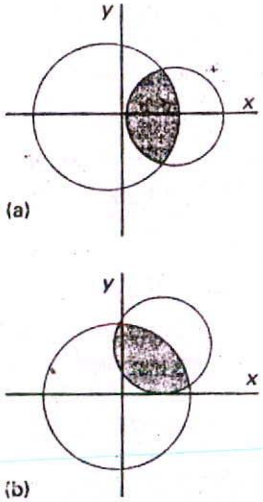
15.5 Vanishing integrals and orbital overlap

Suppose we had to evaluate the integral

$$I = \int f_1 f_2 \, d\tau \tag{7}$$

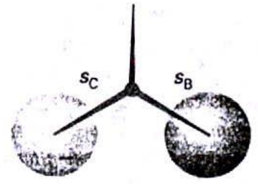
where f_1 and f_2 are functions. For example, f_1 might be an atomic orbital A on one atom and f_2 an atomic orbital B on another atom, in which case I would be their overlap integral. If we knew that the integral was zero, we could say at once that a molecular orbital does not result from (A, B) overlap in that molecule. We shall now see that character tables provide a quick way of judging whether an integral is necessarily zero.

(a) The criteria for vanishing integrals



15.27 The value of an integral I (for example, an area) is independent of the coordinate system used to evaluate it. That is, I is a basis of a representation of symmetry species A_1 (or its equivalent).

The key point in dealing with the integral I is that the value of any integral, and of an overlap integral in particular, is independent of the orientation of the molecule (Fig. 15.27). In group theoretical language we express this by saying that I is invariant under any symmetry operation of the molecule, and that each operation brings about the trivial transformation $I \rightarrow I$. Because the volume element $d\tau$ is invariant under any symmetry operation, it follows that the integral is nonzero only if the integrand itself, the product $f_1 f_2$, is unchanged by any symmetry operation of the molecular point group. If the integrand changed sign under a symmetry operation, the integral would be the sum of equal and opposite contributions, and hence would be zero. It follows that the only contribution to a nonzero integral comes from functions for which, under any symmetry operation of the molecular point group, $f_1 f_2 \rightarrow f_1 f_2$ and hence for which the characters of the operations are all equal to $+1$. Therefore, for I not to be zero, the integrand $f_1 f_2$ must have symmetry species A_1 (or its equivalent in the specific molecular point group).



15.28 A symmetry-adapted linear combination that belongs to the symmetry species E in a C_{3v} molecule such as NH_3. This combination can form a molecular orbital by overlapping with the p_x orbital on the central atom (the orbital with its axis parallel to the width of the page; see Fig. 15.31c).

We use the following procedure to deduce the symmetry species spanned by the product $f_1 f_2$ and hence to see whether it does indeed span A_1.

1. Decide on the symmetry species of the individual functions f_1 and f_2 by reference to the character table, and write their characters in two rows in the same order as in the table.
2. Multiply the numbers in each column, writing the results in the same order.
3. Inspect the row so produced, and see if it can be expressed as a sum of characters from each column of the group. The integral must be zero if this sum does not contain A_1.

For example, if f_1 is the s_N orbital in NH_3 and f_2 is the linear combination $s_3 = s_B - s_C$ (Fig. 15.28) then, because s_N spans A_1 and s_3 is a member of the basis spanning E, we write

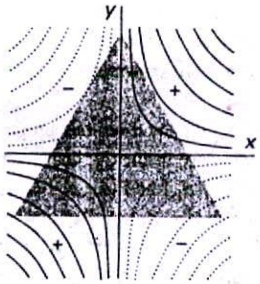
$$\begin{array}{lrrr} f_1: & 1 & 1 & 1 \\ f_2: & 2 & -1 & 0 \\ f_1 f_2: & 2 & -1 & 0 \end{array}$$

The characters 2, −1, 0 are those of E alone, so the integrand does not span A_1. It follows that the integral must be zero. Inspection of the form of the functions (see Fig. 15.28) shows why this is so: s_3 has a node running through s_N. Had we taken $f_1 = s_N$ and $f_2 = s_1$ instead, where $s_1 = s_A + s_B + s_C$, then because each spans A_1 with characters 1, 1, 1:

$$\begin{array}{lrrr} f_1: & 1 & 1 & 1 \\ f_2: & 1 & 1 & 1 \\ f_1 f_2: & 1 & 1 & 1 \end{array}$$

The characters of the product are those of A_1 itself. Therefore, s_1 and s_N may have nonzero overlap. A short cut that works when f_1 and f_2 are bases for irreducible representations of a group is to note their symmetry species: if they are different, the integral of their product must vanish; if they are the same, the integral may be nonzero.

It is important to note that group theory is specific about when an integral *must* be zero, but integrals that it allows to be nonzero *may* be zero for reasons unrelated to symmetry. For example, the N–H distance in ammonia may be so great that the (s_1, s_N) overlap integral is zero simply because the orbitals are so far apart.



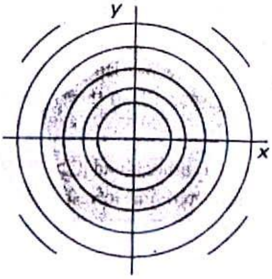
15.29 The integral of the function $f = xy$ over the tinted region is zero. In this case, the result is obvious by inspection, but group theory can be used to establish similar results in less obvious cases.

Example 15.4 Deciding if an integral must be zero (1)

May the integral of the function $f = xy$ be nonzero when evaluated over a region the shape of an equilateral triangle centred on the origin (Fig. 15.29)?

Method First, note that an integral over a single function f is included in the previous discussion if we take $f_1 = f$ and $f_2 = 1$ in eqn 7. Therefore, we need to judge whether f alone belongs to the symmetry species A_1 (or its equivalent) in the point group of the system. To decide that, we identify the point group and then examine the character table to see whether f belongs to A_1 (or its equivalent).

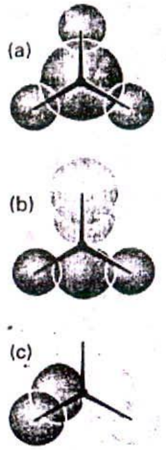
Answer An equilateral triangle has the point-group symmetry D_{3h}. If we refer to the character table of the group, we see that xy is a member of a basis that spans the irreducible representation E′. Therefore, its integral must be zero, because the integrand has no component that spans A_1'.



15.30 The integration of a function over a pentagonal region.

Self-test 15.4 Can the function $x^2 + y^2$ have a nonzero integral when integrated over a regular pentagon centred on the origin?

[Yes, Fig. 15.30]



15.31 Orbitals of the same symmetry species may have non-vanishing overlap. This diagram illustrates the three bonding orbitals that may be constructed from (N2*s*, H1*s*) and (N2*p*, H1*s*) overlap in a C_{3v} molecule. (a) a_1; (b) and (c) the two components of the doubly degenerate *e* orbitals. (There are also three antibonding orbitals of the same species.)

(b) Orbitals with nonzero overlap

The rules just given let us decide which atomic orbitals may have nonzero overlap in a molecule. We have seen that s_N may have nonzero overlap with s_1 (the combination $1s_A + 1s_B + 1s_C$), so bonding and antibonding molecular orbitals can form from (s_N, s_1) overlap (Fig. 15.31). The general rule is that *only orbitals of the same symmetry species may have nonzero overlap*, so *only orbitals of the same symmetry species form bonding and antibonding combinations*. It should be recalled from Chapter 14 that the selection of atomic orbitals that have mutual nonzero overlap is the central and initial step in the construction of molecular orbitals by the LCAO procedure. We are therefore at the point of contact between group theory and the material introduced in that chapter. The molecular orbitals formed from a particular set of atomic orbitals with nonzero overlap are labelled with the lower-case letter corresponding to the symmetry species. Thus, the (s_N, s_1)-overlap orbitals are called a_1 orbitals (or a_1^*, if we wish to emphasize that they are antibonding).

The s_2 and s_3 linear combinations have symmetry species E. Does the N atom have orbitals that have nonzero overlap with them (and give rise to *e* molecular orbitals)? Intuition (as supported by Figs. 15.31b and c) suggests that N2p_x and N2p_y should be suitable. We can confirm this conclusion by noting that the character table shows that in C_{3v}, the functions *x* and *y* jointly belong to the symmetry species E. Therefore, N2p_x and N2p_y also belong to E, so may have nonzero overlap with s_2 and s_3. This conclusion can be verified by multiplying the characters and finding that the product of characters can be expressed as $E \times E = A_1 + A_2 + E$. The two *e* orbitals that result are shown in Fig. 15.31 (there are also two antibonding *e* orbitals).

The power of the method can be illustrated by exploring whether any *d* orbitals on the central atom can take part in bonding. As explained earlier, reference to the C_{3v} character table shows that d_{z^2} has A_1 symmetry and that the pairs $(d_{x^2-y^2}, d_{xy})$ and (d_{yz}, d_{zx}) each transform as E. It follows that molecular orbitals may be formed by (s_1, d_{z^2}) overlap and by overlap of the s_2, s_3 combinations with the E *d* orbitals. Whether or not the *d* orbitals are in fact important is a question group theory cannot answer because the extent of their involvement depends on energy considerations, not symmetry.

Example 15.5 Determining which orbitals can contribute to bonding

The four H1*s* orbitals of methane span $A_1 + T_2$. With which of the C atom orbitals can they overlap? What bonding pattern would be possible if the C atom had *d* orbitals available?

Method Refer to the T_d character table (in the *Data section*) and look for *s*, *p*, and *d* orbitals spanning A_1 or T_2.

Answer An *s* orbital spans A_1, so it may have nonzero overlap with the A_1 combination of H1*s* orbitals. The C2*p* orbitals span T_2, so they may have nonzero overlap with the T_2 combination. The d_{xy}, d_{yz}, and d_{zx} orbitals span T_2, so they may overlap the same combination. Neither of the other two *d* orbitals span A_1 (they span E), so they remain nonbonding orbitals.

Comment It follows that in methane there are (C2*s*,H1*s*)-overlap a_1 orbitals and (C2*p*,H1*s*)-overlap t_2 orbitals. The C3*d* orbitals might contribute to the latter. The lowest energy configuration is probably $a_1^2t_2^6$, with all bonding orbitals occupied.

Self-test 15.5 Consider the octahedral SF_6 molecule, with the bonding arising from overlap of S orbitals and a 2*p* orbital on each F directed towards the central S atom. The latter span $A_{1g} + E_g + T_{1u}$. What S orbitals have nonzero overlap? Suggest what the ground-state configuration is likely to be.

$[3s(A_{1g}), 3p(T_{1u}), 3d(E_g); a_{1g}^2 t_{1u}^6 e_g^4]$

(c) Symmetry-adapted linear combinations

So far, we have only asserted the forms of the linear combinations (such as s_1, etc.) that have a particular symmetry. Group theory also provides machinery that takes an arbitrary basis, or set of atomic orbitals (s_A, etc.), as input and generates combinations of the specified symmetry. Because these combinations are adapted to the symmetry of the molecule, they are called **symmetry-adapted linear combinations** (SALCs). Symmetry-adapted linear combinations are the building blocks of LCAO molecular orbitals, for they include combinations such as $\psi_{1s_A} \pm \psi_{1s_B}$ used to construct molecular orbitals in H_2O (Section 14.8a) and some of the more complex examples that we have seen since then. The construction of SALCs is the first step in any molecular orbital treatment of molecules.

The technique for building SALCs is derived by using the full power of group theory. We shall not show the derivation, which is very lengthy, but present the main conclusions as a set of rules:

1. Construct a table showing the effect of each operation on each orbital of the original basis.
2. To generate the combination of a specified symmetry species, take each column in turn and:
   - (i) Multiply each member of the column by the character of the corresponding operation.
   - (ii) Add together all the orbitals in each column with the factors as determined in (i).
   - (iii) Divide the sum by the order of the group.

	Original basis			
	s_N	s_A	s_B	s_C
Under E	s_N	s_A	s_B	s_C
C_3^+	s_N	s_B	s_C	s_A
C_3^-	s_N	s_C	s_A	s_B
σ_v	s_N	s_A	s_C	s_B
σ_v'	s_N	s_B	s_A	s_C
σ_v''	s_N	s_C	s_B	s_A

For example, from the (s_N, s_A, s_B, s_C) basis in NH_3 we form the table shown in the margin. To generate the A_1 combination, we take the characters for A_1 $(1, 1, 1, 1, 1, 1)$; then rules (i) and (ii) lead to

$$\psi \propto s_N + s_N + \cdots = 6s_N$$

The order of the group (the number of elements) is 6, so the combination of A_1 symmetry that can be generated from s_N is s_N itself. Applying the same technique to the column under s_A gives

$$\psi = \tfrac{1}{6}(s_A + s_B + s_C + s_A + s_B + s_C) = \tfrac{1}{3}(s_A + s_B + s_C)$$

The same combination is built from the other two columns, so they give no further information. The combination we have just formed is the s_1 combination we used before (apart from the numerical factor).

We now form the overall molecular orbital by forming a linear combination of all the SALCs of the specified symmetry species. In this case, therefore, the a_1 molecular orbital is

$$\psi = c_N s_N + c_1 s_1$$

This is as far as group theory can take us. The coefficients must be found by solving the Schrödinger equation; they do not come directly from the symmetry of the system.

We run into a problem when we try to generate an SALC of symmetry species E, because, for representations of dimension 2 or more, the rules generate sums of SALCs. This problem can be illustrated as follows. In C_{3v}, the E characters are $2, -1, -1, 0, 0, 0$, so the column under s_N gives

$$\psi = \tfrac{1}{6}(2s_N - s_N - s_N + 0 + 0 + 0) = 0$$

The other columns give

$$\tfrac{1}{6}(2s_A - s_B - s_C) \qquad \tfrac{1}{6}(2s_B - s_A - s_C) \qquad \tfrac{1}{6}(2s_C - s_B - s_A)$$

However, any one of these three expressions can be written as a sum of the other two (they are not 'linearly independent'). The difference of the second and third gives $\tfrac{1}{2}(s_B - s_C)$, and this combination and the first, $\tfrac{1}{6}(2s_A - s_B - s_C)$, are the two (now linearly independent) SALCs we have used in the discussion of e orbitals.

15.6 Vanishing integrals and selection rules

Integrals of the form

$$I = \int f_1 f_2 f_3 \, d\tau \tag{8}$$

are also common in quantum mechanics for they include matrix elements of operators (Section 11.5d), and it is important to know when they are necessarily zero. For the integral to be nonzero, the product $f_1 f_2 f_3$ must span A_1 (or its equivalent). To test whether this is so, the characters of all three functions are multiplied together in the same way as in the rules set out above.

Example 15.6 Deciding if an integral must be zero (2)

Does the integral $\int (3d_{z^2})x(3d_{xy})\, d\tau$ vanish in a C_{2v} molecule?

Method We must refer to the C_{2v} character table (Table 15.3) and the characters of the irreducible representations spanned by $3z^2 - r^2$ (the form of the d_{z^2} orbital), x, and xy; then we can use the procedure set out above (with one more row of multiplication). Note that $3z^2 - r^2 = 2z^2 - x^2 - y^2$.

Answer We draw up the following table:

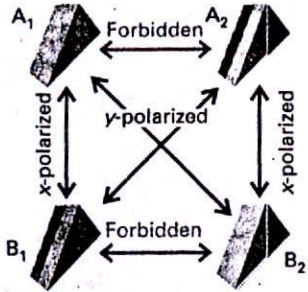
	E	C_2	σ_v	σ_v'	
$f_3 = d_{xy}$	1	1	−1	−1	A_2
$f_2 = x$	1	−1	1	−1	B_1
$f_1 = d_{z^2}$	1	1	1	1	A_1
$f_1 f_2 f_3$	1	−1	−1	1	

The characters are those of B_2. Therefore, the integral is necessarily zero.

Self-test 15.6 Does the integral $\int (2p_x)(2p_y)(2p_z)\, d\tau$ necessarily vanish in an octahedral environment?

[No]

In Chapters 16 and 17 we shall see that the intensity of a spectral line arising from a molecular transition between some initial state $|i\rangle$ with wavefunction ψ_i and a final state $|f\rangle$



15.32 The polarizations of the allowed transitions in a C_{2v} molecule. The shading indicates the structure of the orbitals of the specified symmetry species. The perspective view of the molecule makes it look rather like a door-stop; however, from the side, each 'door-stop' is in fact an isosceles triangle.

with wavefunction ψ_f depends on the (electric) transition dipole moment $\boldsymbol{\mu}_{fi}$. The z-component of this vector is defined through

$$\mu_{z,fi} = \langle f|\mu_z|i\rangle = -e\int \psi_f^* z \psi_i \, d\tau \qquad [9]$$

where $-e$ is the charge of the electron. Stating the conditions for this quantity (and the x- and y-components) to be zero amounts to specifying the **selection rules** for the transition, the rules that specify which transitions are allowed. The transition moment has the form of the integral in eqn 8, so, once we know the symmetry species of the states, we can use group theory to decide which transitions have zero transition dipole moment and therefore are forbidden.

As an example, we investigate whether an electron in an a_1 orbital in H_2O (which belongs to the group C_{2v}) can make an electric dipole transition to a b_1 orbital (Fig. 15.32). We must examine all three components of the transition dipole moment, and take f_2 in eqn 8 as x, y, and z in turn. Reference to the C_{2v} character table shows that these components transform as B_1, B_2, and A_1, respectively. The three calculations run as follows:

	x-component				*y*-component				*z*-component				
	E	C_2	σ_v	σ_v'	E	C_2	σ_v	σ_v'	E	C_2	σ_v	σ_v'	
f_3	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	B_1
f_2	1	−1	1	−1	1	−1	−1	1	1	1	1	1	
f_1	1	1	1	1	1	1	1	1	1	1	1	1	A_1
$f_1f_2f_3$	1	1	1	1	1	1	−1	−1	1	−1	1	−1	

Only the first product (with $f_2 = x$) spans A_1, so only the x-component of the transition dipole moment may be nonzero. Therefore, we conclude that the electric dipole transitions between a_1 and b_1 are allowed. We can go on to state that the radiation emitted (or absorbed) is x-polarized and has its electric field vector in the x-direction, because that form of radiation couples with the x-component of a transition dipole.

Example 15.7 Deducing a selection rule

Is $p_x \rightarrow p_y$ an allowed transition in a tetrahedral environment?

Method We must decide whether the product $p_y q p_x$, with $q = x, y$, or z, spans A_1 by using the T_d character table.

Answer The procedure works out as follows:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$f_3(p_y)$	3	0	−1	−1	1	T_2
$f_2(q)$	3	0	−1	−1	1	T_2
$f_1(p_x)$	3	0	−1	−1	1	T_2
$f_1f_2f_3$	27	0	−1	−1	1	

A_1 occurs (once) in this set of characters, so $p_x \rightarrow p_y$ is allowed.

Comment A more detailed analysis (using the matrix representatives rather than the characters) shows that only $q = z$ gives an integral that may be nonzero, so the transition is z-polarized. That is, the electromagnetic radiation involved in the transition has its electric vector aligned in the z-direction.

Self-test 15.7 What are the allowed transitions, and their polarizations, of a b_1 electron in a C_{4v} molecule?

$[b_1 \rightarrow b_1(z);\ b_1 \rightarrow e(x,y)]$

The following chapters will show many more examples of how the systematic use of symmetry using the techniques of group theory can greatly simplify the analysis of molecular structure and spectra.

Checklist of key ideas

☐ group theory

The symmetry elements of objects

☐ symmetry operation
☐ symmetry element

15.1 Operations and symmetry elements

☐ point groups
☐ space groups
☐ identity
☐ n-fold rotation
☐ principal axis
☐ reflection
☐ mirror plane
☐ inversion
☐ centre of symmetry
☐ n-fold improper rotation
☐ n-fold improper rotation axis

15.2 The symmetry classification of molecules

☐ Schoenflies system
☐ Hermann-Mauguin system
☐ International system
☐ cubic group
☐ icosahedral group

15.3 Some immediate consequences of symmetry

☐ polar molecule
☐ chiral molecule
☐ enantiomeric pair

Character tables

15.4 Character tables and symmetry labels

☐ character table
☐ character
☐ class
☐ order
☐ symmetry species
☐ irreducible representation
☐ representative
☐ basis
☐ matrix representation
☐ block-diagonal form
☐ reduced (representation)
☐ direct sum
☐ spanned (representation)

15.5 Vanishing integrals and orbital overlap

☐ symmetry-adapted linear combinations (SALCs)

15.6 Vanishing integrals and selection rules

☐ criteria for vanishing
☐ overlap integrals
☐ constructing SALCs
☐ selection rule

Further reading

Articles of general interest

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M. Hamermesh, Group theory. In *Encyclopedia of applied physics* (ed. G.L. Trigg), 7, 365. VCH, New York (1993).

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F.A. Cotton, *Chemical applications of group theory.* Wiley, New York (1990).

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P.W. Atkins and R.S. Friedman, *Molecular quantum mechanics.* Oxford University Press (1997).

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B.E. Douglas and C. Hollingsworth, *Symmetry in bonding and structure.* Academic Press, New York (1985).

Exercises

15.1 (a) The CH_3Cl molecule belongs to the point group C_{3v}. List the symmetry elements of the group and locate them in the molecule.

15.1 (b) The CCl_4 molecule belongs to the point group T_d. List the symmetry elements of the group and locate them in the molecule.

15.2 (a) Which of the following molecules may be polar: (a) pyridine (C_{2v}), (b) nitroethane (C_s), (c) gas-phase $HgBr_2$ ($D_{\infty h}$), (d) $B_3N_3H_6$ (D_{3h})?

15.2 (b) Which of the following molecules may be polar: (a) CH_3Cl (C_{3v}), (b) $HW_2(CO)_{10}$ (D_{4h}), (c) $SnCl_4$ (T_d)?

15.3 (a) Use symmetry properties to determine whether or not the integral $\int p_x z p_z \, d\tau$ is necessarily zero in a molecule with symmetry C_{4v}.

15.3 (b) Use symmetry properties to determine whether or not the integral $\int p_x z p_z \, d\tau$ is necessarily zero in a molecule with symmetry D_{6h}.

15.4 (a) Show that the transition $A_1 \rightarrow A_2$ is forbidden for electric dipole transitions in a C_{3v} molecule.

15.4 (b) Is the transition $A_{1g} \rightarrow E_{2u}$ forbidden for electric dipole transitions in a D_{6h} molecule?

15.5 (a) Show that the function xy has symmetry species B_2 in the group C_{4v}.

15.5 (b) Show that the function xyz has symmetry species A_1 in the group D_2.

15.6 (a) Molecules belonging to the point groups D_{2h} or C_{3h} cannot be chiral. Which elements of these groups rule out chirality?

15.6 (b) Molecules belonging to the point groups T_h or T_d cannot be chiral. Which elements of these groups rule out chirality?

15.7 (a) The group D_2 consists of the elements E, C_2, C_2', and C_2'', where the three twofold rotations are around mutually perpendicular axes. Construct the group multiplication table.

15.7 (b) The group C_{4v} consists of the elements E, $2C_4$, C_2, and $2\sigma_v$, $2\sigma_d$. Construct the group multiplication table.

15.8 (a) Identify the point groups to which the following objects belong: (a) a sphere, (b) an isosceles triangle, (c) an equilateral triangle, (d) an unsharpened cylindrical pencil.

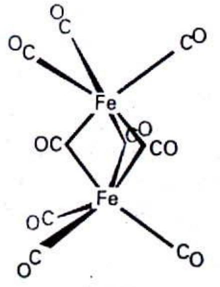
15.8 (b) Identify the point groups to which the following objects belong: (a) a sharpened cylindrical pencil, (b) a three-bladed propellor, (c) a four-legged table, (d) yourself (approximately).

15.9 (a) List the symmetry elements of the following molecules and name the point groups to which they belong: (a) NO_2, (b) N_2O, (c) $CHCl_3$, (d) $CH_2{=}CH_2$, (e) *cis*-CHBr=CHBr, (f) *trans*-CHCl=CHCl.

15.9 (b) List the symmetry elements of the following molecules and name the point groups to which they belong: (a) naphthalene, (b) anthracene, (c) the three dichlorobenzenes.

15.10 (a) Assign (a) *cis*-dichloroethene and (b) *trans*-dichloroethene to point groups.

15.10 (b) Assign the following molecules to point groups: (a) HF, (b) IF_7 (pentagonal bipyramid), (c) XeO_2F_2 (see-saw), (d) $Fe_2(CO)_9$ (**22**), (e) cubane, C_8H_8, (f) tetrafluorocubane, $C_8H_4F_4$ (**23**).



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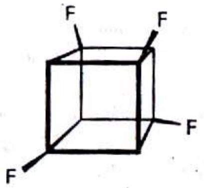

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15.11 (a) Which of the molecules in Exercises 15.9a and 15.10a can be (a) polar, (b) chiral?

15.11 (b) Which of the molecules in Exercises 15.9b and 15.10b can be (a) polar, (b) chiral?

15.12 (a) Consider the C_{2v} molecule NO_2. The combination $p_x(A) - p_x(B)$ of the two O atoms (with x perpendicular to the plane) spans A_2. Is there any orbital of the central N atom that can have a nonzero overlap with that combination of O orbitals? What would be the case in SO_2, where $3d$ orbitals might be available?

15.12 (b) Consider the C_{3v} ion NO_3^-. Is there any orbital of the central N atom that can have a nonzero overlap with the combination $2p_z(A) - p_z(B) - p_z(C)$ of the three O atoms (with z perpendicular to the plane)? What would be the case in SO_3, where $3d$ orbitals might be available?

15.13 (a) The ground state of NO_2 is A_1 in the group C_{2v}. To what excited states may it be excited by electric dipole transitions, and what polarization of light is it necessary to use?

15.13 (b) The ClO_2 molecule (which belongs to the group C_{2v}) was trapped in a solid. Its ground state is known to be B_1. Light polarized parallel to the y-axis (parallel to the OO separation) excited the molecule to an upper state. What is the symmetry of that state?

15.14 (a) What states of (a) benzene, (b) naphthalene may be reached by electric dipole transitions from their (totally symmetrical) ground states?

15.14 (b) What states of (a) anthracene, (b) coronene (**24**) may be reached by electric dipole transitions from their (totally symmetrical) ground states?

24 Coronene

15.15 (a) Write $f_1 = \sin\theta$ and $f_2 = \cos\theta$, and show by symmetry arguments using the group C_s that the integral of their product over a symmetrical range around $\theta = 0$ is zero.

15.15 (b) Determine whether the integral over f_1 and f_2 in Exercise 15.15(a) is zero over a symmetric range about $\theta = 0$ in the group C_{3v}.

Problems

Numerical problems

15.1 List the symmetry elements of the following molecules and name the point groups to which they belong: (a) staggered CH_3CH_3, (b) chair and boat cyclohexane, (c) B_2H_6, (d) $[Co(en)_3]^{3+}$, where en is ethylenediamine (ignore its detailed structure), (e) crown-shaped S_8. Which of these molecules can be (i) polar, (ii) chiral?

15.2 The group C_{2h} consists of the elements E, C_2, σ_h, i. Construct the group multiplication table (the outcome of all multiplications R_iR_j, where R_i and R_j are operations of the group) and find an example of a molecule that belongs to the group.

15.3 The group D_{2h} has a C_2 axis perpendicular to the principal axis and a horizontal mirror plane. Show that the group must therefore have a centre of inversion.

15.4 Consider the H_2O molecule, which belongs to the group C_{2v}. Take as a basis the two H1*s* orbitals and the four valence orbitals of the O atom and set up the 6 × 6 matrices that represent the group in this basis. Confirm by explicit matrix multiplication that the group multiplications (a) $C_2\sigma_v = \sigma_v'$ and (b) $\sigma_v\sigma_v' = C_2$. Confirm, by calculating the traces of the matrices, (a) that symmetry elements in the same class have the same character, (b) that the representation is reducible, and (c) that the basis spans $3A_1 + B_1 + 2B_2$.

15.5 Confirm that the *z*-component of orbital angular momentum is a basis for an irreducible representation of A_2 symmetry in C_{3v}.

15.6 The (one-dimensional) matrices $\mathbf{D}(C_3) = 1$ and $\mathbf{D}(C_2) = 1$, and $\mathbf{D}(C_3) = 1$ and $\mathbf{D}(C_2) = -1$ both represent the group multiplication $C_3C_2 = C_6$ in the group C_{6v} with $\mathbf{D}(C_6) = +1$ and -1, respectively. Use the character table to confirm these remarks. What are the representatives of σ_v and σ_d in each case?

15.7 Construct the multiplication table of the Pauli spin matrices, σ, and the 2 × 2 unit matrix:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Do the four matrices form a group under multiplication (in the sense that $\sigma_i\sigma_j \propto \sigma_k$ for all the matrices)?

15.8 What irreducible representations do the four H1*s* orbitals of CH_4 span? Are there *s* and *p* orbitals of the central C atom that may form molecular orbitals with them? Could *d* orbitals, even if they were present on the C atom, play a role in orbital formation in CH_4?

15.9 Suppose that a methane molecule became distorted to (a) C_{3v} symmetry by the lengthening of one bond, (b) C_{2v} symmetry, by a kind of scissors action in which one bond angle opened and another closed slightly. Would more *d* orbitals become available for bonding?

15.10 The algebraic forms of the *f* orbitals are a radial function multiplied by one of the factors: (a) $z(5z^2 - 3r^2)$, (b) $y(5y^2 - 3r^2)$, (c) $x(5x^2 - 3r^2)$, (d) $z(x^2 - y^2)$, (e) $y(x^2 - z^2)$, (f) $x(z^2 - y^2)$, (g) xyz. Identify the irreducible representations spanned by these orbitals in (a) C_{2v}, (b) C_{3v}, (c) T_d, (d) O_h. Consider a lanthanide ion at the centre of (a) a tetrahedral complex, (b) an octahedral complex. What sets of orbitals do the seven *f* orbitals split into?

15.11 Does the product xyz necessarily vanish when integrated over (a) a cube, (b) a tetrahedron, (c) a hexagonal prism, each centred on the origin?

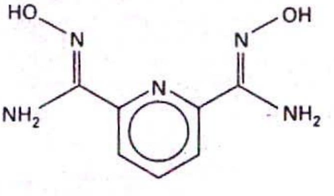
15.12 Treat the naphthalene molecule as belonging to the group C_{2v} with the C_2 axis perpendicular to the plane. Classify the irreducible representations spanned by the carbon $2p_z$ orbitals and find their symmetry-adapted linear combinations.

15.13 The NO_2 molecule belongs to the group C_{2v}, with the C_2 axis bisecting the ONO angle. Taking as a basis the N2*s*, N2*p*, and O2*p* orbitals, identify the irreducible representations they span, and construct the symmetry-adapted linear combinations.

15.14 Construct the symmetry-adapted linear combinations of $C2p_z$ orbitals for benzene, and use them to calculate the Hückel secular determinant. This procedure leads to equations that are much easier to solve than those obtained by using the original orbitals. Show that the Hückel orbitals are those specified in Section 14.9d.

Additional problems supplied by Carmen Giunta and Charles Trapp

15.15 B.A. Bovenzi and G.A. Pearse, Jr (*J. Chem. Soc. Dalton Trans.* accepted, 1997) synthesized coordination compounds of the tridentate ligand pyridine-2,6-diamidoxime ($C_7H_9N_5O_2$, 25). Reaction with $NiSO_4$ produced a complex in which two of the essentially planar ligands are bonded at right angles to a single Ni atom. Name the point group and the symmetry operations of the resulting $[Ni(C_7H_9N_5O_2)_2]^{2+}$ complex cation.



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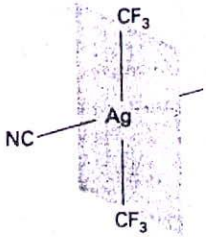
15.16 R. Eujen, B. Hoge, and D.J. Brauer (*Inorg. Chem.* 36, 1464 (1997)) prepared and characterized several square-planar Ag(III) complex anions. In the complex anion [*trans*-$Ag(CF_3)_2(CN)_2]^-$, the Ag–CN groups are collinear. (a) Assuming free rotation of the CF_3 groups (that is, disregarding the AgCF and AgCH angles), name the point group of this complex anion. (b) Now suppose the CF_3 groups cannot rotate freely (because the ion was in a solid, for example). Structure (26) shows a plane which bisects the NC–Ag–CN axis and is perpendicular to it. Name the point group of the complex if each CF_3 group has a CF bond in that plane (so the CF_3 groups do not point to either CN group preferentially) and the CF_3 groups are (i) staggered, (ii) eclipsed.



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15.17 A computational study by C.J. Marsden (*Chem. Phys. Letts.* **245**, 475 (1995)) of AM_x compounds, where A is in Group 14 of the periodic table and M is an alkali metal, shows several deviations from the most symmetric structures for each formula. (a) For example, most of the AM_4 structures were not tetrahedral but had two distinct values for MAM bond angles. They could be derived from a tetrahedron by a distortion shown in (27). What is the point group of the distorted tetrahedron? What is the symmetry species of the distortion considered as a vibration in the new, less symmetric group? (b) Some AM_6 structures are not octahedral, but could be derived from an octahedron by translating a C–M–C axis as in (28). What is the point group of the distorted octahedron? What is the symmetry species of the distortion considered as a vibration in the new, less symmetric group?

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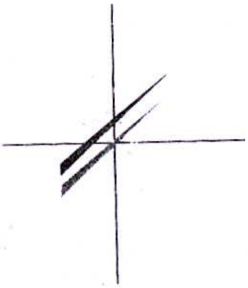

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15.18 In a spectroscopic study of C_{60}, F. Negri, G. Orlandi, and F. Zerbetto (*J. Phys. Chem.* **100**, 10849 (1996)) assigned peaks in the fluorescence spectrum. The molecule has icosahedral symmetry (I_h). The ground electronic state is A_{1g}, and the lowest-lying excited states are T_{1g} and G_g. Are photon-induced transitions allowed from the ground state to either of these excited states? Explain your answer. What if the transition is accompanied by a vibration that breaks the parity?

15.19 The H_3^+ molecule, which plays an important role in chemical reactions occurring in interstellar clouds, is known to be equilateral triangular. (a) Identify the symmetry elements and determine the point group of this molecule. (b) Take as a basis for a representation of this molecule the three H1*s* orbitals and set up the matrices that represent the group in this basis. (c) Obtain the group multiplication table by explicit multiplication of the matrices. (d) Determine if the representation is reducible and, if so, give the irreducible representations obtained.

15.20 The H_3^+ ion has recently been found in the interstellar medium and in the atmospheres of Jupiter, Saturn, and Uranus. The H_4 analogues have not yet been found, and the square planar structure is thought to be unstable with respect to vibration. Take as a basis for a representation of the point group of this molecule the four H1*s* orbitals and determine if this representation is reducible.