12 Approximation Methods in Quantum Mechanics

12.1 THE BORN-OPPENHEIMER APPROXIMATION

In this section the Born–Oppenheimer approximation will be presented in what is necessarily a very simplified form. It has already been introduced without justification in Section 6.5. It is certainly the most important – and most satisfactory – approximation in quantum mechanics, although its rigorous derivation is far beyond the level of this book. Consider, therefore, the following argument.

A stationary state of a polyatomic molecule can be described in quantum mechanics by a wavefunction ψ and an energy ε. Thus, according to Schrödinger,

$$\hat{H}\psi = \varepsilon\psi, \tag{1}$$

where $\hat{H}$ is the total Hamiltonian of the system; it depends on the electronic, nuclear and spin coordinates. Thus, the Hamiltonian is a function of a large number of independent variables that must be separated, at least approximately, to obtain equations that can be solved for variables of each type.

It is usually assumed that the spins that are included in the Hamiltonian can be removed. The variables involving spins of the various particles will thus be eliminated, and the Hamiltonian remains then a function of the positions of the nuclei and the electrons.

The separation of the electronic and nuclear motions depends on the large difference between the mass of an electron and the mass of a nucleus. As the nuclei are much heavier, by a factor of at least 1800, they move much more slowly. Thus, to a good approximation the movement of the electrons in a polyatomic molecule can be assumed to take place in the environment of the nuclei that are fixed in a particular configuration. This argument is the physical basis of the Born–Oppenheimer approximation.

The Hamiltonian for a system composed of a number of nuclei and electrons can be written in the form

$$\hat{H} = -\sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V_{jj'} + V_{ii'} + V_{ij}, \qquad (2)$$

where

$$V_{jj'} = \frac{1}{4\pi\varepsilon_0} \sum_{jj', \ j>j'} \frac{Z_j Z_{j'} e^2}{R_{jj'}}, \qquad (3)$$

$$V_{ii'} = \frac{1}{4\pi\varepsilon_0} \sum_{ii', \ i>i'} \frac{e^2}{r_{ii'}} \qquad (4)$$

and

$$V_{ij} = -\frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{Z_j e^2}{r_{ij}}. \qquad (5)$$

The first two terms in Eq. (2) represent the kinetic energy of the nuclei and the electrons, respectively. The remaining three terms specify the potential energy as a function of the interaction between the particles. Equation (3) expresses the potential function for the interaction of each pair of nuclei. In general, this sum is composed of terms that are given by Coulomb's law for the repulsion between particles of like charge. Similarly, Eq. (4) corresponds to the electron–electron repulsion. Finally, Eq. (5) is the potential function for the attraction between a given electron (i) and a nucleus (j).

It is useful in the present context to separate the Hamiltonian of Eq. (2) into two parts, as given by

$$\hat{H} = \hat{H}_{elec} + \hat{H}_{nucl} = -\sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + V_{ii'} + V_{ij} - \sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 + V_{jj'}. \quad (6)$$

It is then assumed that the wavefunction can be approximated by the relation $\psi = \psi_{elec}\psi_{nucl}$. The first three terms in Eq. (6) are referred to as the electronic part of the Hamiltonian, while the remaining two terms represent the nuclear Hamiltonian. The Schrödinger equation for the general problem can then be written as

$$\hat{H}(\psi_{elec}\psi_{nucl}) = -\sum_j \frac{\hbar^2}{2M_j} \nabla_j^2 (\psi_{elec}\psi_{nucl}) - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 (\psi_{elec}\psi_{nucl})$$

$$+ (V_{jj'} + V_{ii'} + V_{ij})\psi_{elec}\psi_{nucl} = \varepsilon\psi_{elec}\psi_{nucl}. \qquad (7)$$

As the first term on the right-hand side of Eq. (7) expresses the kinetic energy of the nuclei, it is assumed that the wavefunction for the electrons is not modified by the corresponding operator. In other words the movement of the

nuclei takes place within the so-called electron cloud that is developed by the average positions of the ensemble of electrons. Inversely, in the second term of Eq. (7) the operator over the electronic coordinates has no effect on the nuclear wavefunction, as the nuclear positions are taken to be fixed over the period of time of electronic motion.

The imposition of the above approximations on Eq. (7), followed by division by ψ_{nucl}, leads to the relation

$$\frac{\psi_{elec}}{\psi_{nucl}} \sum_j \left(-\frac{\hbar^2}{2M_j} \nabla_j^2 \psi_{nucl} \right) + \left[\sum_i \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 + V_{ii'} + V_{ij} \right) \psi_{elec} \right]$$
$$- (\varepsilon - V_{jj'}) \psi_{elec} = 0. \tag{8}$$

The quantity in square brackets can be readily identified as

$$\hat{H}_{elec} \psi_{elec} = \varepsilon_{elec} \psi_{elec}, \tag{9}$$

where $\varepsilon = \varepsilon_{elec} + \varepsilon_{nucl}$. With the aid of this substitution and multiplication by ψ_{nucl}/ψ_{elec}, the expression

$$\sum_j \left(-\frac{\hbar^2}{2M_j} \nabla_j^2 \psi_{nucl} \right) + V_{jj'} \psi_{nucl} + (\varepsilon_{elec} - \varepsilon) \psi_{nucl} = 0 \tag{10}$$

is obtained. If Eq. (10) is written in the form

$$(\hat{H}_{nucl} + \varepsilon_{elec}) \psi_{nucl} = \varepsilon \psi_{nucl}, \tag{11}$$

it becomes evident that the electronic energy enters the Hamiltonian for the nuclear motion as an effective potential function. Thus, if the "electronic problem", as given by Eq. (9), has been solved as a function of the nuclear geometry, the resulting energy contributes to the potential function that governs internuclear displacements.

The argument presented in the preceding paragraph is perhaps easier to understand with reference to a diatomic molecule. In this case Eq. (9) is solved for each value of the (fixed) interatomic distance. The resulting electronic energy, as a function of this distance, is then substituted in Eq. (10) to yield the Schrödinger equation for the relative nuclear motion, as given by Eq. (6-70). The function $V_{jj'}$ is just the Coulombic repulsion between the two positively charged nuclei, while ε_{elec} is the potential function that describes the forces created by the electron cloud.

It should be emphasized that the Born–Oppenheimer approximation is an extremely good one. Only in certain questions in the interpretation of the molecular spectra of small molecules in the gas phase is it necessary to consider its inherent errors. Therefore, it will not be considered further. There

are, however, other approximations that are important in many areas of physical chemistry and physics.

Several examples of the application of quantum mechanics to relatively simple problems have been presented in earlier chapters. In these cases it was possible to find solutions to the Schrödinger wave equation. Unfortunately, there are few others. In virtually all problems of interest in physics and chemistry, there is no hope of finding analytical solutions, so it is essential to develop approximate methods. The two most important of them are certainly perturbation theory and the variation method. The basic mathematics of these two approaches will be presented here, along with some simple applications.

12.2 PERTURBATION THEORY: STATIONARY STATES

12.2.1 Nondegenerate systems

In many problems for which no direct solution can be obtained, there is a wave equation which differs but slightly from one that can be solved analytically. As an example, consider the hydrogen atom, a problem that was resolved in Section 6.6. Suppose now that an electric field is applied to the atom. The energy levels of the atom are affected by the field, an example of the Stark effect.* If the field (due to the potential difference between two electrodes, for example) is gradually reduced, the system approaches that of the unperturbed hydrogen atom.

With the experiment described above in mind, represent the Hamiltonian of the unperturbed system by $\hat{H}^0$ and that of the perturbed system by

$$\hat{H} = \hat{H}^0 + \lambda\hat{H}'. \tag{12}$$

Assume that the perturbation, $\lambda\hat{H}'$ is small compared with $\hat{H}^0$, where λ is a parameter. As $\lambda \to 0$, the eigenvalues and eigenfunctions are those of the unperturbed system, as given by

$$\hat{H}^0\psi_n^0 = \varepsilon_n^0\psi_n^0 . \tag{13}$$

They are assumed to be known. Furthermore, it should be recalled that the eigenfunctions ψ_n^0 form a complete orthogonal set. The equation of interest is

$$(\hat{H}^0 + \lambda\hat{H}')\psi_n = \varepsilon_n\psi_n. \tag{14}$$

As ψ_n and ε_n are both functions of λ, they can be expanded in power series, *viz.*

*Johannes Stark, German physicist (1874–1957).

$$\psi_n = \psi_n^0 + \lambda \psi_n' + \lambda^2 \psi_n'' + \dots \tag{15}$$

and

$$\varepsilon_n = \varepsilon_n^0 + \lambda \varepsilon_n' + \lambda^2 \varepsilon_n'' + \dots . \tag{16}$$

It will be assumed here, with reasonable assurance, that these two series converge. The substitution of Eqs. (15) and (16) in Eq. (13) leads to the relation

$$\hat{H}^0 \psi_n^0 + \lambda(\hat{H}' \psi_n^0 + \hat{H}^0 \psi_n') + \lambda^2(\hat{H}' \psi_n' + \hat{H}^0 \psi_n'') + \cdots$$
$$= \varepsilon_n^0 \psi_n^0 + \lambda(\varepsilon_n' \psi_n^0 + \varepsilon_n^0 \psi_n') + \lambda^2(\varepsilon_n'' \psi_n^0 + \varepsilon_n' \psi_n' + \varepsilon_n^0 \psi_n'') + \dots .$$
$$\tag{17}$$

The coefficients of the various powers of λ can now be collected to yield a series of equations, namely,

$$\lambda^0 : \hat{H}^0 \psi_n^0 = \varepsilon_n^0 \psi_n^0 \tag{18}$$

$$\lambda^1 : (\hat{H}^0 - \varepsilon_n^0)\psi_n' = \varepsilon_n' \psi_n^0 - \hat{H}' \psi_n^0 \tag{19}$$

$$\lambda^2 : (\hat{H}^0 - \varepsilon_n^0)\psi_n'' = \varepsilon_n'' \psi_n^0 + \varepsilon_n' \psi_n' - \hat{H}' \psi_n' \tag{20}$$

$$\vdots .$$

It has been assumed above that Eq. (18) has been solved. In principle, the resulting eigenvalues and eigenfunctions can then be substituted in Eq. (19) to yield the first-order corrections, and so on, for higher orders of approximation.

12.2.2 First-order approximation

To resolve Eq. (19) an expansion of ψ_n' is made in terms of the zero-order eigenfunctions. Thus,

$$\psi_n' = \sum_\ell a_\ell \psi_\ell^0 \tag{21}$$

and

$$\hat{H}^0 \psi_n' = \hat{H}^0 \sum_\ell a_\ell \psi_\ell^0 = \sum_\ell a_\ell \varepsilon_\ell^0 \psi_\ell^0 . \tag{22}$$

Equation (19) is then written as

$$\sum_\ell a_\ell(\varepsilon_\ell^0 - \varepsilon_n^0)\psi_\ell^0 = (\varepsilon_n' - \hat{H}')\psi_n^0 . \tag{23}$$

The orthonormal properties of the functions ψ_ℓ^0 can now be employed to obtain the desired result. Equation (23) is multiplied by $\psi_n^{0\star}$ and integrated over all

space. The left-hand side of Eq. (23) becomes

$$\int \psi_n^{0\star} \sum_\ell a_\ell (\varepsilon_\ell^0 - \varepsilon_n^0) \psi_\ell^0 \, d\tau = \sum_\ell a_\ell (\varepsilon_\ell^0 - \varepsilon_n^0) \int \psi_n^{0\star} \psi_\ell^0 \, d\tau = 0. \quad (24)$$

The final result is obtained because if $\ell = n$, $\varepsilon_\ell^0 - \varepsilon_n^0 = 0$. Or, if $\ell \neq n$, $\int \psi_n^{0\star} \psi_\ell^0 \, d\tau = 0$, as the functions are orthogonal. After the same operations the right-hand side of Eq. (23) is given by

$$\int \psi_n^{0\star} (\varepsilon_n' - \hat{H}') \psi_n^0 \, d\tau = \varepsilon_n' \int \psi_n^{0\star} \psi_\ell^0 \, d\tau - \int \psi_n^{0\star} \hat{H}' \psi_\ell^0 \, d\tau \quad (25)$$

and, as the zero-order wavefunctions are normalized, Eq. (25) is simply

$$\varepsilon_n' = \int \psi_n^{0\star} \hat{H}' \psi_n^0 \, d\tau. \quad (26)$$

This result stated in words is that ε_n', the first-order correction to energy of the system in a given state n, is just the average value of the perturbation of the Hamiltonian. Equation (26) can be written in the more compact notation of Dirac as

$$\varepsilon_n' = \left\langle n \left| \hat{H}' \right| n \right\rangle. \quad (27)$$

It is often of interest to calculate the corresponding first-order correction to the wavefunctions. The necessary expression can be obtained by returning to Eq. (23). If this equation is now multiplied on each side by $\psi_j^{0\star}$ and the result integrated over all space, the left side will vanish, as before, unless $j = \ell \neq n$. With the application of these conditions, the result is

$$a_j (\varepsilon_j^0 - \varepsilon_n^0) = \varepsilon_n' \int \psi_j^{0\star} \psi_n^0 \, d\tau - \int \psi_j^{0\star} \hat{H}' \psi_n^0 \, d\tau. \quad (28)$$

As $j \neq n$, the first term on the right-hand side of Eq. (28) is equal to zero and the coefficients in Eq. (21) are given by

$$a_j = -\frac{\int \psi_j^{0\star} \hat{H}' \psi_n^0 \, d\tau}{\varepsilon_j^0 - \varepsilon_n^0} = -\frac{\left\langle j \left| \hat{H}' \right| n \right\rangle}{\varepsilon_j^0 - \varepsilon_n^0}. \quad (29)$$

The first-order wavefunctions are then

$$\psi_n = \psi_n^0 + \psi_n' = \psi_n^0 - \sum_{j=0}^{\infty}{}' \frac{\left\langle j \left| \hat{H}' \right| n \right\rangle}{\varepsilon_j^0 - \varepsilon_n^0} \psi_j^0. \quad (30)$$

The prime on the summation in Eq. (30) indicates that the subscript $j = n$ is excluded. It should be noted that the first-order energy given by Eq. (27)

depends only on the diagonal elements of the matrix of $\hat{H}'$. However, the first-order wavefunctions given by Eq. (30) are determined by its off-diagonal elements.

12.2.3 Second-order approximation

Returning to Eq. (20), the coefficients of λ^2 yield the relation

$$(\hat{H}^0 - \varepsilon_n^0)\psi_n'' = (\varepsilon_n' - \hat{H}')\psi_n' + \varepsilon_n'\psi_n^0. \tag{31}$$

Substitution of Eqs. (27) and (30) obtained above with the use of first-order perturbation theory and the expansion

$$\psi_n'' = \sum_i b_i \psi_i^0, \tag{32}$$

as before, will allow Eq. (31) to be written as

$$\sum_i b_i(\varepsilon_i^0 - \varepsilon_n^0)\psi_i^0 = -\sideset{}{'}\sum_j \frac{\langle n|\hat{H}'|j\rangle\langle j|\hat{H}'|n\rangle}{\varepsilon_j^0 - \varepsilon_n^0}\psi_j^0 + \sideset{}{'}\sum_j \frac{\langle j|\hat{H}'|n\rangle}{\varepsilon_j^0 - \varepsilon_n^0}\hat{H}'\psi_j^0$$
$$+ \varepsilon_n''\psi_n^0 . \tag{33}$$

If this expression is multiplied by $\psi_n^{0\star}$ and integrated (with the condition that $n \neq j$), the result is

$$0 = 0 - \sideset{}{'}\sum_j \frac{\langle n|\hat{H}'|j\rangle\langle j|\hat{H}'|n\rangle}{\varepsilon_j^0 - \varepsilon_n^0} + \varepsilon_n'', \tag{34}$$

or

$$\varepsilon_n'' = \sideset{}{'}\sum_j \frac{\langle n|\hat{H}'|j\rangle\langle j|\hat{H}'|n\rangle}{\varepsilon_j^0 - \varepsilon_n^0}. \tag{35}$$

12.2.4 The anharmonic oscillator

The interatomic potential function for the diatomic molecule was described in Section 6.5. In the Taylor-series development of this function [Eq. (6-72)] cubic and higher terms were neglected in the harmonic approximation. It is now of interest to evaluate the importance of these so-called anharmonic terms with the aid of the perturbation theory outlined above. If cubic and quartic terms are added to Eq. (6-74), the potential function becomes

$$V(x) = \tfrac{1}{2}\kappa x^2 + ax^3 + bx^4 \tag{36}$$

where $x = r - r_e$. Clearly, the constants a and b are proportional to the equilibrium values of the third and fourth derivatives of the potential function, respectively.

With the Hamiltonian for the harmonic oscillator,

$$\hat{H}^0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \tfrac{1}{2}kx^2, \tag{37}$$

the Schrödinger equation leads to the solutions in Hermite polynomials (see Section 5.5.1). The zero-order wavefunctions are then

$$\psi_n^0 = \mathcal{N}_n \mathcal{H}_n(\xi)e^{-\frac{1}{2}\xi^2}, \tag{38}$$

where $\xi = 2\pi x\sqrt{v^0 m/\hbar} = \sqrt{\alpha}\,x$, $\varepsilon^0 = hv^0\left(n + \tfrac{1}{2}\right)$ and $\mathcal{N}_n$ is given by Eq. (5-111). The anharmonicity will now be considered as a perturbation, with $\hat{H}' = ax^3 + bx^4$. With the use of Eq. (27) the first-order correction to the energy is equal to

$$\left\langle n|\hat{H}'|n\right\rangle = a\left\langle n|x^3|n\right\rangle + b\left\langle n|x^4|n\right\rangle. \tag{39}$$

The evaluation of the matrix elements in Eq. (39) proceeds as follows.

First of all, consider the parity of the integrands. In the first term on the right-hand side of Eq. (39) both wavefunctions are either odd or even, thus their product is always even, while x^3 is of course odd. The integral between symmetric limits of the resulting odd function of x vanishes and this term makes no contribution to the first-order perturbation. On the other hand the second term is different from zero, as x^4 is an even function.

The matrix elements of x^4 can be evaluated with the use of the recursion relation developed in Section 5.5.1 for the Hermite polynomials (See Appendix IX). In the notation employed here Eq. (5-99) becomes

$$\xi\,\mathcal{H}_n(\xi) = \tfrac{1}{2}\mathcal{H}_{n+1}(\xi) + n\mathcal{H}_{n-1}(\xi). \tag{40}$$

Multiplication of Eq. (40) by ξ yields

$$\xi^2\,\mathcal{H}_n(\xi) = \tfrac{1}{2}\xi\,\mathcal{H}_{n+1}(\xi) + n\xi\,\mathcal{H}_{n-1}(\xi). \tag{41}$$

Equation (40) is then applied twice, *e.g.* with $n \to n + 1$ to give

$$\xi\,\mathcal{H}_{n+1}(\xi) = \tfrac{1}{2}\mathcal{H}_{n+2}(\xi) + (n + 1)\mathcal{H}_n(\xi), \tag{42}$$

and similarly with $n \to n - 1$, to yield

$$\xi^2\,\mathcal{H}_n(\xi) = \tfrac{1}{4}\mathcal{H}_{n+2}(\xi) + \left(n + \tfrac{1}{2}\right)\mathcal{H}_n(\xi) + n(n - 1)\mathcal{H}_{n-2}(\xi). \tag{43}$$

The square of Eq. (43) is given by

$$\xi^4 \mathcal{H}_n^2(\xi) = \tfrac{1}{16}\mathcal{H}_{n+2}^2(\xi) + \left(n + \tfrac{1}{2}\right)^2 \mathcal{H}_n^2(\xi) + n^2(n-1)^2 \mathcal{H}_{n-2}^2(\xi) + \mathcal{O},$$

(44)

where $\mathcal{O}$ represents the cross terms which will vanish on integration due to the orthogonality of the wavefunctions. The second term on the right-hand side of Eq. (39) can be written in the form

$$b\langle n|x^4|n\rangle = \frac{b}{\alpha^2}\mathcal{N}_n^2 \int_{-\infty}^{\infty} e^{-\xi^2}\xi^4 \mathcal{H}_n^2(\xi)\,d\xi.$$

(45)

With the substitution of Eq. (44) in the integrand, Eq. (45) becomes

$$b\langle n\,|x^4|\,n\rangle = \frac{b}{\alpha^2}\mathcal{N}_n^2 \left[\frac{1}{16\mathcal{N}_{n+2}^2} + \frac{\left(n+\tfrac{1}{2}\right)^2}{\mathcal{N}_n^2} + \frac{n^2(n-1)^2}{\mathcal{N}_{n-2}^2}\right]$$

(46)

$$= \frac{3b}{2\alpha^2}\left[\left(n+\tfrac{1}{2}\right)^2 + \tfrac{1}{4}\right]$$

(47)

(problem 7). Thus, the first-order correction to the energy as a result of anharmonicity is proportional to the coefficient b and is quadratic in the vibrational quantum number n.

It was shown above that the cubic term in the potential function for the anharmonic oscillator cannot, for reasons of symmetry, contribute to a first-order perturbation. However, if the matrix elements of $\mathcal{H}' = ax^3$ are evaluated, it is found that this term results in a second-order correction to the energy. The appropriate matrix elements in Eq. (35) must then be evaluated.

The only nonvanishing matrix elements of x^3 are those with $j = n \pm 1$ and $j = n \pm 3$. This result is obtained by repeated application of Eq. (40), as before. Thus, there are four terms that the cubic potential constant contributes to the second-order energy correction, Eq. (35). The final result can be written as

$$\varepsilon_n'' = \frac{15a^2}{4\alpha^3 h\nu^0}\left(n^2 + n + \frac{11}{30}\right) = \frac{15a^2}{4\alpha^3 h\nu^0}\left[\left(n+\tfrac{1}{2}\right)^2 + \frac{17}{60}\right]$$

(48)

(problem 8). This expression, plus the first-order correction given by Eq. (47), indicates that the anharmonicity of the oscillator can be represented in this approximation by a quadratic term in the vibrational quantum number. The vibrational spectra of diatomic molecules are usually interpreted with the addition of an anharmonic term that is proportional to $\left(n + \tfrac{1}{2}\right)^2$. It should be noted

that the application of perturbation theory yields, in addition, a small correction to the zero-point energy.

12.2.5 Degenerate systems

The first-order perturbation theory developed in Section 12.2.2 cannot be employed if the energy level of the unperturbed system is degenerate. In Eq. (12) it was assumed that the perturbed wavefunction ψ_n differed but slightly from a particular zero-order wavefunction, ψ_n^0. However, if the energy level ε_n^0 is α-fold degenerate, there are α linearly independent wavefunctions that satisfy the wave equation for the unperturbed system. Each of these functions is orthogonal to all wavefunctions corresponding to other energy levels. However, they are not necessarily orthogonal to each other.

The simplest example is that of a doubly degenerate level, for which $\hat{H}^0 \psi_{k,1}^0 = \varepsilon_k^0 \psi_{k,1}^0$ and $\hat{H}^0 \psi_{k,2}^0 = \varepsilon_k^0 \psi_{k,2}^0$. Clearly, any linear combination of the two wavefunctions is also a solution, as

$$\hat{H}^0 (c_1 \psi_{k,1}^0 + c_2 \psi_{k,2}^0) = \varepsilon_k^0 (c_1 \psi_{k,1}^0 + c_2 \psi_{k,2}^0). \tag{49}$$

In general, if α_k is the degree of degeneracy, α_k linear combinations of the zero-order wavefunctions can be constructed,

$$\chi_{k,i}^0 = \sum_{j=1}^{\alpha_k} c_{i,j} \psi_{k,j}^0 \qquad i = 1, 2, 3, \ldots, \alpha_k . \tag{50}$$

They are also correct wavefunctions for the zero-order problem. The coefficients can of course be chosen to normalize each result.

Consider a first-order perturbation. The Hamiltonian for the perturbed system is again as given by $\hat{H} = \hat{H}^0 + \lambda \hat{H}'$ [Eq. (12)], but the Schrödinger equation is of the form

$$\hat{H} \psi_{k,j} = \varepsilon_{k,j} \psi_{k,j} . \tag{51}$$

Thus, the effect of the perturbation may be to remove (all or partially) the degeneracies of the unperturbed energy levels. As the perturbation diminishes ($\lambda \to 0$), $\psi_{k,j} \to \chi_{k,i}^0$ and $\varepsilon_{k,j} \to \varepsilon_k^0$. Thus, for the perturbed system,

$$\psi_{k,i} = \chi_{k,i}^0 + \lambda \psi_{k,i}' \tag{52}$$

and

$$\varepsilon_{k,i} = \varepsilon_k^0 + \lambda \varepsilon_{k,i}' . \tag{53}$$

The first-order approximation (equating coefficients of λ) yields the relation

$$\hat{H}^0 \psi_{k,i}' + \hat{H}' \chi_{k,i}^0 = \varepsilon_k^0 \psi_{k,i}' + \varepsilon_{k,i}' \chi_{k,i}^0 . \tag{54}$$

Following the procedure of Section 12.2.2, the expansion

$$\psi'_{k,i} = \sum_{k,j} a_{k,i,k',j} \psi^0_{k',j} \tag{55}$$

is made in terms of the zero-order wavefunctions. Note that the double summation has been employed in Eq. (55) to take into account all wavefunctions associated with a given unperturbed energy level, as well as all energy levels.
   Substitution of Eqs. (52) and (53) in Eq. (51) leads to

$$\sum_{k',j} a_{k,i,k',j} (\varepsilon^0_{k'} - \varepsilon^0_k) \psi'_{k',j} = \sum_j c_{i,j} (\varepsilon'_{i,j} - \hat{H}') \psi^0_{k,j} , \tag{56}$$

which, when multiplied by $\psi^{0*}_{k,n}$ and integrated over all space becomes

$$0 = \sum_{j=1}^{\alpha_k} c_{i,j} \left[\varepsilon'_{k,i} \int \psi^{0\star}_{k,n} \psi^0_{k,j} \, d\tau - \int \psi^{0\star}_{k,n} \hat{H}' \psi^0_{k,j} \, d\tau \right] \tag{57}$$

or

$$\sum_{j=1}^{\alpha_k} c_{i,j} \left[\left\langle n \left| \hat{H}' \right| j \right\rangle - \varepsilon'_{k,i} \left\langle n | j \right\rangle \right] = 0, \qquad i = 1, 2, 3, \ldots, \alpha_k . \tag{58}$$

This result is a system of simultaneous linear, homogeneous equations for the coefficients, $c_{i,j}$. Cramer's rule states that a nontrivial solution exists only if the determinant of the coefficients vanishes (see Section 7.8). Thus,

$$\left| \left\langle n \left| \hat{H}' \right| j \right\rangle - \varepsilon'_{k,i} \left\langle n | j \right\rangle \right| = 0, \qquad i = 1, 2, 3, \ldots, \alpha_k . \tag{59}$$

The determinant in Eq. (59) is of course a secular determinant, a description that refers to its application to the temporal evolution of a mechanical system, historically in astronomy. It will re-appear later in this chapter in the development of the variation method.
   The secular determinant as presented above involves the first-order perturbations of the Hamiltonian and the energy. More generally, it is formulated in terms of the Hamiltonian and the total energies of the perturbed system. From Eqs. (12) and (16),

$$\left\langle n | \hat{H}' | j \right\rangle = \left\langle n | \hat{H}^0 | j \right\rangle + \left\langle n | \hat{H}' | j \right\rangle \tag{60}$$

and

$$\varepsilon_{k,i} \left\langle n | j \right\rangle = \varepsilon^0_k \left\langle n | j \right\rangle + \varepsilon'_{k,i} \left\langle n | j \right\rangle . \tag{61}$$

Their difference, when substituted in Eq. (58) leads to the secular determinant in its more usual form, *viz.*

$$\left| \left\langle n \left| \hat{H} \right| j \right\rangle - \varepsilon_{k,i} \left\langle n | j \right\rangle \right| = 0, \qquad i = 1, 2, 3, \ldots, \alpha_k. \tag{62}$$

12.2.6 The Stark effect of the hydrogen atom

Consider a hydrogen atom under the influence of an electric field, $\mathcal{E}$. The perturbation energy is given by $\hat{H}' = -\boldsymbol{\mu} \cdot \mathcal{E}$, where $\boldsymbol{\mu}$ is the instantaneous dipole moment of the atom. For simplicity, assume that the electric field is directed along the z axis. The perturbation in this case then given by

$$\hat{H}' = ez\mathcal{E}_z = e\mathcal{E}_z r \cos \theta, \tag{63}$$

where e is the electronic charge.

The ground state of the hydrogen atom is nondegenerate and the wavefunction is

$$\psi_{1,0,0} = \frac{1}{\sqrt{4\pi}} R_{1,0}, \tag{64}$$

with the radial part given by

$$R_{1,0} = 2a_0^{-3/2} e^{-r/a_0}. \tag{65}$$

The result of first-order perturbation theory, as given by Eq. (27), is applicable. Clearly, the matrix element $\left\langle 1, 0, 0 \left| \hat{H}' \right| 1, 0, 0 \right\rangle$ vanishes, as $\int_0^\pi \cos \theta \sin \theta \, d\theta = 0$. Thus, there is no first-order Stark effect for the hydrogen atom in the ground state.

However, in the first excited state the degree of degeneracy is equal to four. Hence, the first-order perturbation calculation requires the application of Eq. (62). The wavefunctions for the first excited state can be written in the form

$$\psi_{2,0,0} = \frac{1}{\sqrt{4\pi}} R_{2,0}$$

$$\psi_{2,1,0} = \sqrt{\frac{3}{4\pi}} R_{2,1} \cos \theta$$

$$\psi_{1,1,1} = \sqrt{\frac{3}{4\pi}} R_{2,1} \sin \theta \frac{1}{\sqrt{2}} e^{i\varphi}$$

$$\psi_{1,1,-1} = -\sqrt{\frac{3}{4\pi}} R_{2,1} \sin \theta \frac{1}{\sqrt{2}} e^{-i\varphi}, \tag{66}$$

where the radial parts are given by

$$R_{2,0} = \frac{a_0^{-3/2}}{2\sqrt{2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$R_{2,1} = \frac{a_0^{-3/2}}{2\sqrt{6}} \frac{r}{a_0} e^{-r/2a_0} \tag{67}$$

In Eqs. (67) the quantity a_0 is the radius of the first Bohr orbit (see Section 6.6).

The matrix elements in Eq. (62) are of two types. The diagonal elements involve integrals over θ, all of which vanish. Furthermore, of the off-diagonal elements, only $\langle 2, 0, 0 | \hat{H}' | 2, 1, 0 \rangle = \langle 2, 1, 0 | \hat{H}' | 2, 0, 0 \rangle = -3e\mathscr{E}_z a_0$ are non-zero, as all integrals involving φ vanish. The secular determinant then takes the form

$$\begin{vmatrix} -\varepsilon_2' & -3e\mathscr{E}_z a_0 & 0 & 0 & 0 \\ -3e\mathscr{E}_z a_0 & -\varepsilon_2' & 0 & 0 & 0 \\ 0 & 0 & 0 & -\varepsilon_2' & 0 \\ 0 & 0 & 0 & 0 & -\varepsilon_2' \end{vmatrix} = 0 \tag{68}$$

and the energies of the perturbed levels are obtained as the roots of the expression

$$\varepsilon_2'^2 (\varepsilon_2'^2 - 9e^2 \mathscr{E}_z^2 a_0^2) = 0 \tag{69}$$
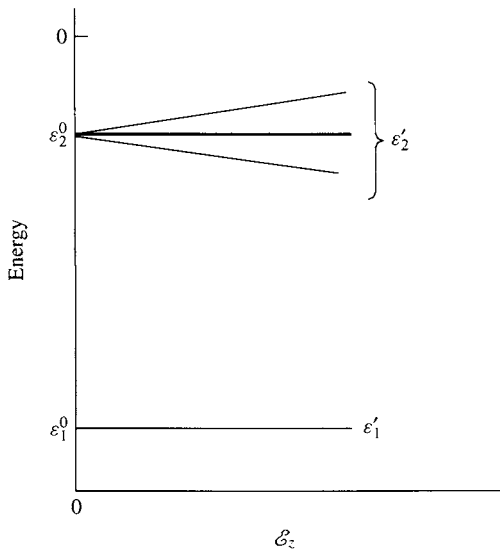
Fig. 1   The Stark effect of the hydrogen atom.

(problem 11). These results are represent in Fig. 1. Note that two of the levels are not perturbed by the applied electric field and their degeneracy is not removed. They correspond to atomic orbitals p_x and p_y, whose maxima lie in the horizontal plane, that is, perpendicular to the direction of the applied field (see Appendix III).

12.3   TIME-DEPENDENT PERTURBATIONS

12.3.1 The Schrödinger equation

To discuss the problem of the interaction of light with an atomic or molecular system, it is essential to consider those perturbations which are functions of time. It is such perturbations that provoke transitions from one stationary state to another in a given system. Thus, specifically, it is the time-dependent Schrödinger equation that must be considered. It can be written in the form

$$\hat{H}\Psi(q_1, q_2, \cdots; t) = i\hbar \frac{\partial \Psi(q_1, q_2, \cdots; t)}{\partial t}, \tag{70}$$

where the Hamiltonian is now a function of time, as well as all of the coordinates of the system.

The separation of the time from the spatial variables can be carried out by the method introduced in Section 6.1.2. Thus, it is sufficient to write

$$\Psi(q_1, q_2, \cdots; t) = \psi(q_1, q_2, \cdots)\vartheta(t) \tag{71}$$

to separate the time from the space variables. The result is given by

$$\Psi(q_1, q_2, \cdots; t) = \psi(q_1, q_2, \cdots)e^{-i\varepsilon_k t/\hbar}. \tag{72}$$

In the problem of interest here, the Hamiltonian in Eq. (62) can be decomposed into a time-independent, unperturbed part $\hat{H}^0$ and a much smaller, time-dependent operator $\hat{H}'(t)$. Then, the Hamiltonian becomes to first order

$$\hat{H}^0 + \hat{H}'(t). \tag{73}$$

The stationary states of the system are described by the eigenfunctions ψ_k and the eigenvalues ε_k of the unperturbed Hamiltonian.

The eigenfunctions ψ_k form a complete set; thus, the wavefunction $\Psi(q_1, q_2, \cdots; t)$ can be expanded in terms of the wavefunctions ψ_k, with the use of the time-dependent coefficients $b_k(t)$. The resulting expression is then

$$\Psi(q_1, q_2, \cdots; t) = \sum_k b_k(t)\psi_k e^{-i\varepsilon_k t/\hbar} \tag{74}$$

which can be substituted into the time-dependent Schrödinger equation to yield

$$\sum_k b_k(t) \hat{H}'(t) \psi_k e^{-i\varepsilon_k t/\hbar} = i\hbar \sum_k \frac{db_k(t)}{dt} \psi_k e^{-i\varepsilon_k t/\hbar}. \tag{75}$$

Multiplication by $\psi_m^\star$ and integration over the spatial coordinates results in the set of differential equations for the coefficients,

$$\frac{db_m(t)}{dt} = -\frac{i}{\hbar} \sum_k b_k(t) \left\langle m \left| \hat{H}'(t) \right| k \right\rangle e^{-(\varepsilon_k - \varepsilon_m)t/\hbar}. \tag{76}$$

It should be noted that in the general case each term in the summation contains three time-dependent factors. Thus, to reduce the complexity of the presentation, only a very simple example will be considered here.

Suppose that at a time $t = 0$, the stationary state of the system is known. That is to say that both its energy ε_n and the corresponding (nondegenerate) wavefunction ψ_n have been determined. Therefore, for $t \leq 0$, all of the coefficients in Eq. (76) are equal to zero, except of course, $b_n = 1$, which identifies the initial state of the system. It is often the ground state, although not necessarily. A perturbation is then applied at $t = 0$. It is then assumed that it is sufficiently weak so that the coefficient b_n does not vary significantly from its initial value of unity over the relatively short duration of the perturbation. With these conditions Eq. (76) can be reduced to

$$\frac{db_m(t)}{dt} = -\frac{i}{\hbar} \left\langle m \left| \hat{H}'(t) \right| n \right\rangle e^{-(\varepsilon_n - \varepsilon_m)t/\hbar}. \tag{77}$$

Normally, the energy difference between the initial and final states, as given in Eq. (77), is equated to $\omega_{nm}\hbar$, where $\nu_{nm} = \omega_{nm}/2\pi$ is the frequency of the transition from the initial state $k = n$ to the final state m.

12.3.2 Interaction of light and matter

The problem of particular interest in physics and chemistry is concerned with the interaction of electromagnetic radiation, and light in particular, with matter. The electric field of the radiation can directly perturb an atomic or molecular system. Then, as in the Stark effect, the energy of interaction – the perturbation – is given by

$$\hat{H}' = -\boldsymbol{\mu} \cdot \boldsymbol{\mathcal{E}}, \tag{78}$$

where $\boldsymbol{\mu}$ is the dipole moment of the system. For simplicity it will be assumed that the light incident on the system is polarized in a particular direction, say x. Then, Eq. (78) becomes simply

$$\hat{H}' = -\mu_x \mathcal{E}_x . \tag{79}$$

If the incident radiation is monochromatic with a frequency $\nu = \omega/2\pi$, as in a laser beam, its electric field can be represented by

$$\mathscr{E}_x = \mathscr{E}_x^0 \cos \omega t, \tag{80}$$

where $\mathscr{E}_x^0$ is the amplitude of the incident radiation. The corresponding component (x) of the dipole moment of the system can be written in the form

$$\mu_x = \sum_i e_i x_i , \tag{81}$$

where e_i is the charge on each particle, and x_i is its position in the x direction. Then the perturbation is given by

$$\hat{H}' = -\mu_x \mathscr{E}_x = -\mathscr{E}_x \sum_i e_i x_i \tag{82}$$

and the matrix elements in Eq. (77) are

$$\left\langle m \left| \hat{H}'(t) \right| n \right\rangle = -\mathscr{E}_x^0 \cos \omega t \sum_i e_i \left\langle m \left| \mu_i \right| n \right\rangle = -\mathscr{E}_x^0 \cos \omega t \left\langle m \left| \mu_x \right| n \right\rangle . \tag{83}$$

The time dependence is in this case due to the oscillation of the imposed electric field as given by Eq. (80), as well as the displacement of the charged particles, electrons and nuclei within the atomic or molecular system.

The expression for the matrix elements given by Eq. (83) is substituted in Eq. (77). The result is

$$\frac{db_m(t)}{dt} = \frac{i}{\hbar} \mathscr{E}_x^0 \cos \omega t \left\langle m \left| \mu_x \right| n \right\rangle e^{-i\omega_{nm}t}. \tag{84}$$

The exponential form of $\cos \omega t$, as given in Eq. (1-36), is then substituted to obtain

$$\frac{db_m(t)}{dt} = \frac{i}{2\hbar} \mathscr{E}_x^0 \left\langle m \left| \mu_x \right| n \right\rangle [e^{-i(\omega_{nm}-\omega)t} + e^{-i(\omega_{nm}+\omega)t}] \tag{85}$$

which can be easily integrated if the matrix element $\langle m | \mu_x | n \rangle$ does not change significantly during the short time of the perturbation. Then, with the initial condition that $b_m = 0$ at $t = 0$, integration yields the time-dependent coefficient

$$b_m(t) = \frac{-\mathscr{E}_x^0 \langle m | \mu_x | n \rangle}{2\hbar} \left[\frac{e^{-i(\omega_{nm}-\omega)t} - 1}{\omega_{nm} - \omega} + \frac{e^{-i(\omega_{nm}-\omega)t} - 1}{\omega_{nm} + \omega} \right]. \tag{86}$$

As the frequency of the incident electromagnetic radiation approaches that of the transition $n \to m$, the first term in the brackets of Eq. (86) dominates; it

becomes very large at resonance.* Thus, the second term in Eq. (79) can be neglected in the spectral region of interest, and the resulting expression for the probability of a transition to the state m can be written as (see problems 14 and 15)

$$b_m b_n^* = \frac{\left|\mathscr{E}_x^0\right|^2 |\langle m |\mu_x| n\rangle|^2 t^2}{4\hbar^2} \left\{ \frac{sin^2[(\omega_{nm} - \omega)t/2]}{[(\omega_{nm} - \omega)t/2]^2} \right\}. \qquad (87)$$

The expression in brackets in Eq. (87) is of the form $(sin\, x/x)^2$, where $x = (\omega_{nm} - \omega)t/2$. Thus, for a given time t for the duration of the perturbation, the spectrum, e.g. the transition probability as a function of the angular frequency ω is as shown in Fig. 2. The width at half-maximum of this spectral feature is represented by Δ for a given value of the time, t. If, for example, the perturbation time is increased by a factor of four, the width of the spectral distribution is reduced by the same factor, as shown by the solid line in Fig. 2. Equation (87) expresses the probability that the system, initially in the state $k = n$, will be in the state m after a sinusoidal perturbation over a relatively short period of time t.

Now to calculate the transition probability in the case in which all frequencies $\nu = \omega/2\pi$ are incident on the molecule, Eq. (87) must be integrated over the frequency range. As the significant frequency variation is due to the factor
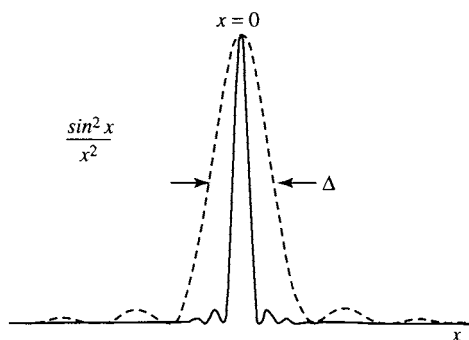
Fig. 2   The function $(sin\, x/x)^2 = sinc^2 x$, where $x = (\omega_{nm} - \omega)t/2$ and t is the duration of the perturbation. The width of the frequency distribution is equal to Δ, which is proportional to $1/t$.

*Note, however, that it does not become infinite, as $lim_{a\to 0}[(e^{iat} - 1)/a] = it$.

in brackets, its integration leads to the approximate expression

$$|b_m|^2 = \frac{\pi \left|\mathscr{E}_x^0\right|^2}{2\hbar^2} |\langle m |\mu_x| n\rangle|^2 t. \tag{88}$$

The quantity $|b_m|^2$ represents the probability of the transition $m \leftarrow n$. Clearly, the number of transitions per unit time depends on the intensity of the incident radiation, which is proportional to $|\mathscr{E}_x^0|^2$, and the square of the matrix element $\langle m|\mu_x|n\rangle$. The latter determines the selection rules for spectroscopic transitions (see the following section).

The result obtained as Eq. (88) can be generalized for the case of isotropic radiation. The light intensity is then proportional to

$$|\mathscr{E}^0|^2 = |\mathscr{E}_x^0|^2 + |\mathscr{E}_y^0|^2 + |\mathscr{E}_z^0|^2, \tag{89}$$

which is in turn proportional to the radiation density, ρ. The square of the matrix elements of the dipole-moment vector are given by

$$| \langle m|\boldsymbol{\mu}|n\rangle |^2 = | \langle m|\mu_x|n\rangle |^2 + | \langle m|\mu_y|n\rangle |^2 + | \langle m|\mu_z|n\rangle |^2, \tag{90}$$

which depends on the molecular orientation. It determines the value of the Einstein coefficient for absorption, which is given by

$$B_{m \leftarrow n} = \frac{2\pi}{(4\pi\varepsilon_0)3c\hbar^2}| \langle m|\boldsymbol{\mu}|n\rangle |^2. \tag{91}$$

The quantity $\langle m|\boldsymbol{\mu}|n\rangle$ is known as the transition (dipole) moment.

In the above rather simplified analysis of the interaction of light and matter, it was assumed that the process involved was the absorption of light due to a transition $m \leftarrow n$. However, the same result is obtained for the case of light emission stimulated by the electromagnetic radiation, which is the result of a transition $m \rightarrow n$. Then the Einstein coefficients for absorption and stimulated emission are identical, viz. $B_{m \leftarrow n} = B_{m \rightarrow n}$.

An important process has not been included in the analysis. It is the possibility of spontaneous emission. Were it not for such a process, in the absence of electromagnetic radiation a molecule in the excited state m would be forced to remain there forever. Thus, in Einstein's analysis of this problem three competing processes were considered to be in equilibrium, leading to the expression

$$B_{m \leftarrow n} N_n \rho = B_{m \rightarrow n} N_m \rho + A_{m \rightarrow n} N_m . \tag{92}$$

The left-hand side of Eq. (92) represents the number of transitions per unit time due to absorption of light. The first term on the right-hand side of Eq. (92)

is due to stimulated emission, while the second term, which remains in the absence of electromagnetic radiation, takes into account the possibility of spontaneous emission. As an equation, this relation expresses the balance between these processes. Furthermore, at equilibrium the relative populations of the upper and lower states is determined by the Boltzmann distribution law,

$$\frac{N_m}{N_n} = e^{-\hbar\omega_{nm}/kT} \tag{93}$$

(see Chapter 10). Substitution of Eq. (93) into Eq. (92) yields the relations between the Einstein coefficients

$$A_{m\to n} = \frac{2\hbar\omega^3}{\pi c^2} B_{m\to n} = \frac{2\hbar\omega^3}{\pi c^2} B_{m\leftarrow n}. \tag{94}$$

It is important to note that all three coefficients depend on the matrix elements of the dipole moment, as expressed by Eq. (90).

12.3.3 Spectroscopic selection rules

General selection rules that govern spectroscopic transitions are derived from the symmetry properties of the dipole moment and the wavefunctions involved. The transition moments can be expressed in general by

$$\langle m|\mu_j|n\rangle = \int \psi_m^\star \mu_j \psi_n \, d\tau, \tag{95}$$

where $j = x, y, z$ identifies space-fixed Cartesian coordinates and ψ_m and ψ_n are the wavefunctions for the states involved in the transition. If any such integral is nonzero, from Eq. (90) it is evident that these transitions are possible. The so-called selection rules are just the answer to the question: Is the transition moment $\langle m|\mu|n\rangle$ equal to zero? If so, transitions between the states m and n are forbidden.

The determination of general selection rules can be made by consideration of the symmetry of the integrand in Eq. (95). For example, it was shown in Section 3.4.5 that the integral over an odd function vanishes. The corresponding group-theoretical expression of this principle was outlined in Section 8.10. The integrand in Eq. (95) is the product of three functions. Thus, if each is characterized by a representation, the direct product provides the needed information concerning the symmetry of the resulting function. In the simplest case each factor may belong to a particular irreducible representation. Then, the resulting direct product can be expressed as

$$\Gamma_m^{(\gamma')} \otimes \Gamma_j^{(\gamma)} \otimes \Gamma_n^{(\gamma'')} = \sum_\ell n^{(\ell)}\Gamma^{(\ell)}. \tag{96}$$

The right-hand side of Eq. (96) is of course the weighted direct sum of the irreducible representations. By convention the totally symmetric irreducible representation corresponds to $\ell = 1$. Thus, if $n^{(1)} = 0$, the integral in Eq. (95) vanishes. The transitions $m \to n$ and $m \leftarrow n$ are then forbidden by the symmetry selection rules. This principle can be illustrated by the following example.

Consider a molecular system of symmetry $\mathcal{C}_{2v}$, whose character table is given in Table 8-11. The irreducible representations for the components of the dipole moment can be easily established, or even read directly from the table. Thus $\Gamma_j^{(\gamma)}$ can be identified as A_1, B_1 or B_2 for $j = z, x$ or y, respectively. Then, if the direct product $\Gamma_m^{(\gamma')} \otimes \Gamma_n^{(\gamma'')}$ contains any of these three irreducible representations, the transitions $m \to n$ and $m \leftarrow n$ are allowed. Furthermore, the polarization of optical transitions can be specified, as each $\Gamma_j^{(\gamma)}$ corresponds to a specific polarization direction.

The selection rules illustrated above are general, as they depend only on the symmetry properties of the functions involved. However, more limiting, selection rules depend on the form of the wavefunctions involved. A relatively simple example of the development of specific selection rules is provided by the harmonic oscillator. The solution of this problem in quantum mechanics, as treated in Section 5.4.4, leads to the wavefunctions given by Eq. (5-103) and the energy levels defined by Eq. (5-92). These results were employed in Section 5.4.4 to describe in a first approximation the vibration of a diatomic molecule. As before, the possibility of transitions between the various energy levels of the system is determined by the matrix elements of the dipole moment.

If r is the internuclear distance in a diatomic molecule and $x = r - r_e$, the dipole moment can be developed in a series in the form

$$\mu = \mu_0 + \left(\frac{d\mu}{dx}\right)_0 x + \dots \ . \tag{97}$$

The first term on the right-hand side of Eq. (97) is the permanent dipole moment. The second term expresses the change in dipole moment with inter-nuclear distance. Often, higher terms are neglected. The derivative $(d\mu/dx)_0$ can then be interpreted as an effective charge carried by the vibrating nuclei. The change in internuclear distance is related to the independent variable employed in Section 5.5.1 by $\xi = 2\pi x \sqrt{v^0 m / h}$, where m is now the reduced mass of the diatomic molecule and $v^0 = \sqrt{k/m}/2\pi$ is the classical frequency of vibration.

The transition moment of interest for process $v' \to v$, is then

$$\langle v'|\mu|v\rangle = \left\langle v' \left| \mu_0 + \left(\frac{d\mu}{dx}\right)_0 x \right| v \right\rangle = \mu_0 \langle v'|v\rangle + \left(\frac{d\mu}{dx}\right)_0 \langle v'|x|v\rangle. \tag{98}$$

For a polar molecule ($\mu_0 \neq 0$) the first term on the far right is nonzero only if the initial and final vibrational states are the same, *viz.* $v = v'$. This case applies to the pure rotational spectra of gaseous molecules, as observed in the microwave region. The second term in Eq. (98) applies to vibrational transitions. The matrix elements of interest are $\langle v'|x|v\rangle$, which are given by

$$\langle v'|x|v\rangle = \alpha^{-1/2}\langle v'|\xi|v\rangle$$

$$= \alpha^{-1/2}\mathcal{N}_{v'}\mathcal{N}_v \int_{-\infty}^{+\infty} (e^{-\xi^2/2}\mathcal{H}_{v'}(\xi))\xi(e^{-\xi^2/2}\mathcal{H}_v(\xi))\,d\xi. \quad (99)$$

To determine the selection rules in this case it is sufficient to recall the relations developed in Section 5.5.1 between the Hermite polynomials. Specifically, Eq. (5-99) can be rewritten in the form

$$\xi\mathcal{H}_v(\xi) = \tfrac{1}{2}\mathcal{H}_{v+1}(\xi) + v\mathcal{H}_{v-1}(\xi). \quad (100)$$

With its substitution in Eq. (99) it becomes evident from the orthogonality of the Hermite polynomials, that all matrix elements are equal to zero, with the exception of $v' = v - 1$ and $v' = v + 1$. Thus, the selection rule for vibrational transitions (in the harmonic approximation) is $\Delta v = \pm 1$. It is not necessary to evaluate the matrix elements unless there is an interest in calculating the intensities of spectral features resulting from vibrational transitions (see problem 18). It should be evident that transitions such as $\Delta v = \pm 3$ are forbidden under this more restrictive selection rule, although they are permitted under the symmetry selection rule developed in the previous paragraphs.

As a second example of the determination of selection rules from the properties of special functions, consider the hydrogen atom. At any given instant the dipole moment is $\boldsymbol{\mu} = e\boldsymbol{r}$, where $\boldsymbol{r}$ describes the position of the electron with respect to the proton and e is the electronic charge. The wavefunctions for the hydrogen atom are given by

$$\psi_{n,\ell,m} = R_{n,\ell}(r)\Theta_{\ell,m}(cos\,\theta)e^{im\varphi}, \quad (101)$$

where the angular-dependent factor is given by Eq. (6-69). If the incident light is polarized in, say, the z direction, the matrix elements of interest are of the form

$$\langle n', \ell', m'|\mu_z|n, \ell, m\rangle = e\langle n', \ell', m'|r\,cos\,\theta|n, \ell, m\rangle$$

$$= e\langle n', \ell'|r|n, \ell\rangle\langle\ell', m'|cos\,\theta|\ell, m\rangle\langle m'|m\rangle. (102)$$

The factor that depends on the radial wavefunctions is in general nonzero. The factor in φ contributes to the integral

$$\langle m'|m\rangle = \frac{1}{2\pi}\int_0^{2\pi} e^{-i(m'-m)}\,d\varphi = \delta_{m',m}, \quad (103)$$

which imposes the condition $\Delta m = 0$, or the integral vanishes. The θ-dependent part of Eq. (102) can be evaluated from the recursion relations for the associated Legendre polynomials. For this example Eq. (5-122) can be written as

$$
cos \, \theta \, P_\ell^{|m|}(cos \, \theta) = \frac{(\ell + |m|)}{(2\ell + 1)} P_{\ell-1}^{|m|}(cos \, \theta) + \frac{(\ell - |m| + 1)}{(2\ell + 1)} P_{\ell+1}^{|m|}(cos \, \theta),
$$

(104)

which leads directly to the selection rule $\Delta \ell = \pm 1$.

For light polarized in the x or y directions, the procedure followed in the preceding paragraph can be employed with $\mu_x = ex = er \, sin \, \theta \, cos \, \varphi$ and $\mu_y = ey = er \, sin \, \theta \, sin \, \varphi$. Then, it is apparent that $\Delta m = \pm 1$ and with the aid of Eqs. (5-123) and (5-124) the selection rule $\Delta \ell = \pm 1$ can be easily established (see problem 19). In conclusion the selection rules for the absorption of unpolarized light are $\Delta m = 0, \pm 1$ and $\Delta \ell = \pm 1$.

12.4 THE VARIATION METHOD

A different approach to obtaining approximation solutions to quantum mechanical problems is provided by the variation method. It is particularly useful when there is no closely related problem that yields exact solutions. The perturbation method is not applicable in such a case.

The variation method is usually employed to determine an approximate value of the lowest energy state (the ground state) of a given atomic or molecular system. It can, furthermore, be extended to the calculation of energy levels of excited states. It forms the basis of molecular orbital theory and that which is often referred to (incorrectly) as "theoretical chemistry".

12.4.1 The variation theorem

Given an acceptable, normalized function ϕ, if the lowest eigenvalue of the Hamiltonian $\hat{H}$ is ε_0, then

$$
W = \int \phi^\star \hat{H} \phi \, d\tau \geq \varepsilon_0,
$$

(105)

which is the variation theorem. This relation may be a bit surprising, as the function ϕ can be any normalized function of the coordinates of the system that satisfies the conditions for an acceptable wavefunction. Although the function ϕ is arbitrary, the more wisely it is chosen the more closely will W approach ε_0, the true energy of the ground state of the system. Thus, if ϕ were chosen to be the correct ground-state wavefunction, ψ_0, Eq. (105) would yield the energy of the ground state.

As a simple proof of the variational theorem, consider the case in which $\phi \neq \psi_0$. The variational function can be expanded in terms of the complete set of normalized, orthogonal functions ψ_n. Thus,

$$\phi = \sum_n a_n \psi_n \ , \tag{106}$$

with

$$\sum_n a_n^\star a_n = 1. \tag{107}$$

Substitution of this expansion in the integral for W [Eq. (103)] leads to the equation

$$W = \sum_n \sum_{n'} a_n^\star a_{n'} \int \psi_n^\star \hat{H} \psi_{n'} \, d\tau = \sum_n a_n^\star a_n \varepsilon_n \ , \tag{108}$$

as the functions ψ_n satisfy the equation

$$\hat{H} \psi_n = \varepsilon_n \psi_n \ . \tag{109}$$

The energy of the ground state, ε_0 is then subtracted from each side of Eq. (108) to yield

$$W - \varepsilon_0 = \sum_n a_n^\star a_n (\varepsilon_n - \varepsilon_0), \tag{110}$$

where Eq. (107) has been employed.

As ε_n is greater than ε_0 for all values of n, and the coefficients $a_n^\star a_n$ are of course positive or zero, the right-hand side of Eq. (108) is positive or zero. It has thus been shown that W is always an upper limit to ε_0, the true energy of the ground state of the system; thus,

$$W \geq \varepsilon_0. \tag{111}$$

Equation (111) is a statement of the variational theorem.

If several variation functions, $\phi_1, \phi_2, \phi_3, \ldots$ are chosen and the corresponding values of the variational energy, $W_1, W_2, W_3, \ldots$ are calculated from Eq. (103), each of these values of W will be greater than the true energy of the ground state, ε_0. Thus, the lowest one is nearest ε_0. In many cases it is convenient to employ a variational function that contains one or more parameters. Then the resulting expression for W can be minimized with respect to the parameters.

12.4.2 An example: The particle in a box

The one-dimensional problem of the particle in a box was treated in Section 5.4.1. Exact solutions were obtained, which were then restricted by the boundary conditions $\psi(0) = \psi(\ell) = 0$. If the exact solutions were not known, the problem

might be attacked with the use of a simple variation function which satisfies the boundary conditions. As an example, take

$$\phi = \mathcal{N}x(\ell - x),$$ (112)

which vanishes at each side of the box. The normalization constant can be evaluated from the relation

$$\int_0^\ell \phi^2 \, d\phi = \mathcal{N}^2 \int_0^\ell x^2(\ell - x)^2 \, dx = \mathcal{N}^2 \ell^5/30,$$ (113)

which leads to $\mathcal{N} = \sqrt{30/\ell^5}$ (problem 21).

In the interior of the box $V(x) = 0$ and the Hamiltonian is simply

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2};$$ (114)

then, Eq. (105) becomes

$$W = -\frac{h^2}{8\pi^2 m}\frac{30}{\ell^5}\int_0^\ell x(\ell - x)\frac{d^2}{dx^2}[x(\ell - x)] \, dx = \frac{5h^2}{4\pi^2 m\ell^2}.$$ (115)

The true energy of the ground state was found in Section 5.4.1 to be equal to $\varepsilon_1 = h/8m\ell^2$. Its comparison with Eq. (108) is

$$W = \frac{10}{\pi^2}\left(\frac{h^2}{8m\ell^2}\right) > \frac{h^2}{8m\ell^2} = \varepsilon_1$$ (116)

and the error is in this case approximately 2%.

Although the variational theorem was expressed in Eq. (111) with respect to the ground state of the system, it is possible to apply it to higher, so-called excited, states. As an example, consider again the particle in a box. In Section 5.4.2 a change in coordinate was made in order to apply symmetry considerations. Thus, the potential function was written as

$$V(x) = \begin{cases} 0, & -\frac{1}{2}\ell < x < \frac{1}{2}\ell \\ \infty, & x = -\frac{1}{2}\ell, \frac{1}{2}\ell \end{cases}.$$ (117)

It is an even function of x and the solutions can be classified as even or odd (Gerade or Ungerade), as given in Eqs. (5-72) and (5-73). It should be noted that the ground state in this case is symmetric. It is then of interest to choose a variation function that is antisymmetric (u) to determine the energy of the first excited state $n = 2$, which is antisymmetric. As an example, consider the variational function

$$\phi = \mathcal{N}x(\ell/2 + x)(\ell/2 - x) = \mathcal{N}x\left[(\ell^2/4) - x^2\right],$$ (118)

which is Ungerade. The normalization leads to the factor $\mathcal{N} = \sqrt{840/\ell^7}$ (see problem 21). The variational energy is then given by

$$W = \frac{42}{\pi^2}\left(\frac{h^2}{8m\ell^2}\right) > 4\left(\frac{h^2}{8m\ell^2}\right), \tag{119}$$

where on the right-hand side the factor $4 = n^2$ specifies the first excited state, $n = 2$.

12.4.3 Linear variation functions

It is often convenient to employ a variation function that it is a linear combination of suitably chosen functions χ_n; thus,

$$\phi = \sum_n^m c_n \chi_n. \tag{120}$$

It should be noted that the functions χ_n need not necessarily form an orthonormal set. The linearly independent coefficients c_n can be considered to be variable parameters that are determined by minimization of the variational energy, W. If the functions χ_n are not orthonormal, Eq. (105) can be rewritten in the form

$$W = \frac{\int \phi^\star \hat{H}\phi \, d\tau}{\int \phi^\star \phi \, d\tau} \geq \varepsilon_0. \tag{121}$$

The variational energy is then given by

$$W = \frac{\sum_n^m \sum_n^m c_{n'}^\star c_n \left\langle n' \left| \hat{H} \right| n \right\rangle}{\sum_n^m \sum_{n'}^m c_{n'}^\star c_n \left\langle n' | n \right\rangle}, \tag{122}$$

where $\langle n'|\hat{H}|n\rangle \equiv \int \chi_{n'}^\star \hat{H}\chi_n \, d\tau$ and $\langle n'|n\rangle \equiv \int \chi_{n'}^\star \chi_n \, d\tau$. The partial derivative of Eq. (122) with respect to a particular coefficient $c_k^\star$ leads to the relation

$$\frac{\partial W}{\partial c_k^\star} \sum_{n'}^m \sum_n^m c_{n'}^\star c_n \left\langle n' | n \right\rangle + W \frac{\partial}{\partial c_k^\star}\left(\sum_{n'}^m \sum_n^m c_{n'}^\star c_n \left\langle n' | n \right\rangle\right)$$

$$= \frac{\partial}{\partial c_k^\star}\left(\sum_{n'}^m \sum_n^m c_{n'}^\star c_n \left\langle n' \left| \hat{H} \right| n \right\rangle\right). \tag{123}$$

If the coefficients are independent, the condition $\partial W/\partial c_k^{\star} = 0$ can be imposed for each value of the index k from 1 to m.* Then,

$$W \sum_n^m c_n \langle k|n \rangle = \sum_n^m c_n \left\langle k|\hat{H}|n \right\rangle, \tag{124}$$

or,

$$\sum_n^m c_n \left(\left\langle k \left| \hat{H} \right| n \right\rangle - W \langle k|n \rangle \right) = 0. \tag{125}$$

Equation (125) applies for all values of the index $k = 1, 2, \ldots, m$. It is a set of m simultaneous, homogeneous, linear equations for the unknown values of the coefficients c_n. Following Cramer's rule (Section 7.8), a nontrivial solution exists only if the determinant of the coefficients vanishes. Thus, the secular determinant takes the form

$$\left| \left\langle k|\hat{H}|n \right\rangle - W \langle k|n \rangle \right| = 0. \tag{126}$$

In the case in which the functions χ_n are orthonormal, $\langle k|n \rangle = \delta_{k,n}$ and the variational energies W are just the eigenvalues of the matrix $\langle k|\hat{H}|n \rangle$. According to the variational theorem, the lowest root of Eq. (124) is the upper limit to the true energy of the ground state of the system, ε_0.

12.4.4 Linear combinations of atomic orbitals (LCAO)

It is often convenient to use atomic orbitals as the basis for molecular-orbital calculations. Thus, in Eq. (120) the atomic orbitals χ_n can serve as the basis, and a given molecular system can be described as a linear combination of such functions. Clearly, the simplest molecule is diatomic and the appropriate molecular orbitals can be formed as linear combinations, viz.

$$\phi = c_a \chi_a + c_b \chi_b, \tag{127}$$

where the functions χ_a and χ_b are the atomic orbitals associated with the atoms a and b, respectively. The coefficients in this linear combination can be determined by application of the variational principle, as illustrated in the following derivation. This method, which is of general application to polyatomic molecules, is referred to in the scientific literature as the method LCAO.

*Note that the equivalent condition $\partial W/\partial c_k = 0$ yields a set of equations which is simply the complex conjugate of Eq. (122).

A given application of the LCAO method is characterized by a set of integrals. For a diatomic molecule they are

$$H_{aa} = \left\langle \chi_a \left| \hat{H} \right| \chi_a \right\rangle, \tag{128}$$

$$H_{bb} = \left\langle \chi_b \left| \hat{H} \right| \chi_b \right\rangle, \tag{129}$$

$$H_{ab} = \left\langle \chi_a \left| \hat{H} \right| \chi_b \right\rangle = \left\langle \chi_b \left| \hat{H} \right| \chi_a \right\rangle \tag{130}$$

and

$$S = \langle \chi_a | \chi_b \rangle. \tag{131}$$

The last is known as the overlap integral, as it is determined by the volume common to the atomic orbitals a and b at a given internuclear distance. In general, $S < 1$, an integral that is often set equal to zero in approximate calculations.

The use of a linear variation function was summarized in the previous section. For the example of a diatomic molecule the set of simultaneous equations [Eq. (125)] becomes

$$c_a(H_{aa} - W) + c_b(H_{ab} - SW) = 0 \tag{132}$$

and

$$c_a(H_{ab} - SW) + c_b(H_{bb} - W) = 0. \tag{133}$$

The expansion of the corresponding secular determinant leads to the relation

$$(H_{aa} - W)(H_{bb} - W) - (H_{ab} - SW)^2 = 0, \tag{134}$$

which is quadratic in W. To evaluate the coefficients c_a and c_b the two values of W are substituted successively in either Eq. (132) or Eq. (133), as described in the classical example of Section 7.11. However, as these equations are homogeneous, only the ratio of the coefficients can be determined. The supplementary condition necessary to resolve this ratio is provided by normalization of the functions ϕ. The atomic orbitals are assumed to be normalized, or can be made so. Thus, normalization of the molecular orbital in this case can be expressed by

$$\langle \phi | \phi \rangle = c_a^2 + c_b^2 + 2c_a c_b S = 1. \tag{135}$$

This example of the LCAO method, as applied to diatomic molecules, is perfectly general. However, it is simpler for homonuclear diatomics, for which $H_{aa} = H_{bb}$. Then, Eq. (134) becomes

$$(H_{aa} - W)^2 - (H_{ab} - SW)^2 = 0, \tag{136}$$

whose roots are

$$W_{\pm} = \frac{H_{aa} \pm H_{ab}}{1 \pm S}. \tag{137}$$

Thus, two values can be evaluated, W_+ and W_-, according to the signs in Eq. (137). If the appropriate integrals are known, these quantities can be calculated for a given interatomic distance in the diatomic molecule. As indicated above the successive substitution of the two values W_+ and W_- yields

$$c_a \mp c_b = 0. \tag{138}$$

With the application of the normalization condition given by Eq. (135), the coefficients in Eq. (138) are found as

$$c_a = c_b = \frac{1}{\sqrt{2(1+S)}} \tag{139}$$

and

$$c_a = -c_b = \frac{1}{\sqrt{2(1-S)}}, \tag{140}$$

respectively, depending on whether the upper or lower sign is employed in the preceding equations. The variational wavefunctions are then of the form

$$\phi_+ = \frac{1}{\sqrt{2(1+S)}} (\chi_a + \chi_b) \tag{141}$$

and

$$\phi_- = \frac{1}{\sqrt{2(1-S)}} (\chi_a - \chi_b), \tag{142}$$

with the corresponding energies given by Eq. (137).

The simplest diatomic species is the molecular ion H_2^+. Its electronic kinetic energy is given by a single term, as that of the protons can be neglected (see Section 12.1). The interaction of the electron with each proton is expressed by Coulomb's law, as is the proton–proton repulsion. With the use of the resulting Hamiltonian the integrals defined by Eqs. (128)–(130) can be evaluated exactly, with the functions χ_a and χ_b the 1s orbitals of atomic hydrogen (see Section 6.6). The resulting energies calculated with the use of Eq. (137) are represented in Fig. 3, as it is the lowest energy level of H_2^+ that is of interest. Clearly, the curve of W_+ exhibits a minimum and, if the corresponding state ϕ_+ is "occupied" by the electron, a stable species can exist. This orbital is then referred to as a bonding orbital. On the other hand the curve of W_- vs. internuclear distance has no minimum, so its occupation by the electron cannot
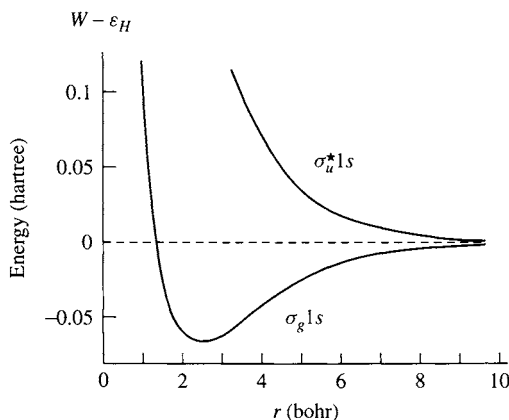
Fig. 3   Variational energy of H_2^+ as a function of internuclear distance.
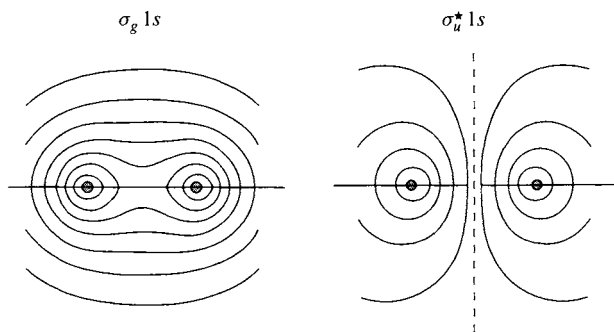
Fig. 4   The wavefunctions $\phi_+(\sigma_g 1s)$ and $\phi_-(\sigma_u^\star 1s)$ for H_2^+. Note that the wavefunction ϕ_- has opposite signs on either side of the dotted line.

result in bonding of the two protons. Thus, the orbital ϕ_- is an antibonding orbital and, if occupied by the electron, the ion is in a so-called excited state.

It should be noted (Fig. 4) that if the bonding orbital, designated σ_g 1s, is occupied, the probability of finding the electron in the region between the nuclei is relatively important. On the other hand, for the antibonding orbital $(\sigma_u^\star 1s)$ there is a nodal plane that passes through the center of symmetry of the ion. It is perpendicular to the internuclear axis. Thus, it can be concluded that it is the electronic probability density that is responsible for bonding. Although this conclusion is correct and can be generalized, the wavefunctions obtained by the LCAO method are usually far from the true functions. Furthermore, although the lower energy level as calculated by the method is an upper limit

to the true energy of the ground state, the variation theorem in its simplest form says nothing about the value of the upper energy level.

The limitation of the above analysis to the case of homonuclear diatomic molecules was made by imposing the relation $H_{aa} = H_{bb}$, as in this case the two nuclei are identical. More generally, $H_{aa} \neq H_{bb}$, and for heteronuclear diatomic molecules Eq. (134) cannot be simplified (see problem 25). However, the polarity of the bond can be estimated in this case. The reader is referred to specialized texts on molecular orbital theory for a development of this application.

12.4.5 The Hückel approximation*

One of the most popular of the semi-empirical LCAO methods is that of Hückel. It is applicable to planar molecules which have π-electron systems. The "delocalization" of these systems, as treated by this method, has particular chemical significance. The traditional application is to the benzene molecule. Historically, different "structures" of this molecule were suggested by Kékulé[†] and by Dewar[‡] that are described in virtually all textbooks of organic chemistry. These structures represented the first efforts to represent the delocalization of the π orbitals in such systems. In the present context the delocalization can be better specified with the use of the method of Hückel.

Consider first the ethylene molecule. Its geometrical structure is shown in Fig. 5. The s, p_y and p_z atomic orbitals of the carbon atoms are assumed to be hybridized. This sp^2 hybridization implies H–C–H bond angles of $120°$, approximately in agreement with experimental results. The remaining two p_x orbitals are thus available to contribute to a π-electron system in the molecule. Here again, the two linear combinations of atomic orbitals yield bonding and
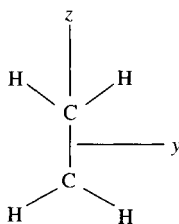
Fig. 5   The ethylene molecule showing only the single (σ) bonds.

*Erich Hückel, German chemist (1896–1980).

†August Kékulé von Stradonitz, German chemist (1829–1896).

‡Sir James Dewar, British chemist and physicist (1842–1923).

antibonding possibilities. The LCAO method presented in the previous section can be employed to obtain a semiquantitative description of the electronic structure.

For a homonuclear diatomic system in the Hückel approximation the integrals given by Eqs. (128)–(131) take the simple forms $H_{aa} = H_{bb} = \alpha$, $H_{ab} = H_{ba} = \beta$ and $S = 0$. The atomic orbitals involved, χ_a and χ_b, are of course the p_x orbitals of carbon atoms a and b, respectively. The resulting secular determinant is then simply

$$\begin{vmatrix} \alpha - W & \beta \\ \beta & \alpha - W \end{vmatrix} = 0, \tag{143}$$

which can be written as

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0, \tag{144}$$

with $x = (\alpha - W)/\beta$. As the roots of Eq. (144) are $x = \pm 1$, the energy levels are determined by $W = \pm(\alpha - \beta)$, as shown in Fig. 6. The corresponding approximate molecular orbitals are also indicated, with the normalizing factor $1/\sqrt{2}$. The coefficients were evaluated as illustrated in the previous section [Eqs. (139) and (140)]. Here again, the occupied lower level will result in an increased electronic density in the region between the nuclei, although the upper level, if occupied, will not.

As the ethylene molecule contains a total of 16 electrons, there are but two that are available to occupy the π system. Two pairs of electrons are assumed to fill the two 1s atomic orbitals of the carbon atoms. Five pairs of electrons contribute to the σ orbitals that represent single bonds in Fig. 5. Thus, the two
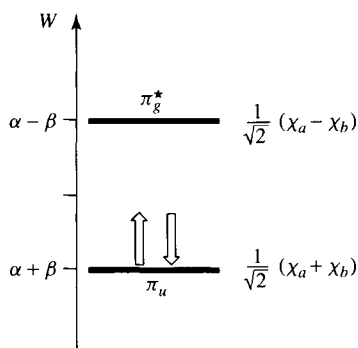
Fig. 6   The π energy levels of ethylene. The asterisk identifies the antibonding orbital, while the two arrows represent the two electrons with antiparallel spins corresponding to the configuration of the ground state (see text).

remaining can occupy the molecular orbitals established by the LCAO method, as outlined above. For the ground state of the molecule these two electrons, with antiparallel spins following the Pauli principle, occupy the lower energy level, as shown in Fig. 6. Excited states can be described by promoting one or both electrons to the higher energy level.

The ethylene molecule in its equilibrium configuration is of symmetry $\mathscr{D}_{2h}$. Its symmetry can then be used to simplify the development of the appropriate molecular orbitals. Thus, the characters of the reducible representation of the π orbitals can be determined, as given in Table 1. With the application of the magic formula (see Section 8.9) it is easy to establish the reduction of the representation for the two π orbitals, namely, $\Gamma_\pi = B_{2g} \oplus B_{3u}$. The appropriate linear combination of atomic orbitals can then be found with the use of the projection operator technique. However, as only two π orbitals are involved, it is sufficient to consider a subgroup of $\mathscr{D}_{2h}$ that is of order two and that includes an operation that exchanges the labels (a,b) on the atomic orbitals. The group $\mathscr{S}_2 \equiv G_i$ is appropriate, as it preserves the g–u property of the molecular orbitals. The characters for this group, as given in Appendix VIII, are in this case just the coefficients of the atomic wavefunctions, χ_a and χ_b. The notation for the irreducible representations shown in Fig. 6 is identified in Table 2.

In conjugated systems the π orbitals become delocalized. The classical example is the butadiene molecule, that is usually described by the formula $CH_2 = CH - CH = CH_2$. This representation of the molecule does not take into consideration the delocalization of the π-electron system formed by the four

Table 1   Symmetry operations of the group $\mathscr{D}_{2h}$ and the characters of Γ_π.

$\mathscr{D}_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
χ_π	2	-2	0	0	0	0	2	-2

Table 2   The character table for the group $\mathscr{S}_2 \equiv G_i$ and the characters of Γ_π.

$\mathscr{S}_2 \equiv G_i$	E	i
$A_g \equiv \pi_g^*$	1	1
$A_u \equiv \pi_u$	1	-1
χ_π	2	0

available p orbitals of the carbon atoms. To treat this problem with the use
of the method of Hückel, it is sufficient to write the secular determinant as a
function of the integrals α and β and to introduce the approximations indicated
above. In addition to the often poor approximation $S = 0$, it is customary to
assume that there is no interaction between nonadjacent atomic orbitals. Thus,
the integrals of the type H_{ab} are set equal to zero if the atoms a and b are not
adjacent. The butadiene molecule provides a good example of this method.

Butadiene exists in two equilibrium structural isomers. They are represented
in Fig. 7. However, with the usual Hückel approximation these two structures
cannot be distinguished, as interactions between nonadjacent atoms have been
neglected. Thus for either isomer, or even a hypothetical structure in which
the carbon skeleton is linear, the secular determinant is the same, namely,

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0, \tag{145}$$

where $x = (\alpha - W)/\beta$, as before. The roots of this equation can be found by
direct expansion of the determinant (see problem 26). However, the application
of group theory allows the determinant to be factored, a technique that is often
useful in more complicated problems.

Consider the *trans* isomer of butadiene. Both the symmetry operations that
define the group $\mathscr{C}_{2h}$ and the characters of the representation Γ_π are given
in Table 3. The reduction of this representation leads to $\Gamma_\pi = 2B_g \oplus 2A_u$.
Thus, two linear combinations of the atomic orbitals can be constructed of
symmetry B_g and two others of symmetry A_u. Their use will factor the secular
determinant into two 2×2 blocks, as described in the following paragraph.

As indicated above, the conventional structure of *trans* butadiene does
not include the delocalization of the π-electron system. This effect can be
analyzed, at least approximately, by application of the Hückel method. As
in the example of ethylene, each carbon atom has an available p orbital–the

(a)   (b)
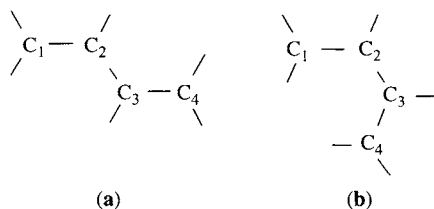
Fig. 7   The equilibrium structures of butadiene: *trans* (a) and *cis* (b). Only the σ
bonds are shown.

Table 3   The symmetry operations
of the group $\mathcal{G}'_{2h}$ and the characters
of Γ_π.

$\mathcal{G}'_{2h}$	E	C_2	i	σ_h
χ_π	4	0	0	-4

p_z orbitals in this case. With the use of the projection operator, the linear combinations of the four atomic orbitals can be constructed, *viz.*

$$B_g \begin{cases} \frac{1}{\sqrt{2}}(\chi_1 - \chi_4) \\[2mm] \frac{1}{\sqrt{2}}(\chi_2 - \chi_3) \end{cases} \tag{146}$$

and

$$A_u \begin{cases} \frac{1}{\sqrt{2}}(\chi_1 + \chi_4) \\[2mm] \frac{1}{\sqrt{2}}(\chi_2 + \chi_3) \end{cases} \tag{147}$$

where the atomic numbering is as shown in Fig. 7. The two diagonal blocks of the factored secular determinant are then of the form

$$B_g : \begin{vmatrix} x & 1 \\ 1 & x-1 \end{vmatrix} = 0 \tag{148}$$
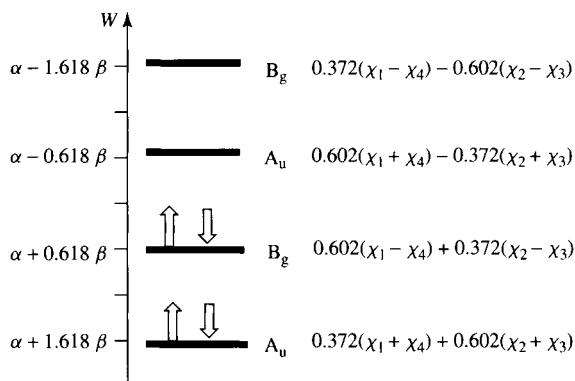
and

$$A_u : \begin{vmatrix} x & 1 \\ 1 & x+1 \end{vmatrix} = 0. \tag{149}$$

The roots of Eqs. (148) and (149) are given by $x = (1 \pm \sqrt{5})/2$ and $x = (-1 \pm \sqrt{5})/2$, respectively.* The results of the above analysis are summarized in Fig. 8.

The benzene molecule in its equilibrium configuration is planar. Its symmetry is described by the point group $\mathcal{D}_{6h}$ as shown in Fig. 8-1(c). The delocalized π system is represented there by dotted lines. The six p_z orbitals contribute to the π system, as simply described by the Hückel approximation. The reduction $\Gamma_\pi = B_{2g} \oplus E_{1g} \oplus A_{2u} \oplus E_{2u}$ can be found as in the previous examples. However, to construct the appropriate linear combinations of the π orbitals, it is sufficient to choose a subgroup of $\mathcal{D}_{6h}$ whose symmetry operations permute all

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*The quantity $(1 + \sqrt{5})/2 = 1.62$ is known as the golden ratio. It appears often in works of art, as for example to determine the approximate ratio of the height to width of a classic painting – and this page.

W

$\alpha - 1.618\,\beta$ ⎯⎯⎯ B_g $0.372(\chi_1 - \chi_4) - 0.602(\chi_2 - \chi_3)$

$\alpha - 0.618\,\beta$ ⎯⎯⎯ A_u $0.602(\chi_1 + \chi_4) - 0.372(\chi_2 + \chi_3)$

$\alpha + 0.618\,\beta$ ⇑ ⇓ ⎯⎯⎯ B_g $0.602(\chi_1 - \chi_4) + 0.372(\chi_2 - \chi_3)$

$\alpha + 1.618\,\beta$ ⇑ ⇓ ⎯⎯⎯ A_u $0.372(\chi_1 + \chi_4) + 0.602(\chi_2 + \chi_3)$

Fig. 8 The energy levels and wavefunctions for the π-orbitals of *trans* butadiene. The arrows define the electron configuration of the ground state.
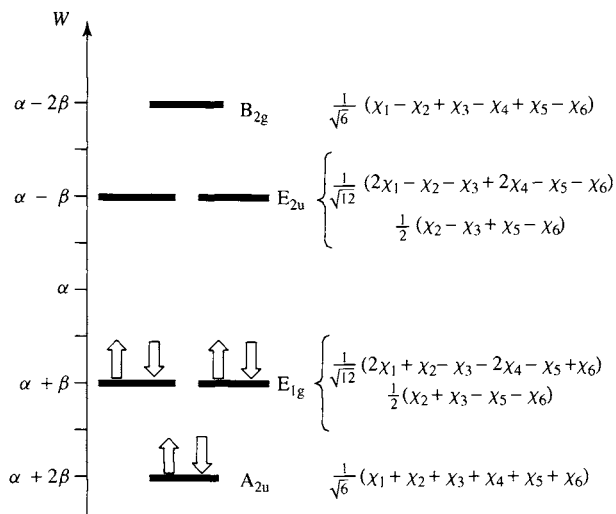
six of the p_z atomic orbitals. For example, the choice of the group G'_6 leads to the equivalent reduction $\Gamma_\pi = A \oplus B \oplus E_1 \oplus E_2$. The character table for this group (see Appendix VII) contains complex elements of the type $\varepsilon = exp(2\pi i/6)$. The application of the projection operator will then yield linear combinations such as

$$E_1 : \begin{cases} \chi_1 + \varepsilon\chi_2 - \varepsilon^\star\chi_3 - \chi_4 - \varepsilon\chi_5 + \varepsilon^\star\chi_6 \\ \chi_1 + \varepsilon^\star\chi_2 - \varepsilon\chi_3 - \chi_4 - \varepsilon^\star\chi_5 + \varepsilon\chi_6 \end{cases} \tag{150}$$

As $\varepsilon + \varepsilon^\star = 1$ in this case, the equivalent linear combinations that involve only real coefficients can be found by adding and subtracting the two functions given in Eq. (150). For the π system of benzene the normalized linear combinations of p_z can then be determined, as given in Fig. 9. It is easily verified that these linear combinations are orthonormal. Furthermore, they result in the desired factoring of the secular determinant. The construction of the energy level diagram is then relatively straightforward (problem 29).

The use of group theory to factor the secular determinant is of increasing importance as the molecule becomes larger, providing of course that it maintains a relatively high symmetry. With the use of available computer programs the advantages of this approach may seem to be of less interest. However, it should be understood that symmetry arguments lead to visualization of the molecular orbitals, as now represented by a number of programs. Their comprehension requires the basic understanding of the elements of group theory, as outlined above.

As a final exercise for the reader, consider the naphthalene molecule (symmetry $\mathscr{D}_{2h}$), as shown in Fig. 10. Application of the Hückel method leads to a 10×10 secular determinant (see problem 30). However, with the application

$$W$$

$$\alpha - 2\beta \quad \blacksquare \quad B_{2g} \quad \tfrac{1}{\sqrt{6}}(\chi_1 - \chi_2 + \chi_3 - \chi_4 + \chi_5 - \chi_6)$$

$$\alpha - \beta \quad \blacksquare \quad \blacksquare \quad E_{2u} \quad \begin{cases} \tfrac{1}{\sqrt{12}}(2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6) \\ \tfrac{1}{2}(\chi_2 - \chi_3 + \chi_5 - \chi_6) \end{cases}$$

$$\alpha$$

$$\alpha + \beta \quad \Uparrow \Downarrow \quad \Uparrow \Downarrow \quad E_{1g} \quad \begin{cases} \tfrac{1}{\sqrt{12}}(2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6) \\ \tfrac{1}{2}(\chi_2 + \chi_3 - \chi_5 - \chi_6) \end{cases}$$

$$\alpha + 2\beta \quad \Uparrow \Downarrow \quad A_{2u} \quad \tfrac{1}{\sqrt{6}}(\chi_1 + \chi_2 + \chi_3 + \chi_4 + \chi_5 + \chi_6)$$

Fig. 9 The energy levels and the LCAO orbitals for the π-electron system of benzene. The electron configuration as represented by the arrows is that of the ground state of the molecule.
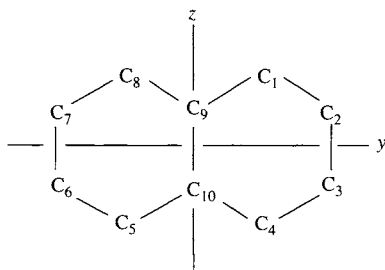
Fig. 10 The naphthalene molecule. Only the σ bonds are represented.

of the method outlined above the reduced representation takes the form $\Gamma_\pi = 2B_{1g} \oplus 3B_{2g} \oplus 2A_u \oplus 3B_{3u}$. The appropriate linear combination of p_x orbitals can be constructed directly with the use of the projection operator.

PROBLEMS

1. Verify Eq. (10).

2. Develop the series of relations given by Eqs. (18)–(. . .).

3. Derive Eq. (26).

4. Derive Eq. (30).

5. Derive Eq. (35).

6. Make the indicated substitutions to obtain Eq. (44).

7. Verify Eq. (47).

8. Derive Eq. (48).

9. Derive the secular equations, Eq. (58).

10. Verify Eq. (62).

11. Verify Eq. (69).

12. Carry out the separation of variables to obtain Eq. (72).

13. Derive Eq. (76).

14. Make the indicated substitution to obtain Eq. (85).

15. Derive Eqs. (86) and (87).

16. Integrate Eq. (87) as indicated.

17. Derive the relation between the Einstein coefficients [Eq. (94)].

18. Evaluate the transition moments in Eq. (99) for $v' = v \pm 1$.

<div align="right">Ans. See Appendix IX.</div>

19. Verify the selection rules for the hydrogen atom as given in the last paragraph of Section 12.3.3.

20. Prove the variation theorem [Eq. (111)].

21. Calculate the normalization factor in Eqs. (113) and (118).

22. Verify Eq. (115).

23. Verify Eq. (119).

24. Derive the secular determinant [Eq. (126)].

25. Show that the variational energies of a homonuclear diatomic molecule are given in the LCAO approximation by Eq. (137) and that the corresponding wavefunctions are as indicated in Eqs. (141) and (142).

26. Find the roots of Eq. (145) by direct expansion of the determinant and compare them with the results given below, Eq. (149).

27. Show that $\Gamma_\pi = 2B_g \oplus 2A_u$ for the π-electron system in *trans* butadiene.

28. Verify Eqs. (146) and (147).

29. Apply the projection-operator method to obtain the molecular orbital expression shown in Fig. 9 and verify the energies.

30. Set up the secular determinant for the π-system of naphthalene and factor it as explained in the last paragraph of this chapter.