6 Computational chemistry

In this chapter we extend the description of the electronic structure of molecules presented in Chapter 5 by introducing methods that harness the power of computers to calculate electronic wavefunctions and energies. These calculations are among the most useful tools used by chemists for the prediction of molecular structure and reactivity. The computational methods we discuss handle the electron–electron repulsion term in the Schrödinger equation in different ways. One such method, the Hartree–Fock method, treats electron–electron interactions in an average and approximate way. This approach typically requires the numerical evaluation of a large number of integrals. Semiempirical methods set these integrals to zero or to values determined experimentally. In contrast, *ab initio* methods attempt to evaluate the integrals numerically, leading to a more precise treatment of electron–electron interactions. Configuration interaction and Møller–Plesset perturbation theory are used to account for electron correlation, the tendency of electrons to avoid one another. Another computational approach, density functional theory, focuses on electron probability densities rather than on wavefunctions. The chapter concludes by comparing results from different electronic structure methods with experimental data and by describing some of the wide range of chemical and physical properties of molecules that can be computed.

The field of **computational chemistry**, the use of computers to predict molecular structure and reactivity, has grown in the past few decades due to the tremendous advances in computer hardware and to the development of efficient software packages. The latter are now applied routinely to compute molecular properties in a wide variety of chemical applications, including pharmaceuticals and drug design, atmospheric and environmental chemistry, nanotechnology, and materials science. Many software packages have sophisticated graphical interfaces that permit the visualization of results. The maturation of the field of computational chemistry was recognized by the awarding of the 1998 Nobel Prize in Chemistry to J.A. Pople and W. Kohn for their contributions to the development of computational techniques for the elucidation of molecular structure and reactivity.

The central challenge

The goal of electronic structure calculations in computational chemistry is the solution of the electronic Schrödinger equation, $\hat{H}\Psi = E\Psi$, where E is the electronic energy and Ψ is the many-electron wavefunction, a function of the coordinates of all the electrons and the nuclei. To make progress, we invoke at the outset the Born–Oppenheimer approximation and the separation of electronic and nuclear motion (Chapter 5). The electronic hamiltonian $\hat{H}$ is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i^{N_e}\nabla_i^2 - \sum_i^{N_e}\sum_I^{N_n}\frac{Z_I e^2}{4\pi\varepsilon_0 r_{Ii}} + \tfrac{1}{2}\sum_{i\neq j}^{N_e}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} \tag{6.1a}$$

where

- the first term is the kinetic energy of the N_e electrons;
- the second term is the potential energy of attraction between each electron and each of the N_n nuclei, with electron i at a distance r_{Ii} from nucleus I of charge $Z_I e$;
- the final term is the potential energy of repulsion between two electrons separated by r_{ij}.

The factor of $\frac{1}{2}$ in the final sum ensures that each repulsion is counted only once. The combination $e^2/4\pi\varepsilon_0$ occurs throughout computational chemistry, and we denote it j_0. Then the hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i^{N_e}\nabla_i^2 - j_0\sum_i^{N_e}\sum_I^{N_n}\frac{Z_I}{r_{Ii}} + \tfrac{1}{2}j_0\sum_{i\neq j}^{N_e}\frac{1}{r_{ij}} \tag{6.1b}$$

We shall use the following labels:

Species	Label	Number used
Electrons	i and $j = 1, 2, \ldots$	N_e
Nuclei	$I = \mathrm{A}, \mathrm{B}, \ldots$	N_n
Molecular orbitals, ψ	$m = a, b, \ldots$	
Atomic orbitals used to construct the molecular orbitals (the 'basis'), χ	$o = 1, 2, \ldots$	N_b

Another general point is that the theme we develop in the sequence of *illustrations* in this chapter is aimed at showing explicitly how to use the equations that we have presented, and thereby give them a sense of reality. To do so, we shall take the simplest possible many-electron molecule, dihydrogen (H_2). Some of the techniques we introduce do not need to be applied to this simple molecule, but they serve to illustrate them in a simple manner and introduce problems that successive sections show how to solve. One consequence of choosing to develop a story in relation to H_2, we have to confess, is that not all the *illustrations* are actually as brief as we would wish; but we decided that it was more important to show the details of each little calculation than to adhere strictly to our normal use of the term 'brief'.

● A BRIEF ILLUSTRATION

The notation we use for the description of H_2 is shown in Fig. 6.1. For this two-electron ($N_e = 2$), two-nucleus ($N_n = 2$) molecule the hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - j_0\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} + \frac{1}{r_{A2}} + \frac{1}{r_{B2}}\right) + \frac{j_0}{r_{12}}$$

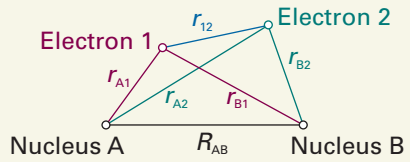


Fig. 6.1 The notation used for the description of molecular hydrogen, introduced in the *brief illustration* preceding Section 6.1 and used throughout the text.

To keep the notation simple, we introduce the one-electron operator

$$h_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - j_0\left(\frac{1}{r_{Ai}} + \frac{1}{r_{Bi}}\right) \tag{6.2}$$

which should be recognized as the hamiltonian for electron i in an H_2^+ molecule-ion. Then

$$\hat{H} = h_1 + h_2 + \frac{j_0}{r_{12}} \tag{6.3}$$

We see that the hamiltonian for H_2 is essentially that of each electron in an H_2^+-like molecule-ion but with the addition of the electron–electron repulsion term. ●

It is hopeless to expect to find analytical solutions with a hamiltonian of the complexity of that shown in eqn 6.1, even for H_2, and the whole thrust of computational chemistry is to formulate and implement numerical procedures that give ever more reliable results.

6.1 The Hartree–Fock formalism

The electronic wavefunction of a many-electron molecule is a function of the positions of all the electrons, $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)$. To formulate one very widely used approximation, we build on the material in Chapter 5, where we saw that in the MO description of H_2 we supposed that each electron occupies an orbital and that the overall wavefunction can be written $\psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)\ldots$. Note that this **orbital approximation** is quite severe and loses many of the details of the dependence of the wavefunction on the relative locations of the electrons. We do the same here, with two small changes of notation. To simplify the appearance of the expressions we write $\psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)\ldots$ as $\psi(1)\psi(2)\ldots$. Next, we suppose that electron 1 occupies a molecular orbital ψ_a with spin α, electron 2 occupies the same orbital with spin β, and so on, and hence write the many-electron wavefunction Ψ as the product $\Psi = \psi_a^\alpha(1)\psi_a^\beta(2)\ldots$. The combination of a molecular orbital and a spin function, such as $\psi_a^\alpha(1)$, is the spinorbital introduced in Section 4.4; for example, the spinorbital ψ_a^α should be interpreted as the product of the spatial wavefunction ψ_a and the spin state α, so $\psi_a^\alpha(1) = \psi_a(1)\alpha(1)$, and likewise

for the other spinorbitals. We shall consider only closed-shell molecules but the techniques we describe can be extended to open-shell molecules.

A simple product wavefunction does not satisfy the Pauli principle and change sign under the interchange of any pair of electrons (Section 4.4). To ensure that the wavefunction does satisfy the principle, we modify it to a sum of all possible permutations, using plus and minus signs appropriately:

$$\Psi = \psi_a^\alpha(1)\psi_a^\beta(2)\cdots\psi_z^\beta(N_e) - \psi_a^\alpha(2)\psi_a^\beta(1)\cdots\psi_z^\beta(N_e) + \cdots \tag{6.4}$$

There are $N_e!$ terms in this sum, and the entire sum can be represented by the Slater determinant (Section 4.4):

$$\Psi = \frac{1}{\sqrt{N_e!}}\begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) & \cdots & \cdots & \psi_z^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) & \cdots & \cdots & \psi_z^\beta(2) \\ \vdots & \vdots & & & \vdots \\ \vdots & \vdots & & & \vdots \\ \psi_a^\alpha(N_e) & \psi_a^\beta(N_e) & \cdots & \cdots & \psi_z^\beta(N_e) \end{vmatrix} \tag{6.5a}$$

The factor $1/\sqrt{N_e!}$ ensures that the wavefunction is normalized if the component molecular orbitals ψ_m are normalized. To save the tedium of writing out large determinants, the wavefunction is normally written by using only its principal diagonal:

$$\Psi = (1/N_e!)^{1/2}|\psi_a^\alpha(1)\psi_a^\beta(2)\cdots\psi_z^\beta(N_e)| \tag{6.5b}$$

A BRIEF ILLUSTRATION

The Slater determinant for H_2 ($N_e = 2$) is

$$\Psi = \frac{1}{\sqrt{2}}\begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) \end{vmatrix}$$

$$= \frac{1}{\sqrt{2}}\{\psi_a^\alpha(1)\psi_a^\beta(2) - \psi_a^\beta(1)\psi_a^\alpha(2)\}$$

$$= \frac{1}{\sqrt{2}}\psi_a(1)\psi_a(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}$$

where both electrons occupy the molecular wavefunction ψ_a. We should recognize the spin factor as that corresponding to a singlet state (eqn 4.31b, $\sigma_- = (1/\sqrt{2})\{\alpha\beta - \beta\alpha\}$), so Ψ corresponds to two spin-paired electrons in ψ_a.

According to the variation principle (Section 5.5), the best form of Ψ is the one that corresponds to the lowest achievable energy as the ψ are varied, that is, we need the wavefunctions ψ that will minimize the expectation value $\int \Psi^* \hat{H} \Psi \, d\tau$. Because the electrons interact with one another, a variation in the form of ψ_a, for instance, will affect what will be the best form of all the other ψs, so finding the best form of the ψs is a far from trivial problem. However, D.R. Hartree and V. Fock showed that the optimum ψs each satisfy an at first sight very simple set of equations:

$$f_1\psi_a(1) = \varepsilon_a\psi_a(1) \tag{6.6}$$

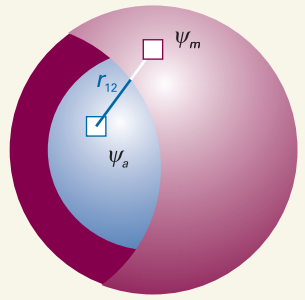


Fig. 6.2 A schematic interpretation of the physical interpretation of the Coulomb repulsion term, eqn 6.7a. An electron in orbital ψ_a experiences repulsion from an electron in orbital ψ_m where it has probability density $|\psi_m|^2$.

where f_1 is called the **Fock operator**. This is the equation to solve to find ψ_a; there are analogous equations for all the other occupied orbitals. This Schrödinger-like equation has the form we should expect (but its formal derivation is quite involved). Thus, f_1 has the following structure:

$$\begin{aligned} f_1 &= \text{core hamiltonian for electron 1 } (h_1) \\ &\quad + \text{average Coulomb repulsion from electrons 2, 3, . . .} \\ &\quad (V_{\text{Coulomb}}) \\ &\quad + \text{average correction due to spin correlation } (V_{\text{Exchange}}) \\ &= h_1 + V_{\text{Coulomb}} + V_{\text{Exchange}} \end{aligned}$$

By the **core hamiltonian** we mean the one-electron hamiltonian h_1 defined by eqn 6.2 and representing the energy of electron 1 in the field of the nuclei. The Coulomb repulsion from all the other electrons contributes a term that acts as follows (Fig. 6.2):

$$J_m(1)\psi_a(1) = j_0\int \psi_a(1)\frac{1}{r_{12}}\psi_m^*(2)\psi_m(2)\,d\tau_2 \tag{6.7a}$$

This integral represents the repulsion experienced by electron 1 in orbital ψ_a from electron 2 in orbital ψ_m, where it is distributed with probability density $\psi_m^*\psi_m$. There are two electrons in each orbital, so we can expect a total contribution of the form

$$V_{\text{Coulomb}}\psi_a(1) = 2\sum_m J_m(1)\psi_a(1)$$

where the sum is over all the occupied orbitals, including orbital a. You should be alert to the fact that counting 2 for the orbital with $m = a$ is incorrect, because electron 1 interacts only with the second electron in the orbital, not with itself. This error will be corrected in a moment. The spin correlation term takes into account the fact that electrons of the same spin tend to avoid each other (Section 4.4), which reduces the net Coulomb interaction between them. This contribution has the following form:

$$K_m(1)\psi_a(1) = j_0\int \psi_m(1)\frac{1}{r_{12}}\psi_m^*(2)\psi_a(2)\,d\tau_2 \tag{6.7b}$$

For a given electron 1 there is only one electron of the same spin in all the occupied orbitals, so we can expect a total contribution of the form

$$V_{\text{Exchange}}\psi_a(1) = -\sum_m K_m(1)\psi_a(1)$$

The negative sign reminds us that spin-correlation keeps electrons apart, and so reduces their classical, Coulombic repulsion. By collecting terms, we arrive at a specific expression for the effect of the Fock operator:

$$f_1\psi_a(1) = h_1\psi_a(1) + \sum_m \{2J_m(1) - K_m(1)\}\psi_a(1) \tag{6.8}$$

with the sum extending over all the occupied orbitals. Note that $K_a(1)\psi_a(1) = J_a(1)\psi_a(1)$, so the term in the sum with $m = a$ loses one of its $2J_a$, which is the correction that avoids the electron repelling itself, which we referred to above.

Equation 6.8 reveals a second principal approximation of the Hartree–Fock formalism (the first being its dependence on the orbital approximation). Instead of electron 1 (or any other electron) responding to the instantaneous positions of the other electrons in the molecule through terms of the form $1/r_{1j}$, it responds to an *averaged* location of the other electrons through integrals of the kind that appear in eqn 6.7. When we look for reasons why the formalism gives poor results, this approximation is a principal reason; it is addressed in Section 6.6.

Although eqn 6.6 is the equation we have to solve to find ψ_a, eqn 6.7 reveals that it is necessary to know all the other occupied wavefunctions in order to set up the operators J and K and hence to find ψ_a. To make progress with this difficulty, we can guess the initial form of all the one-electron wavefunctions, use them in the definition of the Coulomb and exchange operators, and solve the Hartree–Fock equations. That process is then continued using the newly found wavefunctions until each cycle of calculation leaves the energies ε_m and wavefunctions ψ_m unchanged to within a chosen criterion. This is the origin of the term **self-consistent field** (SCF) for this type of procedure in general and of **Hartree–Fock self-consistent field** (HF-SCF) for the approach based on the orbital approximation.

● A BRIEF ILLUSTRATION

We continue with the H_2 example. According to eqn 6.6, the Hartree–Fock equation for ψ_a is $f_1\psi_a(1) = \varepsilon_a\psi_a(1)$ with

$$f_1\psi_a(1) = h_1\psi_a(1) + 2J_a(1)\psi_a(1) - K_a(1)\psi_a(1)$$

because there is only one term in the sum (there is only one occupied orbital). In this expression

$$J_a(1)\psi_a(1) = K_a(1)\psi_a(1) = j_0\int \psi_a(1)\frac{1}{r_{12}}\psi_a{}^*(2)\psi_a(2)\mathrm{d}\tau_2$$

The equation to solve is therefore

$$-\frac{\hbar^2}{2m_e}\nabla_1^2\psi_a(1) - j_0\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}}\right)\psi_a(1)$$
$$+ j_0\int \psi_a(1)\frac{1}{r_{12}}\psi_a{}^*(2)\psi_a(2)\mathrm{d}\tau_2 = \varepsilon_a\psi_a(1)$$

This equation for ψ_a must be solved self-consistently (and numerically) because the integral that governs the form of ψ_a requires us to know ψ_a already. In the following examples we shall illustrate some of the procedures that have been adopted. ●

6.2 The Roothaan equations

The difficulty with the HF-SCF procedure lies in the numerical solution of the Hartree–Fock equations, an onerous task even for powerful computers. As a result, a modification of the technique was needed before the procedure could be of use to chemists. We saw in Chapter 5 how molecular orbitals are constructed as linear combinations of atomic orbitals. This simple approach was adopted in 1951 by C.C.J. Roothaan and G.G. Hall independently, who found a way to convert the Hartree–Fock equations for the molecular orbitals into equations for the coefficients that appear in the LCAO used to simulate the molecular orbital. Thus, they wrote (as we did in eqn 5.34)

$$\psi_m = \sum_{o=1}^{N_b} c_{om}\chi_o \tag{6.9}$$

where c_{om} are unknown coefficients and the χ_o are the atomic orbitals (which we take to be real). Note that this approximation is in addition to those underlying the Hartree–Fock equations because the basis is finite and so cannot reproduce the molecular orbital exactly. The size of the basis set (N_b) is not necessarily the same as the number of atomic nuclei in the molecule (N_n), because we might use several atomic orbitals on each nucleus (such as the four 2s and 2p orbitals of a carbon atom). From N_b basis functions, we obtain N_b linearly independent molecular orbitals ψ.

We show in *Justification 6.1* that the use of a linear combination like in eqn 6.9 leads to a set of simultaneous equations for the coefficients called the **Roothaan equations**. These equations are best summarized in matrix form by writing

$$\boldsymbol{Fc} = \boldsymbol{Sc\varepsilon} \tag{6.10}$$

where $\boldsymbol{F}$ is the $N_b \times N_b$ matrix with elements

$$F_{oo'} = \int \chi_o(1)f_1\chi_{o'}(1)\mathrm{d}\tau_1 \tag{6.11a}$$

$\boldsymbol{S}$ is the $N_b \times N_b$ matrix of overlap integrals:

$$S_{oo'} = \int \chi_o(1)\chi_{o'}(1)\mathrm{d}\tau_1 \tag{6.11b}$$

and $\boldsymbol{c}$ is an $N_b \times N_b$ matrix of all the coefficients we have to find:

$$\boldsymbol{c} = \begin{pmatrix} c_{1a} & c_{1b} & \cdots & c_{1N_b} \\ c_{2a} & c_{2b} & \cdots & c_{2N_b} \\ \vdots & \vdots & \vdots & \vdots \\ c_{N_b a} & c_{N_b b} & \cdots & c_{N_b N_b} \end{pmatrix} \tag{6.11c}$$

The first column is the set of coefficients for ψ_a, the second column for ψ_b, and so on. Finally, $\boldsymbol{\varepsilon}$ is a diagonal matrix of orbital energies $\varepsilon_a, \varepsilon_b, \ldots$:

$$\boldsymbol{\varepsilon} = \begin{pmatrix} \varepsilon_a & 0 & \cdots & 0 \\ 0 & \varepsilon_b & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \varepsilon_{N_b} \end{pmatrix} \tag{6.11d}$$

Justification 6.1 *The Roothaan equations*

To construct the Roothaan equations we substitute the linear combination of eqn 6.9 into eqn 6.6, which gives

$$f_1 \sum_{o=1}^{N_b} c_{om}\chi_o(1) = \varepsilon_m \sum_{o=1}^{N_b} c_{om}\chi_o(1)$$

Now multiply from the left by $\chi_o(1)$ and integrate over the coordinates of electron 1:

$$\sum_{o=1}^{N_b} c_{om} \overbrace{\int \chi_{o'}(1) f_1 \chi_o(1)\mathrm{d}\tau_1}^{F_{o'o}} = \varepsilon_m \sum_{o=1}^{N_b} c_{om} \overbrace{\int \chi_{o'}(1)\chi_o(1)\mathrm{d}\tau_1}^{S_{o'o}}$$

That is,

$$\sum_{o=1}^{N_b} F_{o'o}c_{om} = \varepsilon_m \sum_{o=1}^{N_b} S_{o'o}c_{om}$$

This expression has the form of the matrix equation in eqn 6.10.

A BRIEF ILLUSTRATION

In this *illustration* we show how to set up the Roothaan equations for H_2. To do so, we adopt a basis set of real, normalized functions χ_A and χ_B, centred on nuclei A and B, respectively. We can think of these functions as H1s orbitals on each nucleus, but they could be more general than that, and in a later *illustration* we shall make a computationally more friendly choice. The two possible linear combinations corresponding to eqn 6.9 are

$$\psi_a = c_{Aa}\chi_A + c_{Ba}\chi_B \qquad \psi_b = c_{Ab}\chi_A + c_{Bb}\chi_B$$

so the matrix $\boldsymbol{c}$ is

$$\boldsymbol{c} = \begin{pmatrix} c_{Aa} & c_{Ab} \\ c_{Ba} & c_{Bb} \end{pmatrix}$$

and the overlap matrix $\boldsymbol{S}$ is

$$\boldsymbol{S} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \quad \text{with} \quad S = \int \chi_A(1)\chi_B(1)\mathrm{d}\tau_1$$

The Fock matrix is

$$\boldsymbol{F} = \begin{pmatrix} F_{AA} & F_{AB} \\ F_{BA} & F_{BB} \end{pmatrix} \quad \text{with} \quad F_{oo'} = \int \chi_o(1) f_1 \chi_{o'}(1)\mathrm{d}\tau_1$$

We shall explore the explicit form of the elements of $\boldsymbol{F}$ in a later *illustration*; for now, we just regard them as variable quantities. The Roothaan equations are therefore

$$\begin{pmatrix} F_{AA} & F_{AB} \\ F_{BA} & F_{BB} \end{pmatrix}\begin{pmatrix} c_{Aa} & c_{Ab} \\ c_{Ba} & c_{Bb} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}\begin{pmatrix} c_{Aa} & c_{Ab} \\ c_{Ba} & c_{Bb} \end{pmatrix}\begin{pmatrix} \varepsilon_a & 0 \\ 0 & \varepsilon_b \end{pmatrix} \bullet$$

ANOTHER BRIEF ILLUSTRATION

In this continuation of the preceding *illustration*, we establish the simultaneous equations corresponding to the Roothaan equations we have just established. After multiplying out the matrices constructed in the preceding *illustration*, we obtain

$$\begin{pmatrix} F_{AA}c_{Aa} + F_{AB}c_{Ba} & F_{AA}c_{Ab} + F_{AB}c_{Bb} \\ F_{BA}c_{Aa} + F_{BB}c_{Ba} & F_{BA}c_{Ab} + F_{BB}c_{Bb} \end{pmatrix}$$

$$= \begin{pmatrix} \varepsilon_a c_{Aa} + S\varepsilon_a c_{Ba} & \varepsilon_b c_{Ab} + S\varepsilon_b c_{Bb} \\ \varepsilon_a c_{Ba} + S\varepsilon_a c_{Aa} & \varepsilon_b c_{Bb} + S\varepsilon_b c_{Ab} \end{pmatrix}$$

On equating matching elements, we obtain the following four simultaneous equations:

$$\begin{aligned} F_{AA}c_{Aa} + F_{AB}c_{Ba} &= \varepsilon_a c_{Aa} + S\varepsilon_a c_{Ba} \\ F_{BA}c_{Aa} + F_{BB}c_{Ba} &= \varepsilon_a c_{Ba} + S\varepsilon_a c_{Aa} \\ F_{AA}c_{Ab} + F_{AB}c_{Bb} &= \varepsilon_b c_{Ab} + S\varepsilon_b c_{Bb} \\ F_{BA}c_{Ab} + F_{BB}c_{Bb} &= \varepsilon_b c_{Bb} + S\varepsilon_b c_{Ab} \end{aligned}$$

Thus, to find the coefficients for the molecular orbital ψ_a, we need to solve the first and second equations, which we can write as

$$\begin{aligned} (F_{AA} - \varepsilon_a)c_{Aa} + (F_{AB} - S\varepsilon_a)c_{Ba} &= 0 \\ (F_{BA} - S\varepsilon_a)c_{Aa} + (F_{BB} - \varepsilon_a)c_{Ba} &= 0 \end{aligned}$$

There is a similar pair of equations (the third and fourth) for the coefficients in ψ_b. ●

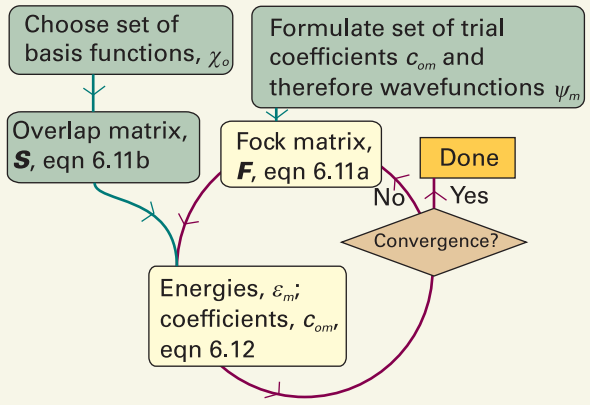


Fig. 6.3 The iteration procedure for a Hartree–Fock self-consistent field calculation.

If we write the Roothaan equations as $(\boldsymbol{F}-\boldsymbol{S\varepsilon})\boldsymbol{c}=0$ we see that they are simply a collection of N_b simultaneous equations for the coefficients. This point was demonstrated explicitly in the preceding *illustration*. Therefore, they have a solution only if

$$|\boldsymbol{F}-\boldsymbol{\varepsilon S}|=0 \tag{6.12}$$

In principle, we can find the orbital energies that occur in $\boldsymbol{\varepsilon}$ by looking for the roots of this secular equation and then using those energies to find the coefficients that make up the matrix $\boldsymbol{c}$ by solving the Roothaan equations. There is a catch, though: the elements of $\boldsymbol{F}$ depend on the coefficients (through the presence of J and K in the expression for f_1). Therefore, we have to proceed iteratively: we guess an initial set of values for $\boldsymbol{c}$, solve the secular equation for the orbital energies, use them to solve the Roothaan equations for $\boldsymbol{c}$, and compare the resulting values with the ones we started with. In general they will be different, so we use those new values in another cycle of calculation, and continue until convergence has been achieved (Fig. 6.3).

● A BRIEF ILLUSTRATION

The two simultaneous equations for the coefficients in ψ_a obtained in the previous *illustration* have a solution if

$$\begin{vmatrix} F_{AA}-\varepsilon & F_{AB}-S\varepsilon \\ F_{BA}-S\varepsilon & F_{BB}-\varepsilon \end{vmatrix}=0$$

The determinant expands to give the following equation:

$$(F_{AA}-\varepsilon)(F_{BB}-\varepsilon)-(F_{AB}-S\varepsilon)(F_{BA}-S\varepsilon)=0$$

On collecting terms, we arrive at

$$(1-S^2)\varepsilon^2-(F_{AA}+F_{BB}-SF_{AB}-SF_{BA})\varepsilon + (F_{AA}F_{BB}-F_{AB}F_{BA})=0$$

This is a quadratic equation for the orbital energies ε, and may be solved by using the quadratic formula. Thus, if we summarize the equation as $a\varepsilon^2+b\varepsilon+c=0$, then

$$\varepsilon=\frac{-b\pm(b^2-4ac)^{1/2}}{2a}$$

With these energies established and taking the lower of the two energies to be ε_a since ψ_a is occupied in ground-state H_2, we can construct the coefficients by using the relation

$$c_{Aa}=-\frac{F_{AB}-S\varepsilon_a}{F_{AA}-\varepsilon_a}c_{Ba}$$

in conjunction with the normalization condition $c_{Aa}^2+c_{Ba}^2+2c_{Aa}c_{Ba}S=1$. (For this homonuclear diatomic molecule, there is, of course, a much simpler method of arriving at $c_{Aa}=c_{Ba}$.) ●

The principal outstanding problem is the form of the elements of the Fock matrix $\boldsymbol{F}$ and its dependence on the LCAO coefficients. The explicit form of $F_{oo'}$ is

$$\begin{aligned} F_{oo'}=&\int\chi_o(1)h_1\chi_{o'}(1)\mathrm{d}\tau_1 \\ &+2j_0\sum_m\int\chi_o(1)\chi_{o'}(1)\frac{1}{r_{12}}\psi_m(2)\psi_m(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &-j_0\sum_m\int\chi_o(1)\psi_m(1)\frac{1}{r_{12}}\psi_m(2)\chi_{o'}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \end{aligned} \tag{6.13}$$

where the sums are over the occupied molecular orbitals. The dependence of $\boldsymbol{F}$ on the coefficients can now be seen to arise from the presence of the ψ_m in the two integrals, for these molecular orbitals depend on the coefficients in their LCAOs.

● A BRIEF ILLUSTRATION

At this point we are ready to tackle the matrix elements that occur in the treatment of H_2, using the LCAOs set up in a previous *illustration*. As we saw there, we need the four matrix elements F_{AA}, F_{AB}, F_{BA}, and F_{BB}. We show here how to evaluate F_{AA}. Only one molecular orbital is occupied (ψ_a), so eqn 6.13 becomes

$$\begin{aligned} F_{AA}=&\int\chi_A(1)h_1\chi_A(1)\mathrm{d}\tau_1 \\ &+2j_0\int\chi_A(1)\chi_A(1)\frac{1}{r_{12}}\psi_a(2)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \\ &-j_0\int\chi_A(1)\psi_a(1)\frac{1}{r_{12}}\psi_a(2)\chi_A(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \end{aligned}$$

With $\psi_a = c_{Aa}\chi_A + c_{Ba}\chi_B$, the second integral on the right is

$$j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\psi_a(2)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$= j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\{c_{Aa}\chi_A(2) + c_{Ba}\chi_B(2)\}$$

$$\times \{c_{Aa}\chi_A(2) + c_{Ba}\chi_B(2)\}\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$= c_{Aa}c_{Aa}j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\chi_A(2)\chi_A(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

$$+ c_{Aa}c_{Ba}j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\chi_A(2)\chi_B(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 + \cdots$$

From now on we shall use the notation

$$(\mathrm{AB}|\mathrm{CD}) = j_0\int \chi_A(1)\chi_B(1)\frac{1}{r_{12}}\chi_C(2)\chi_D(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (6.14)$$

Integrals like this are fixed throughout the calculation because they depend only on the choice of basis, so they can be tabulated once and for all and then used whenever required. Our task later in this chapter will be to see how they are evaluated. For the time being, we can treat them as constants. In this notation, the integral we are evaluating becomes

$$j_0\int \chi_A(1)\chi_A(1)\frac{1}{r_{12}}\psi_a(2)\psi_a(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$
$$= c_{Aa}c_{Aa}(\mathrm{AA}|\mathrm{AA}) + 2c_{Aa}c_{Ba}(\mathrm{AA}|\mathrm{BA}) + c_{Ba}c_{Ba}(\mathrm{AA}|\mathrm{BB})$$

(We have used (AA|BA) = (AA|AB).) There is a similar term for the third integral, and overall

$$F_{AA} = E_A + c_{Aa}^2(\mathrm{AA}|\mathrm{AA}) + 2c_{Aa}c_{Ba}(\mathrm{AA}|\mathrm{BA})$$
$$+ c_{Ba}^2\{2(\mathrm{AA}|\mathrm{BB}) - (\mathrm{AB}|\mathrm{BA})\}$$

where

$$E_A = \int \chi_A(1)h_1\chi_A(1)\mathrm{d}\tau_1 \qquad (6.15)$$

is the energy of an electron in orbital χ_A based on nucleus A, taking into account its interaction with both nuclei. Similar expressions may be derived for the other three matrix elements of F. The crucial point, though, is that we now see how F depends on the coefficients that we are trying to find. ●

Self-test 6.1 Construct the element F_{AB} using the same basis.

$$\left[F_{AB} = \int \chi_A(1)h_1\chi_B(1)\mathrm{d}\tau_1 + c_{Aa}^2(\mathrm{BA}|\mathrm{AA})\right.$$
$$\left. + c_{Aa}c_{Ba}\{3(\mathrm{BA}|\mathrm{AB}) - (\mathrm{AA}|\mathrm{BB})\} + c_{Ba}^2(\mathrm{BA}|\mathrm{BB})\right]$$

6.3 Basis sets

One of the problems with molecular structure calculations now becomes apparent. The basis functions appearing in eqn 6.14 may in general be centred on different atomic nuclei so (AB|CD) is in general a so-called 'four-centre, two-electron integral'. If there are several dozen basis functions used to build the one-electron wavefunctions, there will be tens of thousands of integrals of this form to evaluate (the number of integrals increases as N_b^4). The efficient calculation of such integrals poses the greatest challenge in an HF-SCF calculation but can be alleviated by a clever choice of basis functions.

The simplest approach is to use a **minimal basis set**, in which one basis function is used to represent each of the orbitals in an elementary valence theory treatment of the molecule, that is, we include in the basis set one function each for H and He (to simulate a 1s orbital), five functions each for Li to Ne (for the 1s, 2s, and three 2p orbitals), nine functions each for Na to Ar, and so on. For example, a minimal basis set for CH_4 consists of nine functions: four basis functions to represent the four H1s orbitals, and one basis function each for the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals of carbon. Unfortunately, minimal basis set calculations frequently yield results that are far from agreement with experiment.

Significant improvements in the agreement between electronic structure calculations and experiment can often be achieved by increasing the number of basis set functions. In a **double-zeta** (DZ) basis set, each basis function in the minimal basis is replaced by two functions; in a **triple-zeta** (TZ) basis set, by three functions. For example, a double-zeta basis for H_2O consists of fourteen functions: a total of four basis functions to represent the two H1s orbitals, and two basis set functions each for the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals of oxygen. In a **split-valence** (SV) basis set, each inner-shell (core) atomic orbital is represented by one basis set function and each valence atomic orbital by two basis set functions; an SV calculation for H_2O, for instance, uses thirteen basis set functions. Further improvements to the accuracy of electronic structure calculations can often be achieved by including **polarization functions** in the basis; these functions represent atomic orbitals with higher values of the orbital angular momentum quantum number l than considered in an elementary valence theory treatment. For example, polarization functions in a calculation for CH_4 include basis functions representing d orbitals on carbon or p orbitals on hydrogen. Polarization functions often lead to improved results because atomic orbitals are distorted (or polarized) by adjacent atoms when bonds form in molecules.

One of the earliest choices for basis set functions was that of **Slater-type orbitals** (STO) centred on each of the atomic nuclei in the molecule and of the form

$$\chi = Nr^a e^{-br}Y_{lm_l}(\theta,\phi) \qquad (6.16)$$

N is a normalization constant, a and b are (non-negative) parameters, Y_{lm_l} is a spherical harmonic (Table 3.2), and (r,θ,ϕ) are the spherical polar coordinates describing the location of the electron relative to the atomic nucleus. Several such basis functions are typically centred on each atom, with each basis function characterized by a unique set of values of a, b, l, and m_l. The values of a and b generally vary with the element and there are several rules for assigning reasonable values. For molecules containing hydrogen, there is an STO centred on each proton with $a=0$ and $b=1/a_0$, which simulates the correct behaviour of the 1s orbital at the nucleus (see eqn 4.14). However, using the STO basis set in HF-SCF calculations on molecules with three or more atoms requires the evaluation of so many two-electron integrals (AB|CD) that the procedure becomes computationally impractical.

The introduction of **Gaussian-type orbitals** (GTO) by S.F. Boys largely overcame the problem. Cartesian Gaussian functions centred on atomic nuclei have the form

$$\chi = Nx^i y^j z^k e^{-\alpha r^2} \tag{6.17}$$

where (x,y,z) are the Cartesian coordinates of the electron at a distance r from the nucleus, (i,j,k) are a set of non-negative integers, and α is a positive constant. An **s-type** Gaussian has $i=j=k=0$; a **p-type** Gaussian has $i+j+k=1$; a **d-type** Gaussian has $i+j+k=2$ and so on. Figure 6.4 shows contour plots for various Gaussian-type orbitals. The advantage of GTOs is that the product of two Gaussian functions on different centres is equivalent to a single Gaussian function located at a point between the two centres (Fig. 6.5). Therefore, two-electron integrals on three and four different atomic centres can be reduced to integrals over two different centres, which are much easier to evaluate numerically.

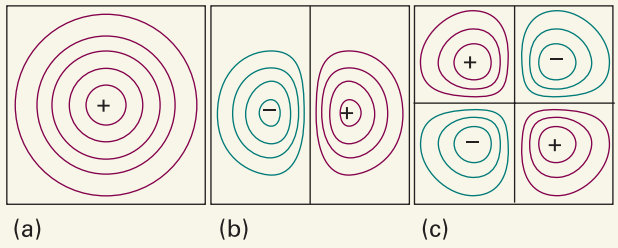


Fig. 6.4 Contour plots for Gaussian-type orbitals. (a) s-type Gaussian, e^{-r^2}; (b) p-type Gaussian xe^{-r^2}; (c) d-type Gaussian, xye^{-r^2}.

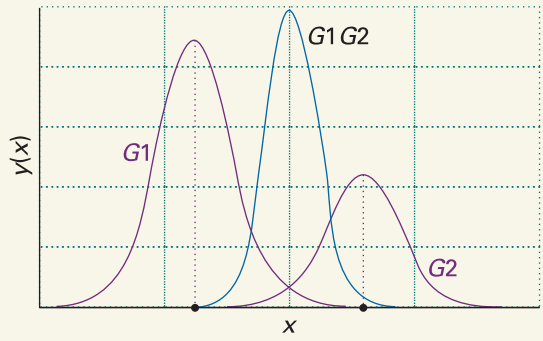


Fig. 6.5 The product of two Gaussian functions on different centres is itself a Gaussian function located at a point between the two contributing Gaussians. The scale of the product has been increased relative to that of its two components.

● A BRIEF ILLUSTRATION

There are no four-centre integrals in H_2, but we can illustrate the principle by considering one of the two-centre integrals that appear in the Fock matrix and, to be definite, we consider

$$(\mathrm{AB}|\mathrm{AB}) = j_0 \int \chi_A(1)\chi_B(1)\frac{1}{r_{12}}\chi_A(2)\chi_B(2)\mathrm{d}\tau_1\mathrm{d}\tau_2$$

We choose an s-type Gaussian basis and write

$$\chi_A(1) = Ne^{-\alpha|r_1-R_A|^2} \qquad \chi_B(1) = Ne^{-\alpha|r_1-R_B|^2}$$

where $\boldsymbol{r}_1$ is the coordinate of electron 1 and $\boldsymbol{R}_I$ is the coordinate of nucleus I. The product of two such Gaussians, one centred on A and one centred on B, for electron 1, is

$$\chi_A(1)\chi_B(1) = N^2 e^{-\alpha|r_1-R_A|^2} e^{-\alpha|r_1-R_B|^2} = N^2 e^{-\alpha\{|r_1-R_A|^2+|r_1-R_B|^2\}}$$

By using the relation

$$|\boldsymbol{r}-\boldsymbol{R}|^2 = (\boldsymbol{r}-\boldsymbol{R})\cdot(\boldsymbol{r}-\boldsymbol{R}) = |\boldsymbol{r}|^2 + |\boldsymbol{R}|^2 - 2\boldsymbol{r}\cdot\boldsymbol{R}$$

we can confirm that

$$|\boldsymbol{r}_1-\boldsymbol{R}_A|^2 + |\boldsymbol{r}_1-\boldsymbol{R}_B|^2 = \tfrac{1}{2}R^2 + 2|\boldsymbol{r}_1-\boldsymbol{R}_0|^2$$

where $\boldsymbol{R}_0 = \frac{1}{2}(\boldsymbol{R}_A+\boldsymbol{R}_B)$ is the midpoint of the molecule and $R = |\boldsymbol{R}_A - \boldsymbol{R}_B|$ is the bond length. Hence

$$\chi_A(1)\chi_B(1) = N^2 e^{-\frac{1}{2}\alpha R^2} e^{-2\alpha|r_1-R_0|^2}$$

The product $\chi_A(2)\chi_B(2)$ is the same, except for the index on $\boldsymbol{r}$. Therefore, the two-centre, two-electron integral (AB|AB) reduces to

$$(\mathrm{AB}|\mathrm{AB}) = N^4 j_0 e^{-\alpha R^2} \int e^{-2\alpha|r_1-R_0|^2}\frac{1}{r_{12}}e^{-2\alpha|r_2-R_0|^2}\mathrm{d}\tau_1\mathrm{d}\tau_2$$

This is a single-centre two-electron integral, with both exponential functions spherically symmetrical Gaussians centred on the midpoint of the bond, and much faster to evaluate than the original two-centre integral. ●

Some of the basis sets that employ Gaussian functions and are commonly used in electronic structure calculations are given in Table 6.1. An STO-*N*G basis is a minimal basis set in which each basis function is itself a linear combination of *N* Gaussians; the STO in the name of the basis reflects the fact that each linear

Table 6.1 Basis set designations and example basis sets for H_2O

General basis	Example basis	Basis functions
STO-*N*G	STO-3G	For each O 1s, 2s, $2p_x$, $2p_y$, $2p_z$ and H 1s orbital:
		One function, a linear combination of 3 Gaussians
*m-np*G	6-31G	For O 1s orbital:
		One linear combination of 6 Gaussians
		For each O 2s, $2p_x$, $2p_y$, $2p_z$ and H 1s orbital:
		2 functions:
		– One Gaussian function
		– One linear combination of 3 Gaussians
*m-np*G*	6-31G*	6-31G plus d-type polarization functions on O
*m-np*G**	6-31G**	6-31G* plus p-type polarization functions on each H
*m-npq*G	6-311G	6-31G plus an additional Gaussian for each
		O 2s, $2p_x$, $2p_y$, $2p_z$ and H 1s orbital
m-npq+G	6-311+G	6-311G plus diffuse s- and p-type Gaussians on O
m-npq++G	6-311++G	6-311+G plus diffuse Gaussians on each H
m-npq+G*	6-311+G*	6-311+G plus d-type polarization functions on O
m-npq+G**	6-311+G**	6-311+G* plus p-type polarization functions on each H

combination is chosen by a least-squares fit to a Slater-type function. An *m-np*G basis is a split-valence basis set in which each core atomic orbital is represented by one function (a linear combination of *m* Gaussians) and each valence orbital is represented by two basis functions, one a linear combination of *n* Gaussians and the other of *p* Gaussian functions. The addition of d-type polarization functions for non-hydrogen atoms to the *m-np*G basis yields an *m-np*G* basis; further addition of p-type polarization functions for hydrogen atoms results in an *m-np*G** basis set. In an *m-npq*G basis, each valence atomic orbital is represented by three basis functions, linear combinations of *n*, *p*, and *q* Gaussians, respectively. Addition of diffuse (small α-valued, eqn 6.17) s- and p-type Gaussians on non-hydrogen atoms results in an *m-npq*+G basis set; additional diffuse functions to hydrogen, *m-npq*++G. A considerable amount of work has gone into the development of efficient basis sets and this is still an active area of research.

We have arrived at the point where we can see that the Hartree–Fock approach, coupled with the use of basis set functions, requires the evaluation of a large number of integrals. There are two approaches commonly taken at this point. In **semiempirical methods**, the integrals encountered are either set to zero or estimated from experimental data. In ***ab initio* methods**, an attempt is made to evaluate the integrals numerically, using as input only the values of fundamental constants and atomic numbers of the atoms present in the molecule.

The first approach: semiempirical methods

In semiempirical methods, many of the integrals that occur in a calculation are estimated by appealing to spectroscopic data or physical properties such as ionization energies, or by using a series of rules to set certain integrals equal to zero. These methods are applied routinely to molecules containing large numbers of atoms because of their computational speed but there is often a sacrifice in the accuracy of the results.

6.4 The Hückel method revisited

Semiempirical methods were first developed for conjugated π systems, the most famous semiempirical procedure being Hückel molecular orbital theory (HMO theory, Section 5.6).

The initial assumption of HMO theory is the separate treatment of π and σ electrons, which is justified by the different energies and symmetries of the orbitals. The secular determinant, from which the π-orbital energies and wavefunctions are obtained, has a form similar to that of eqn 6.12 and is written in terms of overlap integrals and hamiltonian matrix elements. The overlap integrals are set to 0 or 1, the diagonal hamiltonian matrix elements are set to a parameter α, and off-diagonal elements either to 0 or the parameter β. The HMO approach is useful for qualitative, rather than quantitative, discussions of conjugated π systems because it treats repulsions between electrons very poorly.

● A BRIEF ILLUSTRATION

Here we return to the third *illustration* of Section 6.2 and set $S = 0$. The diagonal Fock matrix elements are set equal to α (that is, we set $F_{AA} = F_{BB} = \alpha$), and the off-diagonal elements are set equal to β (that is, we set $F_{AB} = F_{BA} = \beta$). Note that the dependence of these integrals on the coefficients is swept aside, so we do not have to work towards self-consistency. The quadratic equation for the energies

$$(1 - S^2)\varepsilon^2 - (F_{AA} + F_{BB} - SF_{AB} - SF_{BA})\varepsilon + (F_{AA}F_{BB} - F_{AB}F_{BA}) = 0$$

becomes simply

$$\varepsilon^2 - 2\alpha\varepsilon + \alpha^2 - \beta^2 = 0$$

and the roots are $\varepsilon = \alpha \pm \beta$, exactly as we found in Section 5.6. ●

6.5 Differential overlap

In the second most primitive and severe approach, called **complete neglect of differential overlap** (CNDO), all two-electron integrals of the form (AB|CD) are set to zero unless χ_A and χ_B are the same, and likewise for χ_C and χ_D. That is, only integrals of the form (AA|CC) survive and they are often taken to be parameters with values adjusted until the calculated energies are in agreement with experiment. The origin of the term 'differential overlap' is that what we normally take to be a measure of 'overlap' is the integral $\int \chi_A \chi_B d\tau$. The differential of an integral of a function is the function itself, so in this sense the 'differential' overlap is the product $\chi_A \chi_B$. The implication is that we then simply compare orbitals: if they are the same, the integral is retained; if different, it is discarded.

● A BRIEF ILLUSTRATION

The expression for F_{AA} derived in the final *illustration* in Section 6.2 is

$$F_{AA} = E_A + c_{Aa}^2(AA|AA) + 2c_{Aa}c_{Ba}(AA|BA) + c_{Ba}^2\{2(AA|BB) - (AB|BA)\}$$

The last integral has the form

$$(AB|BA) = j_0 \int \chi_A(1)\chi_B(1)\frac{1}{r_{12}}\chi_B(2)\chi_A(2)d\tau_1 d\tau_2$$

The 'differential overlap' term $\chi_A(1)\chi_B(1)$ is set equal to zero, so in the CNDO approximation the integral is set equal to zero. The same is true of the integral (AA|BA). It follows that we write

$$F_{AA} \approx E_A + c_{Aa}^2(AA|AA) + 2c_{Ba}^2(AA|BB)$$

and identify the surviving two two-electron integrals as empirical parameters. ●

Self-test 6.2 Apply the CNDO approximation to F_{AB} for the same system.

$$[F_{AB} = \int \chi_A(1)h_1\chi_B(1)d\tau_1 - c_{Aa}c_{Bb}(AA|BB)]$$

More recent semiempirical methods make less draconian decisions about which integrals are to be ignored, but they are all descendants of the early CNDO technique. Whereas CNDO sets integrals of the form (AB|AB) to zero for all different χ_A and χ_B, **intermediate neglect of differential overlap** (INDO) does not neglect the (AB|AB) for which different basis functions χ_A and χ_B are centred on the same nucleus. Because these integrals are important for explaining energy differences between terms corresponding to the same electronic configuration, INDO is much preferred over CNDO for spectroscopic investigations. A still less severe approximation is **neglect of diatomic differential overlap** (NDDO) in which (AB|CD) is neglected only when χ_A and χ_B are centred on different nuclei or when χ_C and χ_D are centred on different nuclei.

There are other semiempirical methods, with names such as **modified intermediate neglect of differential overlap** (MINDO), **modified neglect of differential overlap** (MNDO), Austin model 1 (AM1), PM3, and **pairwise distance directed Gaussian** (PDDG). In each case, the values of integrals are either set to zero or set to parameters with values that have been determined by attempting to optimize agreement with experiment, such as measured values of enthalpies of formation, dipole moments, and ionization energies. MINDO is useful for the study of hydrocarbons; it tends to give more accurate computed results than MNDO but it gives poor results for systems with hydrogen bonds. AM1, PM3, and PDDG are improved versions of MNDO.

The second approach: *ab initio* methods

In *ab initio* methods, the two-electron integrals are evaluated numerically. However, even for small molecules, Hartree–Fock calculations with large basis sets and efficient and accurate calculation of two-electron integrals can give very poor results because they are rooted in the orbital approximation and the average effect of the other electrons on the electron of interest. Thus, the true wavefunction for H_2 is a function of the form $\Psi(\boldsymbol{r}_1,\boldsymbol{r}_2)$, with a complicated behaviour as $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ vary and perhaps approach one another. This complexity is lost when we write the wavefunction as a simple product of two functions, $\psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)$ and treat each electron as moving in the average field of the other electrons. That is, the approximations of the Hartree–Fock method imply that no attempt is made to take into account **electron correlation**, the tendency of electrons to stay apart in order to minimize their mutual repulsion. Most modern work in electronic structure, such as the approaches discussed in the following two sections as well as more sophisticated approaches that are beyond the scope of this text, tries to take electron correlation into account.

6.6 Configuration interaction

When we work through the formalism described so far using a basis set of N_b orbitals, we generate N_b molecular orbitals. However, if there are N_e electrons to accommodate, in the ground state only $\frac{1}{2}N_e$ of these N_b orbitals are occupied, leaving $N_b - \frac{1}{2}N_e$ so-called **virtual orbitals** unoccupied. The ground state is

$$\Psi_0 = (1/N_e!)^{1/2}|\psi_a^\alpha(1)\psi_a^\beta(2)\psi_b^\alpha(3)\psi_b^\beta(4)\cdots\psi_u^\beta(N_e)|$$

where ψ_u is the HOMO (Section 5.6). We can envisage transferring an electron from an occupied orbital to a virtual orbital ψ_v, and forming the corresponding **singly excited determinant**, such as

$$\Psi_1 = (1/N_e!)^{1/2}|\psi_a^\alpha(1)\psi_a^\beta(2)\psi_b^\alpha(3)\psi_v^\beta(4)\cdots\psi_u^\beta(N_e)|$$

Here a β electron, 'electron 4', has been promoted from ψ_b into ψ_v, but there are many other possible choices. We can also envisage doubly excited determinants, and so on. Each of the Slater determinants constructed in this way is called a **configuration state function** (CSF).

Now we come to the point of introducing these CSFs. In 1959 P.-O. Löwdin proved that the *exact* wavefunction (within the Born–Oppenheimer approximation) can be expressed as a linear combination of CSFs found from the exact solution of the Hartree–Fock equations:

$$\Psi = C_0\Psi_0(\uparrow\uparrow\uparrow\uparrow) + C_1\Psi_1(\uparrow\uparrow\uparrow\downarrow) + C_2\Psi_2(\uparrow\uparrow\downarrow\downarrow) + \cdots \qquad (6.18)$$

The inclusion of CSFs to improve the wavefunction in this way is called **configuration interaction** (CI). Configuration interaction can, at least in principle, yield the exact ground-state wavefunction and energy and thus accounts for the electron correlation neglected in Hartree–Fock methods. However, the wavefunction and energy are exact only if an infinite number of CSFs are used in the expansion in eqn 6.18; in practice, we are resigned to using a finite number of CSFs.

● A BRIEF ILLUSTRATION

We can begin to appreciate why CI improves the wavefunction of a molecule by considering H_2 again. We saw in the first *illustration* in Section 6.1 that, after expanding the Slater determinant, the ground state is

$$\Psi_0 = \psi_a(1)\psi_a(2)\sigma_-(1,2)$$

where $\sigma_-(1,2)$ is the singlet spin state wavefunction. We also know that if we use a minimal basis set and ignore overlap, we can write $\psi_a = (1/\sqrt{2})\{\chi_A + \chi_B\}$. Therefore

$$\begin{aligned}\Psi_0 &= \tfrac{1}{2}\{\chi_A(1) + \chi_B(1)\}\{\chi_A(2) + \chi_B(2)\}\sigma_-(1,2)\\ &= \tfrac{1}{2}\{\chi_A(1)\chi_A(2) + \chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)\\ &\quad + \chi_B(1)\chi_B(2)\}\sigma_-(1,2)\end{aligned}$$

We can see a deficiency in this wavefunction: there are equal probabilities of finding both electrons on A (the first term) or on B (the fourth term) as there are for finding one electron on A and the other on B (the second and third terms). That is, electron correlation has not been taken into account and we can expect the calculated energy to be too high.

From two basis functions we can construct two molecular orbitals: we denote the second one $\psi_b = (1/\sqrt{2})\{\chi_A - \chi_B\}$. We need not consider the singly excited determinant constructed by moving one electron from ψ_a to ψ_b because it will be of ungerade symmetry and therefore not contribute to the gerade ground state of dihydrogen. A doubly excited determinant based on ψ_b would be

$$\begin{aligned}\Psi_2 &= \psi_b(1)\psi_b(2)\sigma_-(1,2)\\ &= \tfrac{1}{2}\{\chi_A(1) - \chi_B(1)\}\{\chi_A(2) - \chi_B(2)\}\sigma_-(1,2)\\ &= \tfrac{1}{2}\{\chi_A(1)\chi_A(2) - \chi_A(1)\chi_B(2) - \chi_B(1)\chi_A(2)\\ &\quad + \chi_B(1)\chi_B(2)\}\sigma_-(1,2)\end{aligned}$$

If we were simply to subtract one CSF from the other, the outer terms would cancel and we would be left with

$$\Psi_0 - \Psi_2 = \{\chi_A(1)\chi_B(2) + \chi_B(1)\chi_A(2)\}\sigma_-(1,2)$$

According to this wavefunction, the two electrons will never be found on the same atom: we have overcompensated for electron configuration. The obvious middle-ground is to form the linear combination $\Psi = C_0\Psi_0 + C_2\Psi_2$ and look for the values of the coefficients that minimize the energy. ●

The *illustration* shows that even a limited amount of CI can introduce some electron correlation; full CI—using orbitals built from a finite basis and allowing for all possible excitations—will take electron correlation into account more fully. The optimum procedure, using orbitals that form an infinite basis and allowing all excitations, is computationally impractical.

The optimum expansion coefficients in eqn 6.18 are found by using the variation principle; as in *Justification 6.1* for the Hartree–Fock method, application of the variation principle for CI results in a set of simultaneous equations for the expansion coefficients.

● A BRIEF ILLUSTRATION

If we take the linear combination $\Psi = C_0\Psi_0 + C_2\Psi_2$, the usual procedure for the variation method (Section 5.5) leads to the secular equation $|\boldsymbol{H} - E\boldsymbol{S}| = 0$, from which we can find the improved energy. Specifically:

$$\boldsymbol{H} = \begin{pmatrix} H_{00} & H_{02} \\ H_{20} & H_{22} \end{pmatrix} \qquad H_{MN} = \int \Psi_M \hat{H} \Psi_N \, d\tau_1 d\tau_2$$

$$\boldsymbol{S} = \begin{pmatrix} S_{00} & S_{02} \\ S_{20} & S_{22} \end{pmatrix} \qquad S_{MN} = \int \Psi_M \Psi_N \, d\tau_1 d\tau_2$$

and the secular equation we must solve to find E is (note that $S_{02} = S_{20}$ and that $H_{02} = H_{20}$ due to hermiticity)

$$\begin{vmatrix} H_{00} - ES_{00} & H_{02} - ES_{02} \\ H_{20} - ES_{20} & H_{22} - ES_{22} \end{vmatrix}$$
$$= (H_{00} - ES_{00})(H_{22} - ES_{22}) - (H_{02} - ES_{02})^2 = 0$$

which is easily rearranged into a quadratic equation for E. As usual, the problem boils down to an evaluation of various integrals that appear in the matrix elements.

The molecular orbitals ψ_a and ψ_b are orthogonal, so S is diagonal and, provided ψ_a and ψ_b are normalized, $S_{00} = S_{22} = 1$. To evaluate the hamiltonian matrix elements, we first write the hamiltonian as in eqn 6.3 ($\hat{H} = h_1 + h_2 + j_0/r_{12}$), where h_1 and h_2 are the core hamiltonians for electrons 1 and 2, respectively, and so

$$H_{00} = \int \Psi_0 \left(h_1 + h_2 + \frac{j_0}{r_{12}} \right) \Psi_0 \, d\tau_1 d\tau_2$$

The first term in this integral (noting that the spin states are normalized) is:

$$\int \Psi_0 h_1 \Psi_0 d\tau_1 d\tau_2 = \int \psi_a(1)\psi_a(2) h_1 \psi_a(1)\psi_a(2) d\tau_1 d\tau_2$$
$$= \int \psi_a(1) h_1 \psi_a(1) d\tau_1$$

Similarly,

$$\int \Psi_0 h_2 \Psi_0 d\tau_1 d\tau_2 = \int \psi_a(2) h_2 \psi_a(2) d\tau_2$$

For the electron–electron repulsion term, using the notation of eqn 6.14,

$$\int \Psi_0 \frac{j_0}{r_{12}} \Psi_0 d\tau_1 d\tau_2 = j_0 \int \psi_a(1)\psi_a(1) \frac{1}{r_{12}} \psi_a(2)\psi_a(2) d\tau_1 d\tau_2$$
$$= c_{Aa}^4 (AA|AA) + c_{Aa}^3 c_{Ba} (AA|AB) + \cdots + c_{Ba}^4 (BB|BB)$$

Expressions of a similar kind can be developed for the other three elements of H, so the optimum energy can be found by substituting the calculated values of the coefficients and the integrals into the expression for the roots of the quadratic equation for E. The coefficients in the CI expression for Ψ can then be found in the normal way by using the lowest value of E and solving the secular equations. ●

6.7 Many-body perturbation theory

The application of perturbation theory to a molecular system of interacting electrons and nuclei is called **many-body perturbation theory**. Recall from discussions of perturbation theory in Chapter 2 (see eqn 2.31) that the hamiltonian is expressed as a sum of a simple, 'model' hamiltonian, $\hat{H}^{(0)}$, and a perturbation $\hat{H}^{(1)}$. Because we wish to find the correlation energy, a natural choice for the model hamiltonian are the Fock operators of the HF-SCF method and for the perturbation we take the difference between the Fock operators and the true many-electron hamiltonian (eqn 6.1). That is,

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} \qquad \text{with } \hat{H}^{(0)} = \sum_{i=1}^{N_e} f_i \tag{6.19}$$

Because the core hamiltonian in the Fock operator in eqn 6.8 cancels the one-electron terms in the full hamiltonian, the perturbation is the difference between the instantaneous interaction between the electrons (the third term in eqn 6.1) and the average interaction (as represented by the operators J and K in the Fock operator). Thus, for electron 1

$$\hat{H}^{(1)}(1) = \sum_i \frac{j_0}{r_{1i}} - \sum_m \{2J_m(1) - K_m(1)\} \tag{6.20}$$

where the first sum (the true interaction) is over all the electrons other than electron 1 itself and the second sum (the average interaction) is over all the occupied orbitals. This choice was first made by C. Møller and M.S. Plesset in 1934 and the method is called **Møller–Plesset perturbation theory** (MPPT). Applications of MPPT to molecular systems were not undertaken until the 1970s and the rise of sufficient computing power.

As usual in perturbation theory, the true wavefunction is written as a sum of the eigenfunction of the model hamiltonian and higher-order correction terms. The **correlation energy**, the difference between the true energy and the HF energy, is given by energy corrections that are second order and higher. If we suppose that the true wavefunction of the system is given by a sum of CSFs like that in eqn 6.18, then (see eqn 2.35)

$$E_0^{(2)} = \sum_{M \neq 0} \frac{|\int \Psi_M \hat{H}^{(1)} \Psi_0 \, d\tau|^2}{E_0^{(0)} - E_M^{(0)}} \tag{6.21}$$

According to **Brillouin's theorem**, only doubly excited Slater determinants have nonzero $\hat{H}^{(1)}$ matrix elements and hence only they make a contribution to $E_0^{(2)}$. The identification of the second-order energy correction with the correlation energy is the basis of the MPPT method denoted MP2. The extension of MPPT to include third- and fourth-order energy corrections are denoted MP3 and MP4, respectively.

● A BRIEF ILLUSTRATION

According to Brillouin's theorem, and for our simple model of H_2 built from two basis orbitals, we write

$$\Psi = C_0 \Psi_0 + C_2 \Psi_2 \qquad \text{with } \Psi_0 = \psi_a(1)\psi_a(2)\sigma_-(1,2)$$
$$\Psi_2 = \psi_b(1)\psi_b(2)\sigma_-(1,2)$$

The only matrix element we need for the sum in eqn 6.21 is

$$\int \Psi_2 \hat{H}^{(1)} \Psi_0 \, d\tau_1 d\tau_2 = j_0 \int \psi_b(1)\psi_b(2) \frac{1}{r_{12}} \psi_a(1)\psi_a(2) d\tau_1 d\tau_2$$

All the integrals over terms based on J and K are zero because these are one-electron operators and so either $\psi_a(1)$ or $\psi_a(2)$ is left unchanged and its orthogonality to ψ_b ensures that the integral vanishes. We now expand each molecular orbital in terms of the basis functions χ_A and χ_B, and obtain

$$\int \Psi_2 \hat{H}^{(1)} \Psi_0 d\tau_1 d\tau_2 = c_{Ab}^2 c_{Aa}^2 (AA|AA)$$
$$+ c_{Ab} c_{Bb} c_{Aa}^2 (BA|AA) + \cdots + c_{Bb}^2 c_{Ab}^2 (BB|BB)$$

If we ignore overlap the coefficients are all equal to $\pm 1/\sqrt{2}$, and if we use symmetries like (AA|AB) = (AA|BA) and (AA|AB) = (BB|BA), this expression simplifies to

$$\int \Psi_2 \hat{H}^{(1)} \Psi_0 \mathrm{d}\tau_1 \mathrm{d}\tau_2 = \tfrac{1}{2}\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AA}|\mathrm{BB})\}$$

It follows that the second-order estimate of the correlation energy is

$$E_0^{(2)} = \frac{\frac{1}{4}\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AA}|\mathrm{BB})\}^2}{E_0^{(0)} - E_2^{(0)}} = \frac{\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AA}|\mathrm{BB})\}^2}{8(\varepsilon_a - \varepsilon_b)}$$

The term (AA|AA) − (AA|BB) is the difference in repulsion energy between both electrons being confined to one atom and each being on a different atom. ●

The third approach: density functional theory

A technique that has gained considerable ground in recent years to become one of the most widely used procedures for the calculation of molecular structure is **density functional theory** (DFT). Its advantages include less demanding computational effort, less computer time, and—in some cases, particularly for d-metal complexes—better agreement with experimental values than is obtained from Hartree–Fock based methods.

6.8 The Kohn–Sham equations

The central focus of DFT is not the wavefunction but the electron probability density, ρ (Section 1.5). The 'functional' part of the name comes from the fact that the energy of the molecule is a function of the electron density and the electron density is itself a function of the positions of the electrons, $\rho(\boldsymbol{r})$. In mathematics a function of a function is called a *functional*, and in this specific case we write the energy as the functional $E[\rho]$. We have encountered a functional before but did not use this terminology: the expectation value of the hamiltonian is the energy expressed as a functional of the wavefunction, for a single value of the energy, $E[\psi]$, is associated with each function ψ. An important point to note is that because $E[\psi]$ is an integral of $\psi H \psi$ over all space, it has contributions from the whole range of values of ψ.

Simply from the structure of the hamiltonian in eqn 6.1 we can suspect that the energy of a molecule can be expressed as contributions from the kinetic energy, the electron–nucleus interaction, and the electron–electron interaction. The first two contributions depend on the electron density distribution. The electron–electron interaction is likely to depend on the same quantity, but we have to be prepared for there to be a modification of the classical electron–electron interaction due to electron exchange (the contribution which in Hartree–Fock theory is expressed by K). That the exchange contribution can be expressed in terms of the electron density is not at all obvious, but in 1964 P. Hohenberg and W. Kohn were able to prove that the exact ground-state energy of an N_e-electron molecule is uniquely determined by the electron probability density. They showed that it is possible to write

$$E[\rho] = E_{\mathrm{Classical}}[\rho] + E_{\mathrm{XC}}[\rho] \tag{6.22}$$

where $E_{\mathrm{Classical}}[\rho]$ is the sum of the contributions of kinetic energy, electron–nucleus interactions, and the classical electron–electron potential energy, and $E_{\mathrm{XC}}[\rho]$ is the **exchange–correlation energy**. This term takes into account all the non-classical electron–electron effects due to spin and applies small corrections to the kinetic energy part of $E_{\mathrm{Classical}}$ that arise from electron–electron interactions. The Hohenberg–Kohn theorem guarantees the existence of $E_{\mathrm{XC}}[\rho]$ but—like so many existence theorems in mathematics—gives no clue about how it should be calculated.

The first step in the implementation of this approach is to calculate the electron density. The relevant equations were deduced by Kohn and L.J. Sham in 1965, who showed that ρ can be expressed as a contribution from each electron present in the molecule, and written

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N_e} |\psi_i(\boldsymbol{r})|^2 \tag{6.23}$$

ψ_i is called a **Kohn–Sham orbital** and is a solution of the **Kohn–Sham equation**, which closely resembles the form of the Schrödinger equation (on which it is based). For a two-electron system,

$$h_1\psi_i(1) + j_0 \int \frac{\rho(2)}{r_{12}} \mathrm{d}\tau_2 \psi_i(1) + V_{\mathrm{XC}}(1)\psi_i(1) = \varepsilon_i \psi_i(1) \tag{6.24}$$

The first term is the usual core term, the second term is the classical interaction between electron 1 and electron 2, and the third term takes exchange effects into account and is called the **exchange–correlation potential**. The ε_i are the Kohn–Sham orbital energies.

6.9 The exchange–correlation energy

The exchange–correlation potential plays a central role in DFT and can be calculated once we know the exchange–correlation energy $E_{\mathrm{XC}}[\rho]$ by forming the following 'functional derivative':

$$V_{\mathrm{XC}}(\boldsymbol{r}) = \frac{\delta E_{\mathrm{XC}}[\rho]}{\delta \rho} \tag{6.25}$$

A functional derivative is defined like an ordinary derivative, but we have to remember that $E_{XC}[\rho]$ is a quantity that gets its value from the entire range of values of $\rho(\boldsymbol{r})$, not just from a single point. Thus, when $\boldsymbol{r}$ undergoes a small change $d\boldsymbol{r}$, the density changes by $\delta\rho$ to $\rho(\boldsymbol{r}+d\boldsymbol{r})$ at each point and $E_{XC}[\rho]$ undergoes a change that is the sum (integral) of all such changes:

$$\delta E_{XC}[\rho] = \int \frac{\delta E_{XC}[\rho]}{\delta\rho}\delta\rho\, d\boldsymbol{r} = \int V_{XC}(\boldsymbol{r})\delta\rho\, d\boldsymbol{r}$$

Note that V_{XC} is an ordinary function of $\boldsymbol{r}$, not a functional: it is the local contribution to the integral that defines the global dependence of $E_{XC}[\rho]$ on $\delta\rho$ throughout the range of integration.

● A BRIEF ILLUSTRATION

The greatest challenge in density functional theory is to find an accurate expression for the exchange–correlation energy. One widely used but approximate form for $E_{XC}[\rho]$ is based on the model of a uniform electron gas, a hypothetical electrically neutral system in which electrons move in a space of continuous and uniform distribution of positive charge. For a uniform electron gas, the exchange–correlation energy can be written as the sum of an exchange contribution and a correlation contribution. The latter is a complicated functional that is beyond the scope of this chapter; we ignore it here. Then the exchange–correlation energy is

$$E_{XC}[\rho] = \int A\rho^{4/3} d\boldsymbol{r} \qquad \text{with } A = -(9/8)(3/\pi)^{1/2} j_0$$

When the density changes from $\rho(\boldsymbol{r})$ to $\rho(\boldsymbol{r}) + \delta\rho(\boldsymbol{r})$ at each point (Fig. 6.6), the functional changes from $E_{XC}[\rho]$ to $E_{XC}[\rho+\delta\rho]$:

$$E_{XC}[\rho+\delta\rho] = \int A(\rho+\delta\rho)^{4/3} d\boldsymbol{r}$$

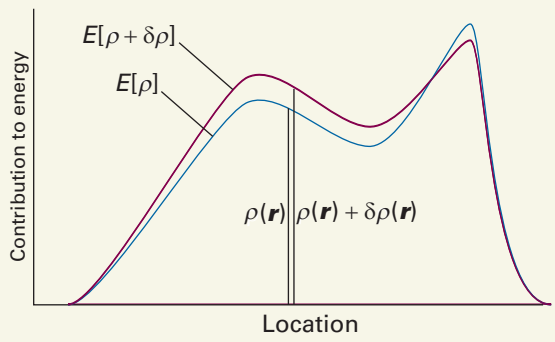


Fig. 6.6 The change in the exchange–correlation energy functional from $E_{XC}[\rho]$ to $E_{XC}[\rho+\delta\rho]$ (the area under each curve) as the density changes from ρ to $\rho+\delta\rho$ at each point $\boldsymbol{r}$.

The integrand can be expanded in a Taylor series (*Mathematical background 1*) and, discarding terms of order $\delta\rho^2$ and higher, we obtain:

$$E_{XC}[\rho+\delta\rho] = \int (A\rho^{4/3} + \tfrac{4}{3}A\rho^{1/3}\delta\rho) d\boldsymbol{r}$$
$$= E_{XC}[\rho] + \int \tfrac{4}{3}A\rho^{1/3}\delta\rho\, d\boldsymbol{r}$$

Therefore, the differential δE_{XC} of the functional (the difference $E_{XC}[\rho+\delta\rho] - E_{XC}[\rho]$ that depends linearly on $\delta\rho$) is

$$\delta E_{XC}[\rho] = \int \tfrac{4}{3}A\rho^{1/3}\delta\rho\, d\boldsymbol{r}$$

and therefore

$$V_{XC}(\boldsymbol{r}) = \tfrac{4}{3}A\rho(\boldsymbol{r})^{1/3} = -\tfrac{3}{2}(3/\pi)^{1/3} j_0 \rho(\boldsymbol{r})^{1/3} \qquad (6.26)$$ ●

Self-test 6.3 Find the exchange–correlation potential if the exchange–correlation energy is given by $E_{XC}[\rho] = \int B\rho^2 d\boldsymbol{r}$. $[V_{XC}(\boldsymbol{r}) = 2B\rho(\boldsymbol{r})]$

The Kohn–Sham equations must be solved iteratively and self-consistently (Fig. 6.7). First, we guess the electron density; it is common to use a superposition of atomic electron probability densities. Second, the exchange–correlation potential is calculated by assuming an approximate form of the dependence of the exchange–correlation energy on the electron density and evaluating the functional derivative. Next, the Kohn–Sham equations are solved to obtain an initial set of Kohn–Sham

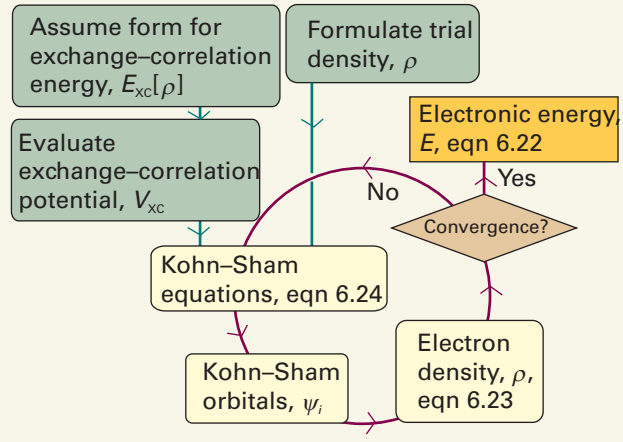


Fig. 6.7 The iteration procedure for solving the Kohn–Sham equations in density functional theory.

orbitals. This set of orbitals is used to obtain a better approximation to the electron probability density (from eqn 6.23) and the process is repeated until the density remains constant to within some specified tolerance. The electronic energy is then computed by using eqn 6.22.

As is the case for the Hartree–Fock one-electron wavefunctions, the Kohn–Sham orbitals can be expanded using a set of basis functions; solving eqn 6.24 then amounts to finding the coefficients in the expansion. Various basis functions, including Slater-type and Gaussian-type orbitals, can be used. Whereas Hartree–Fock methods have computational times that scale as N_b^4, DFT methods scale as N_b^3. Therefore, DFT methods are computationally more efficient, though not necessarily more accurate, than HF methods.

● A BRIEF ILLUSTRATION

In applying DFT to molecular hydrogen, we begin by assuming that the electron density is a sum of atomic electron densities arising from the presence of electrons in the atomic orbitals χ_A and χ_B (which may be STOs or GTOs) and write $\rho(\boldsymbol{r}) = |\chi_A|^2 + |\chi_B|^2$ for each electron. For the exchange–correlation energy E_{XC} we use the form appropriate to a uniform electron gas and the corresponding exchange–correlation potential derived in the previous *illustration* (eqn 6.26).

The Kohn–Sham orbital for the molecule is a solution of

$$\left\{h_1 + j_0\int\frac{\rho(\boldsymbol{r}_2)}{r_{12}}\mathrm{d}\boldsymbol{r}_2 - \tfrac{3}{2}(3/\pi)^{1/3}j_0\rho(\boldsymbol{r}_1)^{1/3}\right\}\psi_1(\boldsymbol{r}_1) = \varepsilon_1\psi_1(\boldsymbol{r}_1)$$

We insert the $\rho(\boldsymbol{r}_1)$ and $\rho(\boldsymbol{r}_2)$ we have assumed and solve this equation numerically for ψ_1. Once we have that orbital, we replace our original guess at the electron density by $\rho(\boldsymbol{r}) = |\psi_1(\boldsymbol{r})|^2$. This density is then substituted back into the Kohn–Sham equation to obtain an improved function $\psi_1(\boldsymbol{r})$ and the process repeated until the density and exchange–correlation energy are unchanged to within a specified tolerance on successive iterations.

When convergence of the iterations has been achieved, the electronic energy (eqn 6.22) is calculated from

$$E[\rho] = 2\int\psi_1(\boldsymbol{r})h_1\psi_1(\boldsymbol{r})\mathrm{d}\boldsymbol{r} + j_0\int\rho(\boldsymbol{r}_1)\frac{1}{r_{12}}\rho(\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2 - \tfrac{9}{8}(3/\pi)^{1/3}j_0\int\rho(\boldsymbol{r})^{4/3}\mathrm{d}\boldsymbol{r}$$

where the first term is the sum of the energies of the two electrons in the field of the two nuclei, the second term is the electron–electron repulsion, and the final term includes the correction due to nonclassical electron–electron effects. ●

Current achievements

Electronic structure calculations provide valuable information about a wide range of important physical and chemical properties. One of the most important is the equilibrium molecular geometry, the arrangement of atoms that results in the lowest energy for the molecule. The calculation of equilibrium bond lengths and bond angles supplements experimental data obtained from structural studies such as X-ray crystallography (Section 9.3), electron diffraction (Section 9.4), and microwave spectroscopy (Section 10.3). Furthermore, analyses of the molecular potential energy curve can yield vibrational frequencies for comparison with results from infrared spectroscopy (Section 10.6) as well as molecular dipole moments.

6.10 Comparison of calculations and experiments

The choice of an electronic structure method to solve a chemical problem is not usually an easy task. Both the chemical accuracy associated with the method and the cost of the calculation (in terms of computational speed and memory) must be taken into account. An *ab initio* method such as full CI or MP2, each of which is capable of yielding accurate results on a molecule with a small number of atoms and electrons, is often computationally impractical for many-electron molecules. In contrast, a semiempirical or DFT calculation might make an electronic structure calculation on the large molecule feasible but with an accompanying sacrifice in reliability. Indeed, no single methodology has been found to be applicable to all molecules. However, the promise that computational chemistry has to enhance our ability to predict chemical and physical properties of a wide range of molecules is sufficient to drive further development of electronic structure methods.

First consider molecular hydrogen, the subject of most of the *illustrations* in this chapter. To compare results from different electronic structure methods, we need to say a few words about the basis set used in the calculations. A minimal basis set uses the fewest possible basis set functions (Section 6.3). However, the **Hartree–Fock limit** is achieved by the use of an infinite number of basis functions. Although this limit is not computationally attainable, a finite basis is considered to have reached the limit if the energy, equilibrium geometry, and other calculated properties have converged and do not vary within a specified tolerance upon further increases in the size of the basis set. The results presented for Hartee–Fock calculations that use such a basis set are labelled 'HF limit' in the accompanying tables. (In practice, the 'HF-limit' in the tables corresponds to a 6-311+G** basis; see Table 6.1.) So that we can compare different electronic structure methods more directly, we report literature results where the same or a similar basis set was used in the different

Table 6.2 Comparison of methods for small H-containing molecules

	Expt	HF limit	MNDO	PM3	CI*	MP2	DFT
R(H—H)/pm	74.2	73.6	66.3	69.9	73.9	73.8	76.7
R(O—H)/pm in H_2O	95.8	94.3	94.3	95.1	95.2	96.0	97.1
Bond angle/° in H_2O	104.5	106.4	106.8	107.7	104.9	103.5	105.1
Dipole moment, $\mu(H_2O)$/D†	1.85	2.2	1.8	1.7	1.9	2.2	2.2

* For dihydrogen, full CI. For water, CI with inclusion of singly and doubly excited determinants.
† 1 D (debye) = 3.336×10^{-30} C m.

types of calculations. The density functional theory calculations to which we refer all used the exchange–correlation potential for a uniform electron gas, including the correlation component neglected in the first *illustration* of Section 6.9.

Table 6.2 compares the equilibrium bond length for dihydrogen determined from various electronic structure methods; the equilibrium geometry corresponds to the minimum in the calculated molecular potential energy. Not surprisingly, the CI and MPPT *ab initio* methods are the most accurate. However, for this simple molecule the Hartree–Fock result is also within chemical accuracy (about 1 pm); the semiempirical methods do not fare as well by comparison but, as also shown in Table 6.2, MNDO and PM3 are more accurate for calculations on water than on dihydrogen. The CI and MP2 methods also achieve chemical accuracy (within 1°) for the bond angle in water. As for the dipole moment of water, the semiempirical methods are found to be slightly more accurate than the Hartree–Fock and density-functional calculations.

Table 6.3 shows some results from semiempirical, MPPT, and DFT calculations of carbon–carbon bond lengths in a variety of small organic molecules as well as the C=C stretching wavenumbers in the alkenes. As we shall see in Section 10.7, vibrational wavenumbers depend on the 'force constants' for displacements from the equilibrium geometry, and they in turn depend on the second derivatives of the potential energy with respect to the displacement. The methods generally do a good job of predicting bond lengths of the single and double bonds and, even though the semiempirical methods do not perform as well in calculating vibrational wavenumbers, the results from Table 6.3 do give us a reasonable level of confidence in the predictive abilities of DFT and semiempirical calculations.

Table 6.3 Comparison of methods for small organic molecules

	Expt	PM3	MP2	DFT
R(C—C)/pm				
propane	152.6	151.2	152.9	151.2
cyclobutane	154.8	154.2	155.0	153.7
R(C=C)/pm				
propene	131.8	132.8	134.1	133.0
cyclobutene	133.2	134.9	135.2	134.1
$\tilde{\nu}$(C=C stretch)/cm^{-1}				
propene	1656	1862	1698	1680
cyclobutene	1570	1772	1598	1600

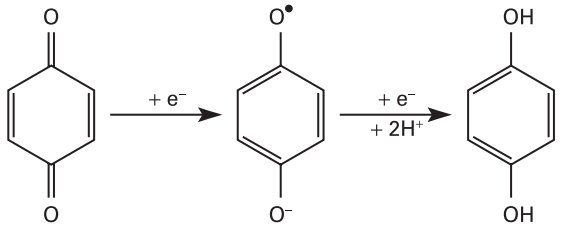
Confidence in DFT and semiempirical methods becomes particularly important when the cost of computations makes *ab initio* methods impractical; such is the case for typical inorganic and organometallic compounds. Hartree–Fock methods generally perform poorly for d-metal complexes and *ab initio* methods can be prohibitively costly. However, DFT and semiempirical methods (such as PM3, which includes parameters for most d metals) have vastly improved the performance of applications of electronic structure theory to inorganic chemistry.

6.11 Applications to larger molecules

In the area of thermodynamics, computational chemistry is becoming the technique of choice for estimating the enthalpies of formation (Section 14.8) of molecules with complex three-dimensional structures. It also opens the way to exploring the effect of solvation on enthalpies of formation by calculating the enthalpy of formation in the gas phase and then including several solvent molecules around the solute molecule. The numerical results should currently be treated as only estimates with the primary purpose of predicting whether interactions with the solvent increase or decrease the enthalpy of formation. As an example, consider the amino acid glycine, which can exist in a neutral (NH_2CH_2COOH) or zwitterionic ($^+NH_3CH_2CO_2^-$) form. It has been found computationally that, whereas in the gas phase the neutral form has a lower enthalpy of formation than the zwitterion, in water the opposite is true because of strong interactions between the polar solvent and the charges in the zwitterion. Therefore, we might suspect that the zwitterionic form is the predominant one in polar media, as is confirmed by protonation/deprotonation calculations of the type carried out in introductory chemistry courses.

Computational chemistry can be used to predict trends in electrochemical properties, such as reduction potentials (Section 17.6). Several experimental and computational studies of aromatic hydrocarbons indicate that decreasing the energy of the lowest unoccupied molecular orbital (LUMO) enhances the ability of the molecule to accept an electron into the LUMO, with an attendant increase in the value of the molecule's reduction potential. The effect is also observed in quinones and flavins, which are co-factors involved in biological electron

transfer reactions. For example, stepwise substitution of the hydrogen atoms in *p*-benzoquinone by methyl groups ($-CH_3$) results in a systematic increase in the energy of the LUMO and a decrease in the reduction potential for formation of the semiquinone radical (**1**):

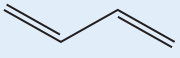
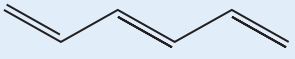
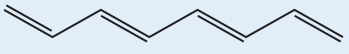


1 Semiquinone radical

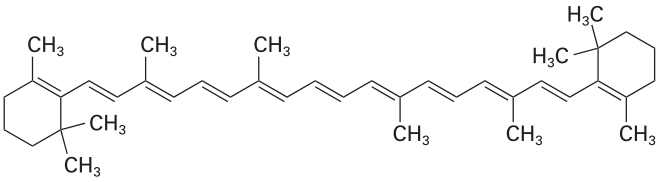
The reduction potentials of naturally occurring quinones are also modified by the presence of different substituents, a strategy that imparts specific functions to specific quinones. For example, the substituents in coenzyme Q are largely responsible for positioning its reduction potential so that the molecule can function as an electron shuttle between specific proteins in the respiratory chain (*Impact I17.3*).

The electronic structure calculations described in this chapter provide insight into spectroscopic properties by correlating the absorption wavelengths and the energy gap between the LUMO and the HOMO in a series of molecules. For example, consider the linear polyenes shown in Table 6.4, all of which absorb in the UV region. The table shows that, as expected, the wavelength of the lowest-energy electronic transition decreases as the HOMO–LUMO energy difference increases. The smallest HOMO–LUMO gap and greatest transition wavelength is found for octatetraene, the longest polyene in the group. The wavelength of the transition increases with increasing number of conjugated double bonds in linear polyenes and extrapolation of the trend suggests that a sufficiently long linear polyene should absorb light in the visible region. This is indeed the case for β-carotene (**2**), which absorbs light with $\lambda \approx 450$ nm. The ability of β-carotene to absorb visible light is part of the strategy employed by plants to harvest solar energy for use in photosynthesis (*Impact I19.1*).

Table 6.4 Electronic structure calculations and spectroscopic data

Polyene	ΔE/eV*	λ/nm
(C_2H_4)	18.1	163
	14.5	217
	12.7	252
	11.8	304

* $\Delta E = E(\text{HOMO}) - E(\text{LUMO})$.



2 β-carotene

IMPACT ON NANOSCIENCE

I6.1 The structures of nanoparticles

Semiconductor oxides, such as TiO_2 and ZnO, are a major area of current research because they can act as *photocatalysts*, substances that accelerate chemical reactions upon absorption of light. Reactions that can be enhanced by photocatalysts include the splitting of water into H_2 and O_2, and the decomposition of pollutants. Among the most popular photocatalytic materials is TiO_2 due to its low cost and catalytic efficiency. The method of preparation of the bulk oxide has a strong influence on its catalytic properties and experiments that attempt to control the form of its crystal lattice have been undertaken widely. Similarly, there is widespread interest in controlling the structure and photocatalytic properties of TiO_2 on the nanometre scale. Computational studies on small clusters of TiO_2 particles can provide insight into effects of size on photochemical properties of nanometre-sized materials, the nature of oxide–substrate interactions, and the growth of larger aggregates.

The most stable form of bulk TiO_2 at atmospheric pressure and room temperature is rutile (Fig. 6.8), in which each titanium atom is surrounded by six oxygen atoms and each O is

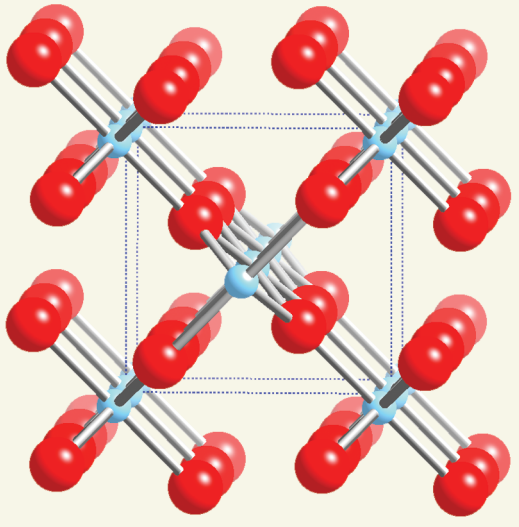


Fig. 6.8 The rutile structure of TiO_2 (blue spheres: Ti; red spheres: O).

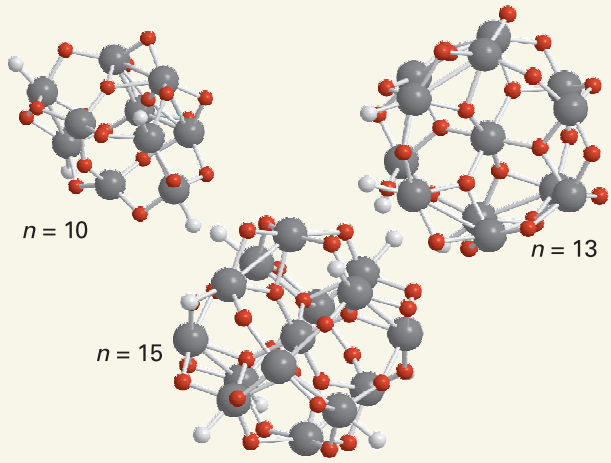


Fig. 6.9 Stable geometries for Ti_nO_{2n} clusters, with $n = 10$, 13, and 15, determined from density functional theory calculations. [From S. Hamad *et al. J. Phys. Chem. B*, 2005, **109**, 15741.]

surrounded by three Ti atoms. Each octahedron composed of the six O atoms around the Ti centre shares two edges with other octahedrons. Some experimental studies on TiO_2 nanoparticles suggest that the nanostructure is anatase, an elongated form of rutile in which the octahedrons share four edges. Other structural distortions appear to be possible as the particle size decreases.

A recent computational study on small Ti_nO_{2n} clusters with $n = 1$–15 has identified the most stable structures for nanoparticles with sizes less than 1 nm. To accomplish the challenging computational task of finding the most probable cluster structures, density functional theory was used to evaluate the energy as a function of geometry and specialized minimization algorithms were used to find equilibrium structures. The calculations revealed compact equilibrium structures with coordination numbers of the Ti atoms increasing with particle size. These structures were found not to be related to anatase. For $Ti_{11}O_{22}$ up to $Ti_{15}O_{30}$, the largest nanoparticle studied, the structures with lower energies consisted of a central octahedron surrounded by square base pyramids, trigonal bipyramids, and tetrahedra (Fig. 6.9). The DFT calculations revealed that structures with a small number of square base pyramids are particularly stable. The stable structures found for the various cluster sizes can be used in further computational work to study the effects of nanostructure on the photochemical properties of TiO_2.

IMPACT ON MEDICINE

I6.2 Molecular recognition and drug design

A drug is a small molecule or protein that binds to a specific receptor site of a target molecule, such as a larger protein or nucleic acid, and inhibits the progress of disease. To devise efficient therapies, we need to know how to characterize and optimize both the three-dimensional structure of the drug and the molecular interactions between the drug and its target.

The binding of a ligand, or *guest*, to a biopolymer, or *host*, is also governed by molecular interactions. Examples of biological *host–guest complexes* include enzyme–substrate complexes, antigen–antibody complexes, and drug–receptor complexes. In all these cases, a site on the guest contains functional groups that can interact with complementary functional groups of the host. Many specific intermolecular contacts must in general be made in a biological host–guest complex and, as a result, a guest binds only to hosts that are chemically similar. The strict rules governing molecular recognition of a guest by a host control every biological process, from metabolism to immunological response, and provide important clues for the design of effective drugs for the treatment of disease.

A full assessment of molecular recognition between a drug and its target requires knowledge of the full spectrum of interactions discussed in Chapter 8. But we can already anticipate some of the factors that optimize the formation of host–guest complexes. For example, a hydrogen bond donor group of the guest must be positioned near a hydrogen bond acceptor group of the host for tight binding to occur. We also expect that an electron-poor region in a host should interact strongly with an electron-rich region of a guest. Computational studies of the types described in this chapter can identify regions of a molecule that have high or low electron densities. Furthermore, graphical representation of numerical results allows for direct visualization of molecular properties, such as the distribution of electron density, thereby enhancing our ability to predict the nature of intermolecular contacts between host and guest.

Consider a protein host with the amino acid serine in a site that binds guests. Electronic structure methods on the serine molecule can provide electronic wavefunctions and electron probability densities at any point in the molecule. From the electron probability densities and the charges of the atomic nuclei, one can compute the electric potential (*Fundamentals F.6*) at any point in the molecule (except at the nuclei themselves). The resulting electric potential can be displayed as an **electrostatic potential surface** (an 'elpot surface') in which net positive potential is shown in one colour and net negative potential is shown in another, with intermediate gradations of colour. Such an elpot surface for serine ($NH_2CH(CH_2OH)COOH$) is shown in Fig. 6.10 where net positive potential is shown in blue and net negative potential in red. The electron-rich regions of the amino acid are susceptible to attack by an electropositive species and the electron-poor regions to attack by an electronegative species.

There are two main strategies for the discovery of a drug. In *structure-based design*, new drugs are developed on the basis of the known structure of the receptor site of a known target. However, in many cases a number of so-called *lead compounds* are known to have some biological activity but little information is available about the target. To design a molecule with improved

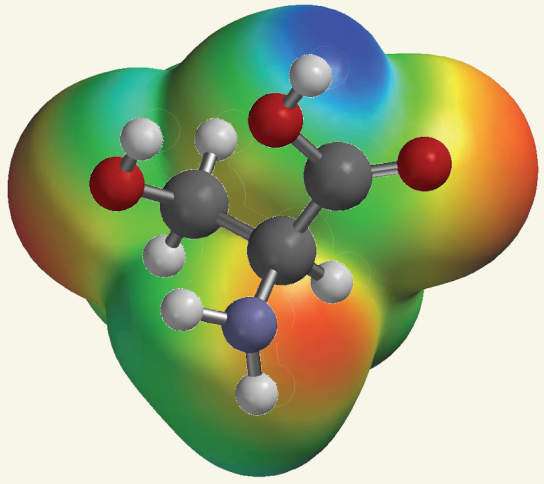


Fig. 6.10 An electrostatic potential surface for the amino acid serine. Positive charge is shown in blue and negative charge in red, with intermediate gradations of colour. The red regions of the molecule are electron-rich and the blue regions are electron-poor.

pharmacological efficacy, **quantitative structure–activity relationships** (QSAR) are often established by correlating data on activity of lead compounds with molecular properties, also called *molecular descriptors*, which can be determined either experimentally or computationally.

In broad terms, the first stage of the QSAR method consists of compiling molecular descriptors for a very large number of lead compounds. Descriptors such as molar mass, molecular dimensions and volume, and relative solubility in water and nonpolar solvents are available from routine experimental procedures. Quantum mechanical descriptors determined by calculations of the type described in this chapter include bond orders and HOMO and LUMO energies.

In the second stage of the process, biological activity is expressed as a function of the molecular descriptors. An example of a QSAR equation is:

$$\text{Activity} = c_0 + c_1 d_1 + c_2 d_1^2 + c_3 d_2 + c_4 d_2^2 + \cdots \qquad (6.27)$$

where d_i is the value of the descriptor and c_i is a coefficient calculated by fitting the data by regression analysis. The quadratic terms account for the fact that biological activity can have a maximum or minimum value at a specific descriptor value. For example, a molecule might not cross a biological membrane and become available for binding to targets in the interior of the cell if it is too hydrophilic, in which case it will not partition into the hydrophobic layer of the cell membrane (see *Impact I16.1* for details of membrane structure), or too hydrophobic, for then it may bind too tightly to the membrane. It follows that the activity will peak at some intermediate value of a parameter that measures the relative solubility of the drug in water and organic solvents.

In the final stage of the QSAR process, the activity of a drug candidate can be estimated from its molecular descriptors and the QSAR equation either by interpolation or extrapolation of the data. The predictions are more reliable when a large number of lead compounds and molecular descriptors are used to generate the QSAR equation.

The traditional QSAR technique has been refined into **3D QSAR**, in which sophisticated computational methods are used to gain further insight into the three-dimensional features of drug candidates that lead to tight binding to the receptor site of a target. The process begins by using a computer to superimpose three-dimensional structural models of lead compounds and looking for common features, such as similarities in shape, location of functional groups, and electrostatic potential plots. The key assumption of the method is that common structural features are indicative of molecular properties that enhance binding of the drug to the receptor. The collection of superimposed molecules is then placed inside a three-dimensional grid of points. An atomic probe, typically an sp^3-hybridized carbon atom, visits each grid point and two energies of interaction are calculated: E_{steric}, the steric energy reflecting interactions between the probe and electrons in uncharged regions of the drug, and E_{elec}, the electrostatic energy arising from interactions between the probe and a region of the molecule carrying a partial charge. The measured equilibrium constant for binding of the

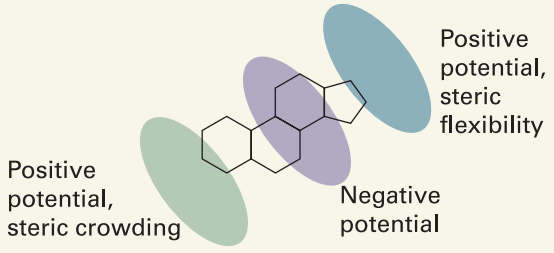


Fig. 6.11 A 3D QSAR analysis of the binding of steroids, molecules with the carbon skeleton shown, to human corticosteroid-binding globulin (CBG). The ellipses indicate areas in the protein's binding site with positive or negative electrostatic potentials and with little or much steric crowding. It follows from the calculations that addition of large substituents near the left-hand side of the molecule (as it is drawn on the page) leads to poor affinity of the drug to the binding site. Also, substituents that lead to the accumulation of negative electrostatic potential at either end of the drug are likely to show enhanced affinity for the binding site. [Adapted from P. Krogsgaard-Larsen, T. Liljefors, U. Madsen (ed.), *Textbook of drug design and discovery*, Taylor & Francis, London (2002).]

drug to the target, K_{bind}, is then assumed to be related to the interaction energies at each point $\boldsymbol{r}$ by the 3D QSAR equation

$$\log K_{\text{bind}} = c_0 + \sum_{\boldsymbol{r}} \{c_s(\boldsymbol{r})E_{\text{steric}}(\boldsymbol{r}) + c_e(\boldsymbol{r})E_{\text{elec}}(\boldsymbol{r})\} \tag{6.28}$$

where the $c(\boldsymbol{r})$ are coefficients calculated by regression analysis, with the coefficients c_s and c_e reflecting the relative importance of steric and electrostatic interactions, respectively, at the grid point $\boldsymbol{r}$. Visualization of the regression analysis is facilitated by colouring each grid point according to the magnitude of the coefficients. Figure 6.11 shows results of a 3D QSAR analysis of the binding of steroids, molecules with the carbon skeleton shown, to human corticosteroid-binding globulin (CBG). Indeed, we see that the technique lives up to the promise of opening a window into the chemical nature of the binding site even when its structure is not known.

The QSAR and 3D QSAR methods, though powerful, have limited power: the predictions are only as good as the data used in the correlations are both reliable and abundant. However, the techniques have been used successfully to identify compounds that deserve further synthetic elaboration, such as addition or removal of functional groups, and testing.

Checklist of key ideas

- ☐ 1. A spinorbital is the product of a molecular orbital and a spin function.
- ☐ 2. The Hartree–Fock (HF) method uses a single Slater determinant, built from molecular orbitals that satisfy the HF equations, to represent the ground-state electronic wavefunction.
- ☐ 3. The Hartree–Fock equations involve the Fock operator, which consists of the core hamiltonian and terms representing the average Coulomb repulsion (J) and average correction due to spin correlation (K). The equations must be solved self-consistently.
- ☐ 4. The Hartree–Fock method neglects electron correlation, the tendency of electrons to avoid one another to minimize repulsion.
- ☐ 5. The Roothaan equations are a set of simultaneous equations, written in matrix form, that result from using a basis set of functions to expand the molecular orbitals.
- ☐ 6. In a minimal basis set, one basis set function represents each of the valence orbitals of the molecule.
- ☐ 7. Slater-type orbitals (STO) and Gaussian-type orbitals (GTO) centred on each of the atomic nuclei are commonly used as basis set functions; the product of two Gaussians on different centres is a single Gaussian function located between the centres.
- ☐ 8. In semiempirical methods, the two-electron integrals are set to zero or to empirical parameters; *ab initio* methods attempt to evaluate the integrals numerically.
- ☐ 9. The Hückel method is a simple semiempirical method for conjugated π systems.
- ☐ 10. In the complete neglect of differential overlap (CNDO) approximation, two-electron integrals are set to zero unless the two basis set functions for electron 1 are the same and the two basis functions for electron 2 are the same.
- ☐ 11. Other semiempirical methods include INDO (intermediate neglect of differential overlap), NDDO (neglect of diatomic differential overlap), MINDO (modified intermediate neglect of differential overlap), MNDO (modified neglect of differential overlap), AM1, and PM3.
- ☐ 12. Virtual orbitals are molecular orbitals that are unoccupied in the HF ground-state electronic wavefunction.
- ☐ 13. A singly excited determinant is formed by transferring an electron from an occupied orbital to a virtual orbital, a doubly excited determinant by transferring two electrons, and so on. Each of these Slater determinants (including the HF wavefunction) is a configuration state function (CSF).
- ☐ 14. Configuration interaction (CI) expresses the exact electronic wavefunction as a linear combination of configuration state functions.
- ☐ 15. Configuration interaction and Møller–Plesset perturbation theory are two popular *ab initio* methods that accommodate electron correlation.
- ☐ 16. Full CI uses molecular orbitals built from a finite basis set and allows for all possible excited determinants.
- ☐ 17. Many-body perturbation theory is the application of perturbation theory to a molecular system of interacting electrons and nuclei.
- ☐ 18. Møller–Plesset perturbation theory (MPPT) uses the sum of the Fock operators from the HF method as the simple, model hamiltonian $\hat{H}^{(0)}$.
- ☐ 19. According to Brillouin's theorem, only doubly excited determinants contribute to the second-order energy correction.
- ☐ 20. In density functional theory (DFT), the electronic energy is written as a functional of the electron probability density.
- ☐ 21. The exchange–correlation energy takes into account nonclassical electron–electron effects.
- ☐ 22. The electron density is computed from the Kohn–Sham orbitals, the solutions to the Kohn–Sham (KS) equations. The latter equations are solved self-consistently.
- ☐ 23. The exchange–correlation potential is the functional derivative of the exchange–correlation energy.

☐24. One commonly used but approximate form for the exchange–correlation energy is based on the model of an electron gas, a hypothetical system in which electrons move in a uniform distribution of positive charge.

☐25. Both the chemical accuracy and the computational cost of a particular method should be considered when deciding which electronic structure method to use in a given application.

☐26. The Hartree–Fock limit refers to an infinite basis set or, in practical terms, a finite basis set for which the energy and equilibrium geometry of the molecule do not vary as the size of the basis set is increased.

Discussion questions

6.1 Describe the physical significance of each of the terms that appears in the Fock operator.

6.2 Explain why the Hartree–Fock formalism does not account for electron correlation but the methods of configuration interaction and many-body perturbation theory do.

6.3 Outline the computational steps used in the Hartree–Fock self-consistent field approach to electronic structure calculations.

6.4 Explain how the Roothaan equations arise in the Hartree–Fock method. What additional approximations do they represent?

6.5 Discuss the role of basis set functions in electronic structure calculations. What are some commonly used basis sets? Why are polarization functions often included?

6.6 Explain why the use of Gaussian-type orbitals is generally preferred over the use of Slater-type orbitals in basis sets.

6.7 Distinguish between semiempirical, *ab initio*, and density functional theory methods of electronic structure determination.

6.8 Discuss how virtual orbitals are useful in CI and MPPT electronic structure calculations.

6.9 Is DFT a semiempirical method? Justify your answer.

Exercises

6.1(a) Write down the electronic hamiltonian for the helium atom.

6.1(b) Write down the electronic hamiltonian for the lithium atom.

6.2(a) Write the expression for the potential energy contribution to the electronic hamiltonian for LiH.

6.2(b) Write the expression for the potential energy contribution to the electronic hamiltonian for BeH_2.

6.3(a) Write down the electronic hamiltonian for HeH^+.

6.3(b) Write down the electronic hamiltonian for LiH^{2+}.

6.4(a) Write down the Slater determinant for the ground state of HeH^+.

6.4(b) Write down the Slater determinant for the ground state of LiH^{2+}.

6.5(a) Write down the Hartree–Fock equation for HeH^+.

6.5(b) Write down the Hartree–Fock equation for LiH^{2+}.

6.6(a) Set up the Roothaan equations for HeH^+ and establish the simultaneous equations corresponding to the Roothaan equations. Adopt a basis set of two real normalized functions, one centred on H and one on He; denote the molecular orbitals ψ_a and ψ_b.

6.6(b) Set up the Roothaan equations for LiH^{2+} and establish the simultaneous equations corresponding to the Roothaan equations. Adopt a basis set of two real normalized functions, one centred on H and one on Li; denote the molecular orbitals ψ_a and ψ_b.

6.7(a) Construct the elements F_{AA} and F_{AB} for the species HeH^+ and express them in terms of the notation in eqn 6.14.

6.7(b) Construct the elements F_{AA} and F_{AB} for the species LiH^{2+} and express them in terms of the notation in eqn 6.14.

6.8(a) Using the integral notation in eqn 6.14, identify all of the four-centre two-electron integrals that are equal to (AA|AB).

6.8(b) Using the integral notation in eqn 6.14, identify all of the four-centre two-electron integrals that are equal to (BB|BA).

6.9(a) How many basis functions are needed in an electronic structure calculation on CH_3Cl using a (a) minimal basis set, (b) split-valence basis set, (c) double-zeta basis set?

6.9(a) How many basis functions are needed in an electronic structure calculation on CH_2Cl_2 using a (a) minimal basis set, (b) split-valence basis set, (c) double-zeta basis set?

6.10(a) What is the general mathematical form of a p-type Gaussian?

6.10(b) What is the general mathematical form of a d-type Gaussian?

6.11(a) A one-dimensional Gaussian (in x) has the form $e^{-\alpha x^2}$ or $x^n e^{-\alpha x^2}$; one-dimensional Gaussians in y and z have similar forms. Show that the s-type Gaussian (eqn 6.17) can be written as a product of three one-dimensional Gaussians.

6.11(b) A one-dimensional Gaussian (in x) has the form $e^{-\alpha x^2}$ or $x^n e^{-\alpha x^2}$; one-dimensional Gaussians in y and z have similar forms. Show that a p-type Gaussian (eqn 6.17) can be written as a product of three one-dimensional Gaussians.

6.12(a) Show that the product of s-type Gaussians on He and H in HeH^+ is a Gaussian at an intermediate position. Note that the Gaussians have different exponents.

6.12(b) Show that the product of s-type Gaussians on Li and H in LiH^{2+} is a Gaussian at an intermediate position. Note that the Gaussians have different exponents.

6.13(a) How many basis functions are needed in an electronic structure calculation on CH_3Cl using a (a) 6-31G* basis set, (b) 6-311G** basis set, (c) 6-311++G basis set?

6.13(b) How many basis functions are needed in an electronic structure calculation on CH_2Cl_2 using a (a) 6-31G* basis set, (b) 6-311G** basis set, (c) 6-311++G basis set?

6.14(a) Identify the quadratic equation for the coefficient of the basis function centred on H in HeH^+ starting from the Fock matrix and making the Hückel approximations.

6.14(b) Identify the quadratic equation for the coefficient of the basis function centred on H in LiH^{2+} starting from the Fock matrix and making the Hückel approximations.

6.15(a) Identify the two-electron integrals that are set to zero in the semiempirical method known as (a) CNDO, (b) INDO.

6.15(b) Identify the two-electron integrals that are set to zero in the semiempirical method known as NDDO.

6.16(a) In a Hartree–Fock calculation on the silicon atom using 20 basis set functions, how many of the molecular orbitals generated would be unoccupied and could be used as virtual orbitals in a configuration interaction calculation?

6.16(b) In a Hartree–Fock calculation on the sulfur atom using 20 basis set functions, how many of the molecular orbitals generated would be unoccupied and could be used as virtual orbitals in a configuration interaction calculation?

6.17(a) Give an example of a singly excited determinant in a CI calculation of H_2.

6.17(b) Give an example of a doubly excited determinant in a CI calculation of H_2.

6.18(a) Using eqn 6.18, write down the expression for the ground-state wavefunction in a CI calculation on HeH^+ involving the ground-state determinant and a singly excited determinant.

6.18(b) Using eqn 6.18, write down the expression for the ground-state wavefunction in a CI calculation on LiH^{2+} involving the ground-state determinant and a doubly excited determinant.

6.19(a) The second-order energy correction (eqn 6.21) in MPPT arises from the doubly excited determinant (the $M = 2$ term). Derive an expression for the integral that appears in the numerator of eqn 6.21 in terms of the integrals (AB|CD) for HeH^+.

6.19(b) The second-order energy correction (eqn 6.21) in MPPT arises from the doubly excited determinant (the $M = 2$ term). Derive an expression for the integral that appears in the numerator of eqn 6.21 in terms of the integrals (AB|CD) for LiH^{2+}.

6.20(a) Which of the following are functionals: (a) $d(x^3)/dx$, (b) $d(x^3)/dx$ evaluated at $x = 1$, (c) $\int x^3 dx$, (d) $\int_1^3 x^3 dx$?

6.20(b) Which of the following are functionals: (a) $d(3x^2)/dx$, (b) $d(3x^3)/dx$ evaluated at $x = 4$, (c) $\int 3x^2 dx$, (d) $\int_1^3 3x^2 dx$?

6.21(a) Using eqn 6.23, write the expression for the electron density in terms of the Kohn–Sham orbitals in a DFT calculation on LiH.

6.21(b) Using eqn 6.23, write the expression for the electron density in terms of the Kohn–Sham orbitals in a DFT calculation on BeH_2.

6.22(a) Write the two Kohn–Sham equations for the Kohn–Sham orbitals in a DFT calculation on HeH^+. Use the exchange–correlation potential of eqn 6.26.

6.22(b) Write the two Kohn–Sham equations for the Kohn–Sham orbitals in a DFT calculation on LiH^{2+}. Use the exchange–correlation potential of eqn 6.26.

6.23(a) Which of the following basis sets should give a result closer to the Hartree–Fock limit in an electronic structure calculation on ethanol, C_2H_5OH: (a) double-zeta, (b) split-valence, (c) triple zeta?

6.23(b) Which of the following basis sets should give a result closer to the Hartree–Fock limit in an electronic structure calculation on methanol CH_3OH: (a) 4-31G, (b) 6-311+G**, (c) 6-31G*?

Problems*

Many of the following problems call on the use of commercially available software. Use versions that are available with this text or the software recommended by your instructor.

Numerical problems

6.1 Using appropriate electronic structure software, perform Hartree–Fock self-consistent field calculations for the ground electronic states of H_2 and F_2 using (a) 6-31G* and (b) 6-311+G** basis sets. Determine ground-state energies and equilibrium geometries. Compare computed equilibrium bond lengths to experimental values.

6.2 Using approprite electronic structure software and a basis set of your choice or on the advice of your instructor, perform calculations for: (a) the ground electronic state of H_2; (b) the ground electronic state of F_2; (c) the first electronic state of H_2; (d) the first electronic state of F_2. Determine energies and equilibrium geometries and compare to experimental values where possible.

6.3 Use the AM1 and PM3 semiempirical methods to compute the equilibrium bond lengths and standard enthalpies of formation of (a) ethanol, C_2H_5OH, (b) 1,4-dichlorobenzene, $C_6H_4Cl_2$. Compare with experimental values and suggest reasons for any discrepancies.

6.4 Molecular orbital calculations based on semiempirical (Section 6.5), *ab initio*, and DFT methods describe the spectroscopic properties of conjugated molecules better than simple Hückel theory (Section 6.4). (a) Using the computational method of your choice (semiempirical, *ab initio*, or density functional methods), calculate the energy separation between the HOMO and LUMO of ethene, butadiene, hexatriene, and octatetraene. (b) Plot the HOMO–LUMO energy separations against the experimental frequencies for $\pi^* \leftarrow \pi$ ultraviolet absorptions for these molecules (61 500, 46 080, 39 750, and 32 900 cm^{-1}, respectively). Use mathematical software to find the polynomial equation that best fits the data. (c) Use your polynomial fit from part (b) to estimate the wavenumber and wavelength of the $\pi^* \leftarrow \pi$ ultraviolet absorption of decapentaene from the calculated HOMO–LUMO energy separation. (d) Discuss why the calibration procedure of part (b) is necessary.

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

6.5 Molecular electronic structure methods may be used to estimate the standard enthalpy of formation of molecules in the gas phase. (a) Using a semiempirical method of your choice, calculate the standard enthalpy of formation of ethene, butadiene, hexatriene, and octatetraene in the gas phase. (b) Consult a database of thermochemical data, and, for each molecule in part (a), calculate the difference between the calculated and experimental values of the standard enthalpy of formation. (c) A good thermochemical database will also report the uncertainty in the experimental value of the standard enthalpy of formation. Compare experimental uncertainties with the relative errors calculated in part (b) and discuss the reliability of your chosen semiempirical method for the estimation of thermochemical properties of linear polyenes.

6.6‡ Luo *et al.* (*J. Chem. Phys.* **98**, 3564 (1993)) reported experimental observation of He_2, a species that had escaped detection for a long time. The observation required temperatures in the neighbourhood of 1 mK. Perform configuration interaction and MPPT electronic structure calculations and compute the equilibrium bond length R_e of the dimer as well as the energy of the dimer at R_e relative to the separated He + He atomic limit. (High level, accurate computational studies suggest that the well depth for He_2 is about 0.0151 zJ at a distance R_e of about 297 pm.)

6.7 An important quantity in nuclear magnetic resonance spectroscopy (Chapter 12), which should be familiar from ^{13}C-NMR spectra of organic molecules, is the chemical shift; this experimentally determined quantity is influenced by the details of the electronic structure near the ^{13}C nucleus of interest. Consider the following series of molecules: benzene, methylbenzene, trifluoromethylbenzene, benzonitrile, and nitrobenzene in which the substituents *para* to the C atom of interest are H, CH_3, CF_3, CN, and NO_2, respectively. (a) Using the computational method of your choice, calculate the net charge at the C atom *para* to these substituents in the series of organic molecules given above. (b) It is found empirically that the ^{13}C chemical shift of the *para* C atom increases in the order: methylbenzene, benzene, trifluoromethylbenzene, benzonitrile, nitrobenzene. Is there a correlation between the behaviour of the ^{13}C chemical shift and the computed net charge on the ^{13}C atom? (This problem is revisited in Problem 12.17.)

Theoretical problems

6.8 Show that the Slater determinant in eqn 6.5a is normalized assuming that the spinorbitals from which it is constructed are orthogonal and normalized.

6.9 In a configuration interaction calculation on the ground ^2S state of Li, which of the following Slater determinants can contribute to the ground-state wavefunction?

(a) $|\psi_{1s}^{\alpha}\psi_{1s}^{\beta}\psi_{2s}^{\alpha}|$ (b) $|\psi_{1s}^{\alpha}\psi_{1s}^{\beta}\psi_{2s}^{\beta}|$ (c) $|\psi_{1s}^{\alpha}\psi_{1s}^{\beta}\psi_{2p}^{\alpha}|$

(d) $|\psi_{1s}^{\alpha}\psi_{2p}^{\alpha}\psi_{2p}^{\beta}|$ (e) $|\psi_{1s}^{\alpha}\psi_{3d}^{\alpha}\psi_{3d}^{\beta}|$ (f) $|\psi_{1s}^{\alpha}\psi_{2s}^{\alpha}\psi_{3s}^{\alpha}|$

6.10 In a configuration interaction calculation on the excited $^3\Sigma_u^+$ electronic state of H_2, which of the following Slater determinants can contribute to the excited-state wavefunction?

(a) $|1\sigma_g^{\alpha}1\sigma_u^{\alpha}|$ (b) $|1\sigma_g^{\alpha}1\pi_u^{\alpha}|$ (c) $|1\sigma_u^{\alpha}1\pi_g^{\beta}|$

(d) $|1\sigma_g^{\beta}2\sigma_u^{\beta}|$ (e) $|1\pi_u^{\alpha}1\pi_g^{\alpha}|$ (f) $|1\pi_u^{\beta}2\pi_u^{\beta}|$

6.11 Use MPPT to obtain an expression for the ground-state wavefunction corrected to first order in the perturbation.

6.12 It is often necessary during the course of an electronic structure calculation to take derivatives of the basis functions with respect to nuclear coordinates. Show that the derivative of an s-type Gaussian with respect to x yields a p-type Gaussian and that the derivative of a p-type Gaussian ($i = 1$, $j = k = 0$ in eqn 6.17) yields a sum of s- and d-type Gaussians.

6.13 (a) In a continuation of Exercise 6.6a for HeH^+, proceed to determine the energies of the two molecular orbitals as well as the relation between the two coefficients for ψ_a and the relation between the two coefficients for ψ_b. (b) Repeat for LiH^{2+} (in a continuation of Exercise 6.6b).

6.14 (a) Continuing the Hartree–Fock calculation on HeH^+ in Problem 6.13(a), give the expressions for all four of the elements of the Fock matrix in terms of four-centre, two-electron integrals; the latter are defined in eqn 6.14. (b) Repeat for LiH^{2+} (in a continuation of Problem 6.13(b)).

6.15 (a) In a continuation of Problem 6.14(a) for HeH^+, use Hückel molecular orbital theory to express the energies of the molecular orbitals in terms of α and β. (b) Repeat for LiH^{2+} (in a continuation of Problem 6.14(b)).

6.16 (a) Using the expressions for the four elements of the Fock matrix for HeH^+ determined in Problem 6.14(a), show how these expressions simplify if the CNDO semiempirical method is used. (b) Repeat for LiH^{2+}, beginning with the expressions determined in Problem 6.14(b).

6.17 Consider a four-centre integral in an electronic structure calculation on NH_3 involving s-type Gaussian functions centred on each atomic nucleus. Show that the four-centre, two-electron integral reduces to an integral over two different centres.

6.18 (a) Show why configuration interaction gives an improved ground-state wavefunction for HeH^+ compared to the Hartree–Fock ground-state wavefunction. Use a minimal basis set and ignore overlap. Follow along the lines of the argument presented in the first *illustration* in Section 6.6 but recognize the complication introduced by the fact that HeH^+ does not have inversion symmetry. (b) Repeat for LiH^{2+}.

6.19 In the second *illustration* of Section 6.6, the secular equation for a CI calculation on molecular hydrogen using the ground-state Slater determinant and the doubly excited determinant was presented as well as the expression for one of the hamiltonian matrix elements. Develop similar expressions for the remaining hamiltonian matrix elements.

6.20 Show that in MPPT first-order energy corrections do not contribute to the correlation energy.

6.21 Prove Brillouin's theorem, which states that the hamiltonian matrix elements between the ground-state Hartree–Fock Slater determinant and singly excited determinants are zero.

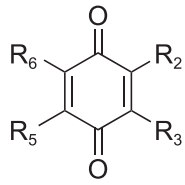
6.22 Derive an expression for the second-order estimate of the correlation energy for H_2 if, in a CI calculation using a minimal basis set, the overlap between the two basis set functions is not ignored but set equal to a constant S.

6.23 Find the DFT exchange–correlation potential if the exchange–correlation energy is given by $\int C\rho^{5/3}\mathrm{d}\boldsymbol{r}$.

Applications: to biology

6.24 Molecular orbital calculations may be used to predict trends in the standard potentials of conjugated molecules, such as the quinones and flavins, that are involved in biological electron transfer reactions (Section 20.8). It is commonly assumed that decreasing the energy of the LUMO enhances the ability of a molecule to accept an electron into the LUMO, with an accompanying increase in the value of the molecule's standard potential. Furthermore, a number of studies indicate that there is a linear correlation between the LUMO energy and the reduction

potential of aromatic hydrocarbons. (a) The standard potentials at pH 7 for the one-electron reduction of methyl-substituted 1,4-benzoquinones (**3**) to their respective semiquinone radical anions are:

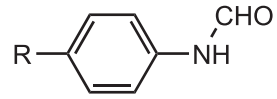


3

R_2	R_3	R_5	R_6	$E^{\ominus}$/V
H	H	H	H	0.078
CH_3	H	H	H	0.023
CH_3	H	CH_3	H	−0.067
CH_3	CH_3	CH_3	H	−0.165
CH_3	CH_3	CH_3	CH_3	−0.260

Using the computational method of your choice (semiempirical, *ab initio*, or density functional theory methods), calculate E_{LUMO}, the energy of the LUMO of each substituted 1,4-benzoquinone, and plot E_{LUMO} against $E^{\ominus}$. Do your calculations support a linear relation between E_{LUMO} and $E^{\ominus}$? (b) The 1,4-benzoquinone for which $R_2 = R_3 = CH_3$ and $R_5 = R_6 = OCH_3$ is a suitable model of ubiquinone, a component of the respiratory electron transport chain (*Impact I17.3*). Determine E_{LUMO} of this quinone and then use your results from part (a) to estimate its standard potential. (c) The 1,4-benzoquinone for which $R_2 = R_3 = R_5 = CH_3$ and $R_6 = H$ is a suitable model of plastoquinone, a component of the photosynthetic electron transport chain (*Impact I19.1*). Determine E_{LUMO} of this quinone and then use your results from part (a) to estimate its standard potential. Is plastoquinone expected to be a better or worse oxidizing agent than ubiquinone? (d) Based on your predictions and on basic concepts of biological electron transport (Section 20.8), suggest a reason why ubiquinone is used in respiration and plastoquinone is used in photosynthesis.

6.25 This problem gives a simple example of a quantitative structure–activity relation (QSAR), *Impact I6.2*, showing how to predict the affinity of non-polar groups for hydrophobic sites in the interior of proteins. (a) Consider a family of hydrocarbons R—H. The hydrophobicity constants, π, for R = CH_3, CH_2CH_3, $(CH_2)_2CH_3$, $(CH_2)_3CH_3$, and $(CH_2)_4CH_3$ are, respectively, 0.5, 1.0, 1.5, 2.0, and 2.5. Use these data to predict the π value for $(CH_2)_6CH_3$. (b) The equilibrium constants K_I for the dissociation of inhibitors (**4**) from the enzyme chymotrypsin were measured for different substituents R:



4

R	CH_3CO	CN	NO_2	CH_3	Cl
π	−0.20	−0.025	0.33	0.5	0.9
$\log K_I$	−1.73	−1.90	−2.43	−2.55	−3.40

Plot $\log K_I$ against π. Does the plot suggest a linear relationship? If so, what are the slope and intercept to the $\log K_I$ axis of the line that best fits the data? (c) Predict the value of K_I for the case R = H.