

commutes with the total spin operator  $\hat{S}$  corresponding to  $\sum_{i=1}^A \mathbf{s}_i$  for  $A$  particles. Yet we see that the general HF equations (11.65) and (11.66) derived from this Hamiltonian do not reflect this symmetry: in principle both spin-up and spin-down components may be present in the HF sp states,

$$\phi_n(\mathbf{r}, m_s) = \delta_{m_s, +\frac{1}{2}} u_n(\mathbf{r}) + \delta_{m_s, -\frac{1}{2}} v_n(\mathbf{r}), \quad (11.69)$$

because the Fock term mixes both components. The HF Slater determinant built with such sp states would not even be an eigenstate of the  $\hat{S}_z$  operator; a typical example where the mean-field approximation may break a symmetry of the exact Hamiltonian.

In fact, the most general two-component sp states in Eq. (11.69) are almost never used in a molecular context. One imposes from the beginning that each HF sp state is either a pure spin-up or a pure spin-down state. The two types of HF sp states corresponding to  $m_s = \pm\frac{1}{2}$  will be denoted by  $\phi_n^{(m_s)}$ , where  $n = 1, \dots, N^{(m_s)}$  so that  $\sum_{m_s} N^{(m_s)} = N$ . The single spin component structure implies

$$\langle \mathbf{r} m'_s | \phi_n^{(m_s)} \rangle = \delta_{m_s, m'_s} \phi_n^{(m_s)}(\mathbf{r}). \quad (11.70)$$

A Slater determinant built with such sp states is automatically an eigenstate of the  $\hat{S}_z$  operator (but not necessarily of  $\hat{S}^2$ ) with eigenvalue  $S_z = \frac{1}{2}[N^{(+\frac{1}{2})} - N^{(-\frac{1}{2})}]$ , and the corresponding one-body density matrix is diagonal in spin,

$$\begin{aligned} n^{HF}(\mathbf{r}' m'_s, \mathbf{r} m_s) &= \delta_{m_s, m'_s} n_{HF}^{(m_s)}(\mathbf{r}', \mathbf{r}) \\ &= \delta_{m_s, m'_s} \sum_{n=1}^{N^{(m_s)}} \phi_n^{(m_s)}(\mathbf{r}) \phi_n^{(m_s)*}(\mathbf{r}'). \end{aligned} \quad (11.71)$$

Using the ansatz (11.70) the HF equations for the spin-up and spin-down type of orbitals become

$$\begin{aligned} \varepsilon_n^{(m_s)} \phi_n^{(m_s)}(\mathbf{r}) &= -\frac{\hbar^2}{2m} \nabla^2 \phi_n^{(m_s)}(\mathbf{r}) + v_H(\mathbf{r}) \phi_n^{(m_s)}(\mathbf{r}) \\ &\quad - \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') n_{HF}^{(m_s)}(\mathbf{r}', \mathbf{r}) \phi_n^{(m_s)}(\mathbf{r}'). \end{aligned} \quad (11.72)$$

This incarnation of HF goes under the name of unrestricted Hartree-Fock or UHF (though it is not the most general mean-field treatment), in order to distinguish it from restricted Hartree-Fock discussed below. Note that in Eq. (11.72) the Fock term acts only between same-spin particles, and

that the only coupling between the two spin types occurs through the total density in the Hartree term.

In restricted Hartree-Fock or RHF one assumes that the HF sp states come in pairs of opposite spin, both members of the pair having the same spatial wave function. RHF is eminently suitable for most neutral molecules, which have an even number of electrons and a spin-singlet ( $S = 0$ ) ground state. In this case the ground state is well-approximated by a closed-shell configuration: a single Slater determinant consisting of  $A/2$  spatial orbitals which are doubly occupied by a spin-up and a spin-down electron. Such a RHF closed-shell configuration is then automatically an  $S = 0$  eigenstate of  $\hat{S}^2$ . The RHF ansatz

$$\phi_n^{(m_s)}(\mathbf{r}) = \phi_n(\mathbf{r}), \text{ for } n = 1, \dots, N/2 \text{ and } m_s = \pm \frac{1}{2}, \quad (11.73)$$

when substituted in Eq. (11.72), leads to the RHF equations for the spatial orbitals,

$$\begin{aligned} \varepsilon_n \phi_n(\mathbf{r}) = & -\frac{\hbar^2}{2m} \nabla^2 \phi_n(\mathbf{r}) + v_H(\mathbf{r}) \phi_n(\mathbf{r}) \\ & - \frac{1}{2} \int d\mathbf{r}' V(\mathbf{r} - \mathbf{r}') n_{HF}(\mathbf{r}', \mathbf{r}) \phi_n(\mathbf{r}'), \end{aligned} \quad (11.74)$$

where the spin-integrated one-body density matrix is related to Eq. (11.66) as

$$n_{HF}(\mathbf{r}', \mathbf{r}) = \sum_{m_s} n^{HF}(\mathbf{r}' m_s, \mathbf{r} m_s) = 2 \sum_{n=1}^{A/2} \phi_n(\mathbf{r}) \phi_n^*(\mathbf{r}'). \quad (11.75)$$

There is of course a trade-off to be made going from the most general Eq. (11.69) to UHF and RHF: less restrictions on the allowed HF sp states means a lower HF energy, but also worse symmetry properties of the HF ground state. The UHF Eqs. (11.72) are commonly used for situations with unpaired electrons (e.g. ionic or radical molecular species with a non-singlet ground state), and can be combined with projection techniques to cure possible spin contamination of the HF ground state. However, when a serious break-down of RHF stability occurs (as happens e.g. in the molecular dissociation limit discussed in Sec.11.3.3), this usually signals the inadequacy of a description in terms of a single Slater determinant, and it is better to give up such a starting point altogether.

For electrons in atoms there is a higher symmetry, since the external potential is spherically symmetric and the Hamiltonian also commutes with

the total orbital angular momentum operator  $\hat{\mathbf{L}}$  corresponding to  $\sum_i \hat{\ell}_i$ . Similar considerations can be made as in the molecular case. In unrestricted HF the radial parts of the HF sp states are allowed to depend on the projection quantum numbers  $m_\ell$  and  $m_s$ , and the HF ground state is an eigenstate of  $\hat{L}_z$  and  $\hat{S}_z$ , but not of  $\hat{\mathbf{L}}^2$  and  $\hat{\mathbf{S}}^2$ . Restricted HF, where the radial part of the HF sp states does not depend on  $m_\ell$  and  $m_s$ , provides a good approximation to describe the  $L = S = 0$  ground state of closed-shell atoms. All  $n\ell$ -shells are assumed to be filled with  $2(2\ell + 1)$  electrons, and the HF Slater determinant is an  $L = S = 0$  eigenstate.

## 11.2 Atoms

### 11.2.1 Closed-shell configurations

The HF equations for an atomic closed-shell configuration can be derived from the RHF equations in Eq. (11.74) with the spherical ansatz

$$\phi_i(\mathbf{r}) = \varphi_{n\ell}(r)Y_{\ell m_\ell}(\hat{\mathbf{r}}), \quad (11.76)$$

for the HF sp states. Multiplying Eq. (11.74) with  $Y_{\ell m_\ell}^*(\hat{\mathbf{r}})$  and integrating over  $\hat{\mathbf{r}}$  leads to equations for the radial wave functions  $\varphi_{n\ell}(r)$ ,

$$\begin{aligned} \varepsilon_{n\ell} \varphi_{n\ell}(r) = \int d\hat{\mathbf{r}} Y_{\ell m_\ell}^*(\hat{\mathbf{r}}) \left\{ \left[ -\frac{1}{2} \nabla^2 - \frac{Z}{r} + v_H(\mathbf{r}) \right] \varphi_{n\ell}(r) Y_{\ell m_\ell}(\hat{\mathbf{r}}) \right. \\ \left. - \frac{1}{2} \int d\mathbf{r}' \frac{n_{HF}(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \varphi_{n\ell}(r') Y_{\ell m_\ell}(\hat{\mathbf{r}}') \right\}, \end{aligned} \quad (11.77)$$

provided the right-hand side of Eq. (11.77) is independent of  $m_\ell$ . This independence is obvious for the kinetic and central potential term, *e.g.*

$$\nabla^2 [\varphi_{n\ell}(r) Y_{\ell m_\ell}(\hat{\mathbf{r}})] = \left( \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\ell(\ell+1)}{r^2} \right) \varphi_{n\ell}(r) Y_{\ell m_\ell}(\hat{\mathbf{r}}), \quad (11.78)$$

but the Hartree and Fock terms require a bit more consideration.

Since each  $(n\ell)$ -shell is fully occupied, the spin-integrated one-body density matrix in Eq. (11.75) can be expressed as

$$\begin{aligned} n_{HF}(\mathbf{r}', \mathbf{r}) &= 2 \sum_{n\ell} \varphi_{n\ell}(r) \varphi_{n\ell}(r') \sum_{m_\ell=-\ell}^{\ell} Y_{\ell m_\ell}(\hat{\mathbf{r}}) Y_{\ell m_\ell}^*(\hat{\mathbf{r}}') \\ &= 2 \sum_{n\ell} \varphi_{n\ell}(r) \varphi_{n\ell}(r') \frac{2\ell+1}{4\pi} P_\ell(\cos \omega), \end{aligned} \quad (11.79)$$

where  $P_\ell(x)$  is the Legendre polynomial of order  $\ell$  and  $\omega$  is the angle between  $\hat{\mathbf{r}}$  and  $\hat{\mathbf{r}}'$ . The electron density is the diagonal part of  $n_{HF}(\mathbf{r}, \mathbf{r}')$  and becomes [note that  $P_\ell(1) = 1$ ],

$$n^{HF}(\mathbf{r}) = n_{HF}(\mathbf{r}, \mathbf{r}) = \frac{1}{4\pi} \sum_{n\ell} 2(2\ell + 1) \varphi_{n\ell}^2(r). \quad (11.80)$$

The closed-shell density in Eq. (11.80) is spherically symmetric, only depending on  $r = |\mathbf{r}|$ .

We can now evaluate the Hartree potential [see Eq. (11.67)],

$$v_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n_{HF}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (11.81)$$

To work out the angular integration, one needs the following expansion for the reciprocal distance between  $\mathbf{r}$  and  $\mathbf{r}'$ ,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L=0}^{\infty} \frac{r_{<}^L}{r_{>}^{L+1}} P_L(\cos\omega), \quad (11.82)$$

where  $r_{<}$  is the smaller and  $r_{>}$  is the larger of the pair  $(r, r')$ . Only the  $L = 0$  contribution in Eq. (11.82) survives the angular integration in Eq. (11.81), because of the orthogonality properties of the Legendre polynomials,

$$\int d\hat{\mathbf{r}}' P_L(\cos\omega) = 2\pi \int_{-1}^{+1} dx P_L(x) = 4\pi\delta_{L,0}. \quad (11.83)$$

As a consequence, the Hartree potential is spherically symmetric,

$$v_H(r) = 4\pi \int dr' r'^2 \frac{n_{HF}(r')}{r_{>}}, \quad (11.84)$$

and the Hartree term in Eq. (11.77) is seen to be independent of  $m_l$ .

Finally, the Fock term in Eq. (11.77) becomes, with the aid of expressions (11.79) and (11.82),

$$\begin{aligned} (\hat{v}_F \varphi_{n\ell})(r) &= \frac{1}{2} \int d\hat{\mathbf{r}} Y_{\ell m_\ell}^*(\hat{\mathbf{r}}) \int d\mathbf{r}' \frac{n_{HF}(\mathbf{r}', \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \varphi_{n\ell}(r') Y_{\ell m_\ell}(\hat{\mathbf{r}}') \\ &= \sum_{n'\ell'} \varphi_{n'\ell'}(r) \sum_{L=0}^{\infty} \int dr' r'^2 \varphi_{n'\ell'}(r') \varphi_{n\ell}(r') \frac{r_{<}^L}{r_{>}^{L+1}} C_{\ell\ell'L}, \end{aligned} \quad (11.85)$$

where the angular integrations have been combined into coefficients

$$C_{\ell\ell'L} = \sum_{m'_L M_L} \frac{4\pi}{2L+1} \int d\hat{\mathbf{r}} Y_{\ell m_\ell}^*(\hat{\mathbf{r}}) Y_{LM_L}(\hat{\mathbf{r}}) Y_{\ell' m'_\ell}(\hat{\mathbf{r}}) \int d\hat{\mathbf{r}}' Y_{\ell' m'_\ell}^*(\hat{\mathbf{r}}') Y_{LM_L}^*(\hat{\mathbf{r}}') Y_{\ell m_\ell}(\hat{\mathbf{r}}'). \quad (11.86)$$

The integrated product of three spherical harmonics is a real number, which can be expressed as

$$\int d\hat{\mathbf{r}} Y_{\ell m_\ell}^*(\hat{\mathbf{r}}) Y_{LM_L}(\hat{\mathbf{r}}) Y_{\ell' m'_\ell}(\hat{\mathbf{r}}) = \frac{\sqrt{(2\ell+1)(2\ell'+1)(2L+1)}}{\sqrt{4\pi}} (-1)^{m_\ell} \begin{pmatrix} \ell & L & \ell' \\ -m_\ell & M_L & m'_\ell \end{pmatrix} \begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix}. \quad (11.87)$$

in terms of the  $3j$ -symbols of standard angular momentum algebra. This implies that the summation over  $L$  in Eq. (11.85) is restricted to the finite interval  $|\ell - \ell'| \leq L \leq \ell + \ell'$ . Using the normalization property

$$\sum_{m'_L M_L} \begin{pmatrix} \ell & L & \ell' \\ -m_\ell & M_L & m'_\ell \end{pmatrix}^2 = \frac{1}{2\ell+1} \quad (11.88)$$

one arrives at

$$C_{\ell\ell'L} = (2\ell'+1) \begin{pmatrix} \ell & L & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2, \quad (11.89)$$

which is indeed independent of  $m_\ell$ .

Combining all of the above results, the HF equations for an atomic closed-shell configuration become

$$\varepsilon_{n\ell} \varphi_{n\ell}(r) = \left\{ -\frac{1}{2} \left[ \frac{1}{r} \frac{\partial^2}{\partial r^2} r - \frac{\ell(\ell+1)}{r^2} \right] - \frac{Z}{r} + v_H(r) \right\} \varphi_{n\ell}(r) - (\hat{v}_F \varphi_{n\ell})(r). \quad (11.90)$$

This represents a set of non-linear integro-differential equations, which can be solved by a variety of methods.

Near  $r = 0$  the HF orbitals have the usual behaviour for a central potential problem, i.e.  $\varphi_{n\ell}(r) \sim r^\ell$ . The asymptotic behaviour ( $r \rightarrow \infty$ ) is a bit more tricky, due to the presence of the non-local Fock potential and the long range of the Coulomb force. One can show that for occupied HF orbitals the asymptotic potential behaves as  $(A - Z - 1)/r + w(r)$ , where  $Z$  is the central charge,  $N$  is the number of electrons, and  $w(r)$  is

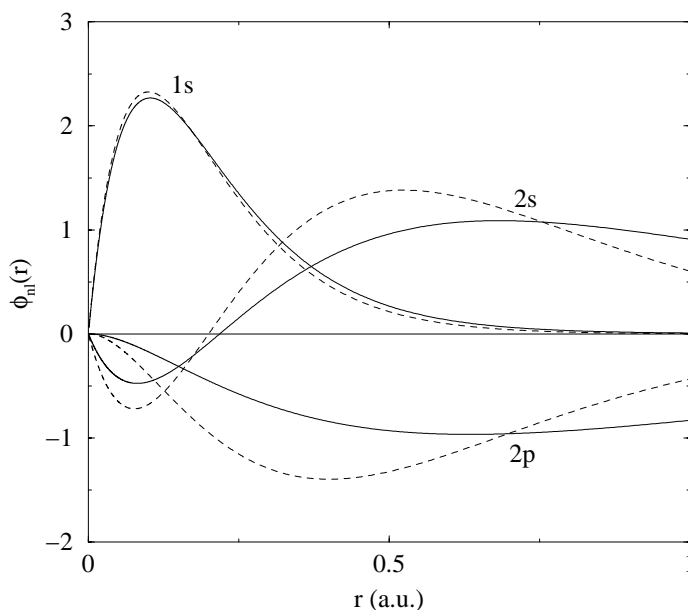


Fig. 11.2 The HF  $1s$ ,  $2s$ , and  $2p$  orbitals in the Ne atom ( $Z = 10$ ) represented by full lines are compared with the corresponding hydrogenic orbitals (dashed lines).

a residual contribution decreasing faster than  $1/r$ . Moreover, all occupied orbitals have the same decay,  $\varphi_{nl}(r) \sim e^{-\kappa r}$ , where  $\kappa = \sqrt{2\varepsilon}$  is determined by the largest occupied HF sp energy  $\varepsilon$ . For unoccupied orbitals there is no cancellation between the Hartree and Fock contributions. The asymptotic potential is less attractive and behaves as  $(A - Z)/r + w(r)$ . As a result, HF typically cannot predict bound unoccupied states for neutral atoms ( $A = Z$ ).

In Fig. 11.2 the occupied HF sp orbitals in the Ne atom are compared with the corresponding hydrogenic orbitals. The most deeply bound orbitals ( $1s$ ) are very similar. In contrast, the HF valence orbitals  $2s$  and  $2p$  are pushed outward compared to the hydrogenic  $2s$  and  $2p$ , because the central charge is screened by the  $1s$  electrons.

### 11.2.2 Comparison with experimental data

In Table 11.1 experimental results for the binding energy and the removal energies in a number of  $L = S = 0$  closed-shell atoms are compared with

Table 11.1 Hartree-Fock results and experimental data

		Removal energies		Total energy	
		HF	Exp.	HF	Exp.
He	1s	-0.918	-0.9040	-2.862	-2.904
Be	1s	-4.733	-4.100	-14.573	-14.667
	2s	-0.309	-0.343		
Ne	1s	-32.77	-31.70	-128.547	-128.928
	2s	-1.930	-1.782		
	2p	-0.850	-0.793		
Mg	1s	-49.03	-47.91	-199.615	-200.043
	2s	-3.768	-3.26		
	2p	-2.283	-1.81		
	3s	-0.253	-0.2811		
Ar	1s	-118.6	-117.87	-526.818	-527.549
	2s	-12.32	-12.00		
	2p	-9.571	-9.160		
	3s	-1.277	-1.075		
	3p	-0.591	-0.579		

Hartree-Fock results for a number of  $L = S = 0$  atoms, compared with experimental data. All energies are in atomic units (Hartree).

the Hartree-Fock predictions.

It is clear that HF in atomic systems is a good starting point, which is able to explain the bulk of the binding energy. In accordance with Koopman's theorem, the removal energies are in reasonable agreement with the data as well. Results are somewhat worse for Be and Mg, for which a representation as a pure closed-shell system is less adequate.

Yet there is little reason to be smug about the performance of HF. The total energy, e.g., is dominated by the rather inert core electrons. Chemical binding between atoms, however, is determined by the valence electrons and is sensitive to small energy differences. In electronic systems the deviations from HF can therefore be crucial, and one often defines the *correlation energy* as the difference between the exact and the HF energy.

The spectroscopic factors associated with the removal states also point to the presence of small but nonnegligible deviations from the HF picture. Experimentally one finds in  $(e, 2e)$  reactions spectroscopic factors  $S \approx 0.90 - 0.95$  for the valence states, whereas HF predicts  $S = 1$ .

To explain these discrepancies one has to go beyond the mean-field and include higher-order contributions to the self-energy.

### 11.2.3 Numerical details

In a numerical solution of the HF equations (11.90) one usually chooses a grid of radial points  $r_i$ , in order to convert the continuous equations to a discrete (matrix) problem. Since the sp wave functions vary much more rapidly near the central charge (the region of small  $r$ ) than in the tail region, an equidistant  $r_i$  grid is not practical. Defining a new independent variable through a logarithmic transformation  $u = \ln(r)$  is therefore quite useful in atomic problems. The  $u$ -variable, which has a range  $-\infty < u < +\infty$ , can then be sampled on an equidistant grid. In practice, one takes a finite interval  $[u_{min}, u_{max}]$ , supplemented with suitable boundary conditions at the edges.

In combination with new dependent variables  $h_{n\ell}(u)$  defined as

$$h_{n\ell}(u) = r^{\frac{3}{2}} \varphi_{n\ell}(r), \quad (11.91)$$

the HF equations (11.90) transform as

$$\begin{aligned} \varepsilon_{n\ell} h_{n\ell}(u) = & \left\{ -\frac{1}{2} \left[ \frac{\partial^2}{r \partial u^2} \frac{1}{r} - \frac{(\ell + \frac{1}{2})^2}{r^2} \right] - \frac{Z}{r} + v_H(u) \right\} h_{n\ell}(u) \\ & - (\hat{v}_F h_{n\ell})(u). \end{aligned} \quad (11.92)$$

The sp wave functions  $h_{n\ell}(u)$  are now normalized as

$$\int_{-\infty}^{\infty} du h_{n\ell}(u) h_{n'\ell'}(u) = \delta_{n,n'} \delta_{\ell,\ell'}. \quad (11.93)$$

The Hartree term in Eq. (11.92) reads

$$v_H(u) = \int du' \frac{1}{r_{>}} \sum_{n\ell} 2(2\ell + 1) h_{n\ell}^2(u), \quad (11.94)$$

and the Fock term can be written as

$$\begin{aligned} (\hat{v}_F h_{n\ell})(u) &= \sum_{n'\ell'} h_{n'\ell'}(u) \sum_L \int du' \frac{r_{<}^L}{r_{>}^{L+1}} C_{\ell\ell'L} h_{n'\ell'}(u') h_{n\ell}(u'). \\ &= \int du' v_F^{(\ell)}(u, u') h_{n\ell}(u'), \end{aligned} \quad (11.95)$$

in terms of a nonlocal potential

$$v_F^{(\ell)}(u, u') = \sum_{n'\ell'} h_{n'\ell'}(u) \sum_L \frac{r_{<}^L}{r_{>}^{L+1}} C_{\ell\ell'L} h_{n'\ell'}(u'). \quad (11.96)$$

Tackling the nonlinear equations (11.92) with iterative methods implies that one has to solve repeatedly equations of the form

$$\left[ \hat{T} - \frac{Z}{r} + v_H(u) - \hat{v}_F \right] h(u) = \epsilon h(u), \quad (11.97)$$

where  $\hat{T}$  is the kinetic energy, and the local Hartree potential  $v_H(u)$  and the non-local Fock potential  $v_F^{(\ell)}(u, u')$  are fixed by the sp wave functions  $\{h_n^{old}\}$  of the previous iteration step. The eigenvalue problem in Eq. (11.97) then determines both the new energy  $\epsilon$  and the new wave function  $h(u)$ . After transposing the Eq. (11.97) on the discrete  $u$ -grid, this is simply a matter of matrix diagonalization. However, the presence of the non-local Fock potential  $v_F^{(\ell)}(u, u')$  would require diagonalization of a matrix with dimension equal to the number of grid points. It is technically much easier to treat the Fock term as an inhomogeneous term. This can be done by replacing Eq. (11.97) with the following consistency loop:

$$h^{(1)}(u) = h^{old}(u) \quad (\text{Initialization}) \quad (11.98)$$

$$y^{(i)}(u) = (\hat{v}_F h^{(i)})(u) \quad (11.99)$$

$$\epsilon^{(i)} = \int du h^{(i)}(u) \left[ \left( \hat{T} - \frac{Z}{r} + v_H(u) \right) h^{(i)}(u) - y^{(i)}(u) \right] \quad (11.100)$$

$$\left( \hat{T} - \frac{Z}{r} + v_H(u) - \epsilon^{(i)} \right) x^{(i)}(u) = y^{(i)}(u) \quad (11.101)$$

$$h^{(i+1)}(u) = x^{(i)}(u) / \sqrt{\int du' |x^{(i)}(u')|^2}. \quad (11.102)$$

After convergence of the sequence  $(h^{(1)}, h^{(2)}, \dots)$ , this is obviously equivalent to Eq. (11.97). The advantage is that Eq.(11.101) only involves the kinetic term and purely local contributions. On a grid this gives rise to a tridiagonal matrix structure, and the resulting linear system can be easily solved by recursion techniques (see also the computer exercise in Sec.11.2.4).

#### 11.2.4 Computer exercise

Reproduce the HF results in Table 11.1 using the ideas in Sec. 11.2.3, combined with the (quick and dirty) discretization techniques explained below.

- Introduce boundaries  $r_{min} = 10^{-7}/Z$  and  $r_{max} = 25$  for the radial

distance  $r$ , and a corresponding grid for  $u = \ln(r)$ ,

$$u_i = c + (i - 1)\Delta, \quad i = 1, \dots, M, \quad (11.103)$$

where  $M \approx 1000$ ,  $c = \ln(r_{min})$  and

$$\Delta = \frac{1}{M - 1} \ln \left( \frac{r_{max}}{r_{min}} \right). \quad (11.104)$$

- For integrations use the crude approximation

$$\int du G(u) \rightarrow \Delta \sum_{i=1}^M G(u_i). \quad (11.105)$$

As a result, integral transformations of the type

$$F(u) = \int du' \frac{r_i^L}{r_i^{L+1}} G(u'), \quad (11.106)$$

which appear in the Hartree and Fock term, can be done in only  $\mathcal{O}(M)$  operations by means of the following recursion relations:

$$V_0 = 0; \quad V_i = V_{i-1} + G(u_i) r_i^L, \quad i = 1, \dots, M \quad (11.107)$$

$$W_0 = 0; \quad W_i = W_{i-1} + G(u_i) / r_i^{L+1}, \quad i = 1, \dots, M \quad (11.108)$$

$$F(u_i) = \Delta \left[ \frac{V_i}{r_i^{L+1}} + r_i^L (W_M - W_i) \right], \quad i = 1, \dots, M \quad (11.109)$$

- Approximate the second-order differential operator in Eq.(11.92) on the grid as

$$\left( \frac{1}{r} \frac{\partial^2}{\partial u^2} \frac{1}{r} \right) h(u) \rightarrow \left( -\frac{2h(u_i)}{r_i^2} + \frac{h(u_{i+1})}{r_i r_{i+1}} + \frac{h(u_{i-1})}{r_i r_{i-1}} \right) \frac{1}{\Delta^2}, \quad (11.110)$$

which gives rise to a symmetric tridiagonal matrix. Corrections at the boundaries can be neglected.

- If  $A_{ij}$  is a symmetric tridiagonal matrix with nonzero elements

$$A_{ii} = a_i, \quad i = 1, \dots, M; \quad A_{i,i+1} = A_{i+1,i} = b_i, \quad i = 1, \dots, M - 1, \quad (11.111)$$

then linear systems of the type

$$\sum_{j=1}^M A_{ij} X_j = Y_i, \quad i = 1, \dots, M \quad (11.112)$$

can be solved for  $X_i$  by means of the following recursion relations:

$$U_M = a_M; U_i = a_i - \frac{b_i^2}{U_{i+1}}, \quad i = M-1, \dots, 1 \quad (11.113)$$

$$V_M = \frac{Y_M}{U_M}; V_i = Y_i - \frac{b_i V_{i+1}}{U_i}, \quad i = M-1, \dots, 1 \quad (11.114)$$

$$X_1 = V_1; X_i = (V_i - \frac{b_{i-1}}{U_i})X_{i-1}, \quad i = 2, \dots, M. \quad (11.115)$$

- Between successive iterations an orthogonalization step should be performed for the sp wave functions having the same  $\ell$ . For a given set of  $K$  non-orthogonal vectors  $(X^{(1)}, X^{(2)}, \dots, X^{(K)})$  construct the  $K \times K$  overlap matrix

$$S_{\mu\nu} = \sum_{i=1}^M X_i^{(\mu)} X_i^{(\nu)}, \quad (11.116)$$

and define the new orthonormal set  $(X'^{(1)}, X'^{(2)}, \dots, X'^{(K)})$  as

$$X'^{(\mu)} = \sum_{\nu=1}^K [S^{-\frac{1}{2}}]_{\mu\nu} X^{(\nu)}. \quad (11.117)$$

- The complete program flow should look like this:

1. Initialize the sp wavefunctions  $\{h_{nl}^{old}(u)\}$  with hydrogenic orbitals.
2. With a fixed set of  $\{h_{nl}^{old}(u)\}$ :
  - (a) For each  $nl$ : construct a new orbital  $h_{nl}(u)$  as a solution of Eq. (11.92), with  $v_H$  and  $\hat{v}_F$  evaluated using the set  $\{h_{nl}^{old}(u)\}$ . To do this, iterate the consistency loop in Eqs. (11.99-11.102) until  $h_{nl}(u)$  has converged. Supplement Eq. (11.101) with an extra statement, setting the sp energy  $\epsilon$  to zero if the value obtained through Eq. (11.101) is positive. This is needed to guide the solution through the rough terrain of the first few iterations.
3. Orthogonalize the set of new  $\{h_{nl}(u)\}$
4. Monitor the convergence of all wave functions. If needed, set  $\{h_{nl}^{old}(u)\} = \{h_{nl}(u)\}$  and repeat step 2.

### 11.3 Molecules

#### 11.3.1 Molecular problems

The total (electrostatic) hamiltonian for a molecular system consisting of  $M$  atomic nuclei and  $N$  electrons is

$$H = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A<B=1}^M \frac{Z_A Z_B}{|\mathbf{r}_A - \mathbf{r}_B|} - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|}, \quad (11.118)$$

where  $M_A, Z_A, \mathbf{r}_A$  ( $A = 1, \dots, M$ ) are the mass, charge and position vectors of the nuclei (considered as point particles) and  $\mathbf{r}_i$  ( $i = 1, \dots, N$ ) are the electron coordinates.

The nuclear masses are much larger than the electron mass, and the velocities of the nuclei are consequently much smaller than the electronic velocities. It is therefore an excellent approximation to assume that the electrons move in a static field generated by the nuclei at fixed positions  $\mathbf{r}_A, \mathbf{r}_B, \dots$ . This is the so-called Born-Oppenheimer approximation, which allows to decouple the nuclear and electronic motion into separate problems.

First one has to find the electronic ground state for fixed nuclear positions  $\{\mathbf{r}_A\}$ , which are considered as external parameters for the electronic problem. Let's denote with  $\Psi_{el}(\{\mathbf{r}_A\})$  the ground state of the many-electron Hamiltonian

$$H_{el}(\{\mathbf{r}_A\}) = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{r}_A|}, \quad (11.119)$$

corresponding to the ground-state energy

$$E_{el}(\{\mathbf{r}_A\}) = \langle \Psi_{el}(\{\mathbf{r}_A\}) | \hat{H}_{el}(\{\mathbf{r}_A\}) | \Psi_{el}(\{\mathbf{r}_A\}) \rangle. \quad (11.120)$$

The motion of the nuclei is then governed by the nuclear Hamiltonian

$$H_{nuc} = - \sum_{A=1}^M \frac{1}{2M_A} \nabla_A^2 + \sum_{A<B=1}^M \frac{Z_A Z_B}{|\mathbf{r}_A - \mathbf{r}_B|} + E_{el}(\{\mathbf{r}_A\}), \quad (11.121)$$

where the electronic ground-state energy  $E_{el}(\{\mathbf{r}_A\})$  plays the role of a (3M-dimensional) potential surface for the nuclei. The Hamiltonian (11.121) can be treated classically or quantummechanically, and determines completely

the rotational and vibrational properties of the molecule, or the dynamical behaviour in chemical reactions.

In a general situation, a complete scan of the multidimensional potential surface is out of the question, but it is possible to perform geometry optimization, i.e. to find the set of nuclear positions  $\{\mathbf{r}_A\}$  which minimize the potential energy

$$V_{nuc}(\{\mathbf{r}_A\}) = \left( E_{el}(\{\mathbf{r}_A\}) + \sum_{A < B=1}^M \frac{Z_A Z_B}{|\mathbf{r}_A - \mathbf{r}_B|} \right). \quad (11.122)$$

This is the classical equilibrium geometry, which determines the spatial structure of the molecule (bond lengths and bond angles). Moreover, it provides a good starting point to describe intramolecular motion in terms of small departures from the equilibrium geometry, using the standard normal mode approximation.

### 11.3.2 Hartree-Fock with a finite discrete basis set

Finding the electronic structure in the complicated external potential generated by the nuclear charges can be exceedingly difficult. In fact, except for some simple cases like diatomic molecules even the single-electron problem is impossible to solve in coordinate space. One therefore introduces a finite number of (well-chosen) basis functions of known analytic form, usually resembling the orbitals of the isolated atoms present in the molecule. The adopted basis set, which determines the sp space in the problem, is by nature non-orthogonal, as it contains atomic orbitals centered on different nuclei.

Expanding the RHF spatial orbitals  $\phi_n(\mathbf{r})$  of Eq.(11.74) in such a non-orthogonal basis set  $\{\zeta_\alpha(\mathbf{r})\}$ ,

$$\phi_n(\mathbf{r}) = \sum_{\alpha} x_{n\alpha} \zeta_{\alpha}(\mathbf{r}), \quad (11.123)$$

the RHF equations become, after projection on  $\zeta_{\beta}(\mathbf{r})$ ,

$$\epsilon_n \sum_{\alpha} x_{n\alpha} S_{\beta\alpha} = \sum_{\alpha} x_{n\alpha} [H_{HF}]_{\beta\alpha}. \quad (11.124)$$

The non-orthogonality of the basis set is reflected in the presence of the overlap matrix,

$$S_{\beta\alpha} = \int d\mathbf{r} \zeta_{\alpha}(\mathbf{r}) \zeta_{\beta}(\mathbf{r}), \quad (11.125)$$

and the matrix elements of the HF hamiltonian,

$$[H_{HF}]_{\beta\alpha} = \int d\mathbf{r} \zeta_{\beta}(\mathbf{r}) \left( -\frac{\nabla^2}{2} - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{r}_A|} \right) \zeta_{\alpha}(\mathbf{r}) \quad (11.126)$$

$$+ \sum_{\gamma\delta} x_{n\gamma} x_{n\delta} \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} [2\zeta_{\alpha}(\mathbf{r})\zeta_{\beta}(\mathbf{r})\zeta_{\gamma}(\mathbf{r}')\zeta_{\delta}(\mathbf{r}') - \zeta_{\alpha}(\mathbf{r}')\zeta_{\beta}(\mathbf{r}')\zeta_{\gamma}(\mathbf{r})\zeta_{\delta}(\mathbf{r})], \quad (11.127)$$

can be expressed in terms of spatial integrals involving only the basis functions. The equations (11.126) are called the Roothaan equations, and represent a set of non-linear algebraic equations in the unknown expansion parameters  $x_{n\alpha}$ . Obviously, the Roothaan equations with any finite basis set will yield a HF energy higher than the exact HF energy (usually called the *HF limit* in this context), but quite reliable results can be obtained by a careful choice of a limited number of basis functions.

A basis function centered on atom  $A$  has the generic form

$$\zeta(\mathbf{r}) = \varphi(\mathbf{r} - \mathbf{r}_A). \quad (11.128)$$

Two choices are commonly adopted for the shape of the atomic orbital  $\varphi$ :

$$\varphi(\mathbf{r}) = P(x, y, z)e^{-\kappa r} \text{ (Slater type)} \quad (11.129)$$

$$\varphi(\mathbf{r}) = P(x, y, z)e^{-\alpha r^2} \text{ (Gaussian type)}. \quad (11.130)$$

Here  $P(x, y, z)$  is a polynomial representing the symmetry character ( $\ell$  value) of the orbital. The global shape is either exponential (Slater type) or Gaussian. The Slater type is more physical, as atomic orbitals do decrease exponentially, and have a cusp at the position of the central charge. The Gaussian type therefore has an unphysical behaviour both at  $r = 0$  and at large  $r$ .

In practice, the numerical advantage of Gaussian-type wave functions is so great, that these are used in most of the present-day applications in quantum chemistry. This is because the use of Gaussians allows a fast computation of the matrix elements of the Coulomb interaction, even when orbitals centered on four different nuclei are involved. Moreover, the unphysical behaviour of the single Gaussian orbital in Eq. (11.130) can be largely overcome by representing the orbital a sum of (minimally three) Gaussians with different exponents, chosen so as to mimic a Slater-type orbital.

Fig. 11.3 The surface of equal electron density in fullerene.

Tremendous effort has been put into the determination of optimum basis sets for molecular calculations. Together with the availability of increased computing power, such techniques have led to the present-day ability of performing ab-initio modelling of quite complicated molecules, within Hartree-Fock or within the framework of density functional theory. An example of this is shown in Fig. 11.3, representing the electron density of the fullerene  $C_{60}$  molecule, obtained in the HF approximation and using a standard Gaussian basis.

### 11.3.3 *The hydrogen molecule*

As an example of molecular problems we discuss a highly simplified - but very instructive - model of the hydrogen molecule.

The two protons  $P_1$  and  $P_2$  are at fixed positions  $\mathbf{R}_1$  and  $\mathbf{R}_2$  (Born-Oppenheimer approximation). The two-electron ground state will be a spin singlet, and the  $S = 0$  spin part from the wave function can be split off,

$$\Psi(\mathbf{x}_1 m_{s_1}, \mathbf{x}_2 m_{s_2}) = \Phi(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{\sqrt{2}} \left( \delta_{m_{s_1}, +\frac{1}{2}} \delta_{m_{s_2}, -\frac{1}{2}} - \delta_{m_{s_1}, -\frac{1}{2}} \delta_{m_{s_2}, +\frac{1}{2}} \right). \quad (11.131)$$

Since the spin part is antisymmetric, the spatial part  $\Phi(\mathbf{r}_1, \mathbf{r}_2)$  must be symmetric under  $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$  interchange.

The finite sp basis set we consider consists of atomic 1s orbitals centered on either one of the two protons  $P_1$  and  $P_2$ , i.e.

$$\phi_i(\mathbf{r}) = \varphi_{1s}(\mathbf{r} - \mathbf{R}_i). \quad (11.132)$$

The following three symmetric combinations can be formed

$$\phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2); \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2); [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)]. \quad (11.133)$$

Because of an additional spatial symmetry (the mirror plane between the two protons) the two-electron wave function should be symmetric under  $P_1 \leftrightarrow P_2$  interchange as well. Consequently there are only two two-electron states in the problem,

$$\Phi_I(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2), \quad (11.134)$$

$$\Phi_{II}(\mathbf{r}_1, \mathbf{r}_2) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2). \quad (11.135)$$

The  $\Phi_I$  configuration is called *ionic*, since both electrons are on the same atom, and has a higher energy than the  $\Phi_{II}$  configuration. The ground state will nevertheless be a mixture of  $\Phi_I$  and  $\Phi_{II}$  due to the interaction between both configurations. In the dissociation limit (for large distances  $|\mathbf{R}_1 - \mathbf{R}_2|$  between the two nuclei) we do expect to reach a pure  $\Phi_{II}$  configuration, because it is energetically more favorable to have two isolated neutral hydrogen atoms than a  $H^-$  negative ion.

Of course we have the freedom to use, instead of the  $\Phi_I$  and  $\Phi_{II}$  two-electron states, any pair of linear independent combinations. Since  $\Phi_I$  and  $\Phi_{II}$  have equal norm, their sum and difference will be orthogonal,

$$\Phi_B(\mathbf{r}_1, \mathbf{r}_2) = \Phi_I(\mathbf{r}_1, \mathbf{r}_2) + \Phi_{II}(\mathbf{r}_1, \mathbf{r}_2) \quad (11.136)$$

$$\Phi_A(\mathbf{r}_1, \mathbf{r}_2) = \Phi_I(\mathbf{r}_1, \mathbf{r}_2) - \Phi_{II}(\mathbf{r}_1, \mathbf{r}_2). \quad (11.137)$$

Looking in detail at the spatial two-electron wave functions  $\Phi_B$  and  $\Phi_A$ , one can easily check that they have the structure of a doubly occupied molecular sp orbital,

$$\Phi_B(\mathbf{r}_1, \mathbf{r}_2) = \phi_b(\mathbf{r}_1)\phi_b(\mathbf{r}_2), \quad \Phi_A(\mathbf{r}_1, \mathbf{r}_2) = \phi_a(\mathbf{r}_1)\phi_a(\mathbf{r}_2), \quad (11.138)$$

where the sp orbitals

$$\phi_b(\mathbf{r}) = \phi_1(\mathbf{r}) + \phi_2(\mathbf{r}), \quad \phi_a(\mathbf{r}) = \phi_1(\mathbf{r}) - \phi_2(\mathbf{r}), \quad (11.139)$$

are the bonding and antibonding orbital, familiar from the description of the single-electron hydrogen molecular ion  $H_2^+$ .

The "exact" solution of the two-electron problem in this two-dimensional model space then follows from diagonalization of the Hamilto-

nian matrix in the  $(\Phi_A, \Phi_B)$  tp basis. The ground-state energy is

$$E_0 = \frac{E_A + E_B}{2} - \sqrt{\left(\frac{E_A - E_B}{2}\right)^2 + \Delta^2}, \quad (11.140)$$

where

$$E_A = \frac{\langle \Phi_A | \hat{H} | \Phi_A \rangle}{\langle \Phi_A | \Phi_A \rangle}, \quad E_B = \frac{\langle \Phi_B | \hat{H} | \Phi_B \rangle}{\langle \Phi_B | \Phi_B \rangle}, \quad (11.141)$$

$$\Delta = \frac{\langle \Phi_A | \hat{H} | \Phi_B \rangle}{\sqrt{\langle \Phi_A | \Phi_A \rangle \langle \Phi_B | \Phi_B \rangle}}. \quad (11.142)$$

In order to obtain the RHF results we would now have to solve the Roothaan equations (11.126) in the adopted sp space by means of an iterative procedure. Fortunately, the present model is so simple that we can skip this. The sp space contains only  $\phi_1$  and  $\phi_2$ , and the only spatial sp wave functions which are compatible with the symmetry requirements are precisely the bonding and antibonding combinations of Eq. (11.139). These must therefore coincide with the RHF sp basis, the bonding orbital being the doubly occupied orbital and the antibonding orbital being unoccupied. As a consequence, the RHF ground state is the  $\Phi_B$  configuration of Eq. (11.136), which together with the  $S = 0$  spin wave function can be written as a single Slater determinant, and the RHF energy is given by  $E_B$  in Eq. (11.141). This implies immediately that the molecular dissociation limit, where the spatial wave function is

$$\Phi_{II}(\mathbf{r}_1, \mathbf{r}_2) = [\Phi_B(\mathbf{r}_1, \mathbf{r}_2) - \Phi_A(\mathbf{r}_1, \mathbf{r}_2)], \quad (11.143)$$

cannot be described in RHF, since  $\Phi_{II}$  is an equal mixture of two closed-shell Slater determinants  $\Phi_A$  and  $\Phi_B$ .

For a numerical illustration we approximate the atomic  $1s$  orbital by means of a single Gaussian<sup>3</sup>

$$\varphi_{1s}(\mathbf{r}) = e^{-\alpha r^2}, \quad (11.144)$$

with  $\alpha = 0.42$ . The matrix elements  $E_B$ ,  $E_A$  and  $\Delta$  in Eq. (11.141), which are functions of the internuclear distance  $R = |\mathbf{R}_1 - \mathbf{R}_2|$ , can all be expressed in terms of exponentials and of the function

$$f(x) = \int_0^1 du e^{-xu^2} = \frac{\sqrt{\pi}}{2\sqrt{x}} \text{Erf}(\sqrt{x}), \quad (11.145)$$

<sup>3</sup>A single Gaussian is sufficient for illustrative purposes, but should of course never be used in genuine calculations.

related to the error function

$$\text{Erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dy e^{-y^2}. \quad (11.146)$$

Taking symmetries of the spatial integrals into account, the one-electron integrals needed for the evaluation of  $E_B$ ,  $E_A$  and  $\Delta$  are

$$\begin{aligned} \langle \phi_1 | \phi_2 \rangle &= \int d\mathbf{r} e^{-\alpha(\mathbf{r}-\mathbf{R}_1)^2} e^{-\alpha(\mathbf{r}-\mathbf{R}_2)^2} \\ &= \left( \frac{\pi}{2\alpha} \right)^{\frac{3}{2}} e^{-\frac{\alpha}{2}R^2} \end{aligned} \quad (11.147)$$

$$\langle \phi_1 | -\frac{1}{2}\nabla^2 | \phi_2 \rangle = \left( \frac{\pi}{2\alpha} \right)^{\frac{3}{2}} \frac{\alpha}{2} (3 - \alpha R^2) e^{-\frac{\alpha}{2}R^2} \quad (11.148)$$

$$\langle \phi_1 | \frac{1}{|\mathbf{r} - \mathbf{R}_1|} | \phi_2 \rangle = \frac{\pi}{\alpha} e^{-\frac{\alpha}{2}R^2} f(2\alpha R^2), \quad (11.149)$$

and the two-electron integrals are

$$\begin{aligned} (\phi_1 \phi_1 | V | \phi_2 \phi_2) &= \int d\mathbf{r}_1 d\mathbf{r}_2 e^{-\alpha(\mathbf{r}_1-\mathbf{R}_1)^2} e^{-\alpha(\mathbf{r}_2-\mathbf{R}_1)^2} \\ &\quad \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-\alpha(\mathbf{r}_1-\mathbf{R}_2)^2} e^{-\alpha(\mathbf{r}_2-\mathbf{R}_2)^2} \\ &= \frac{1}{4} \left( \frac{\pi}{\alpha} \right)^{\frac{5}{2}} e^{-\alpha R^2} \end{aligned} \quad (11.150)$$

$$(\phi_1 \phi_2 | V | \phi_1 \phi_2) = \frac{1}{4} \left( \frac{\pi}{\alpha} \right)^{\frac{5}{2}} f(\alpha R^2) \quad (11.151)$$

$$(\phi_1 \phi_1 | V | \phi_1 \phi_2) = \frac{1}{4} \left( \frac{\pi}{\alpha} \right)^{\frac{5}{2}} e^{-\frac{\alpha}{2}R^2} f\left(\frac{\alpha}{4}R^2\right). \quad (11.152)$$

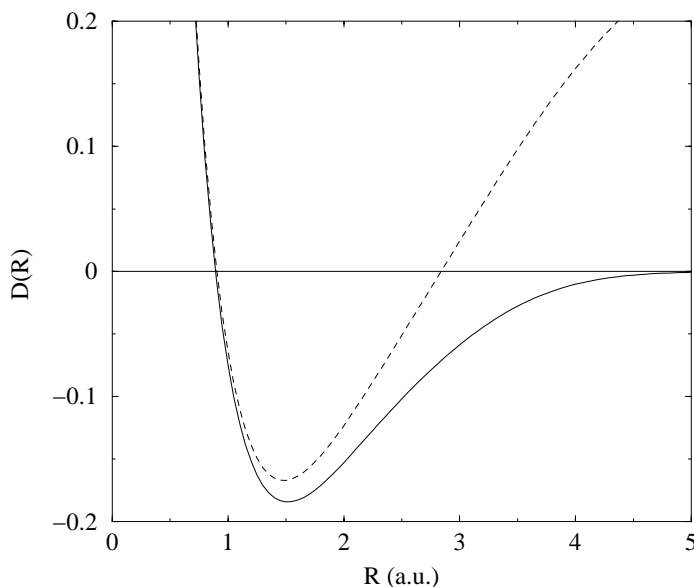
The potential energy  $V$  of the  $\text{H}_2$  molecule is the sum of the electronic ground-state energy  $E_0$  and the Coulomb repulsion between the protons,

$$V(R) = E_0(R) + \frac{1}{R}. \quad (11.153)$$

The dissociation curve  $D(R)$ , defined as

$$D(R) = V(R) - 2E(\text{H-atom}), \quad (11.154)$$

is the potential energy minus the energy of the dissociation products (in this case twice the energy of the H-atom). The position  $R_e$  of the minimum in  $V(R)$  or  $D(R)$  determines the equilibrium geometry, i.e. the bond length of the  $\text{H}_2$  molecule. The depth of the minimum,  $D_e = D(R_e)$ , is the dissociation energy.

Fig. 11.4 Dissociation curves for the  $H_2$  molecule.

The dissociation curve obtained in the present model, using Eqs. (11.130,11.141) and the  $1s$  Gaussian orbital in Eq. (11.144), is shown in Fig. 11.4. It contains all the essential features of a more exact treatment: strong repulsion as  $R \rightarrow 0$ , a minimum corresponding to the equilibrium geometry of bound  $H_2$ , and a correct dissociation limit  $D(R) \rightarrow 0$  as  $R \rightarrow \infty$ . Note that the use of a single Gaussian (having no cusp and bad asymptotics) for the  $1s$  orbital leads to an energy of the hydrogen atom,

$$E(\text{H-atom}) = \frac{\langle \phi | -\frac{\nabla^2}{2} - \frac{1}{r} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{3\alpha}{2} - 2\sqrt{\frac{2\alpha}{\pi}} = -0.404, \quad (11.155)$$

which deviates 20% from the exact value,  $E_H = -0.500$ . Since similar errors are made for the  $H_2$  electronic energy, the final result for the dissociation curve is very reasonable: a bond length  $R_e = 1.51$  and dissociation energy  $D_e = -0.184$ , to be compared with the exact values<sup>4</sup>  $R_e = 1.40$  and  $D_e = -0.175$ .

<sup>4</sup>The experimental value for the dissociation energy of  $H_2$  is  $D_0 = -0.164$ . The difference with the equilibrium value  $D_e = -0.175$  comes mainly from the zero-point energy of the vibrational mode

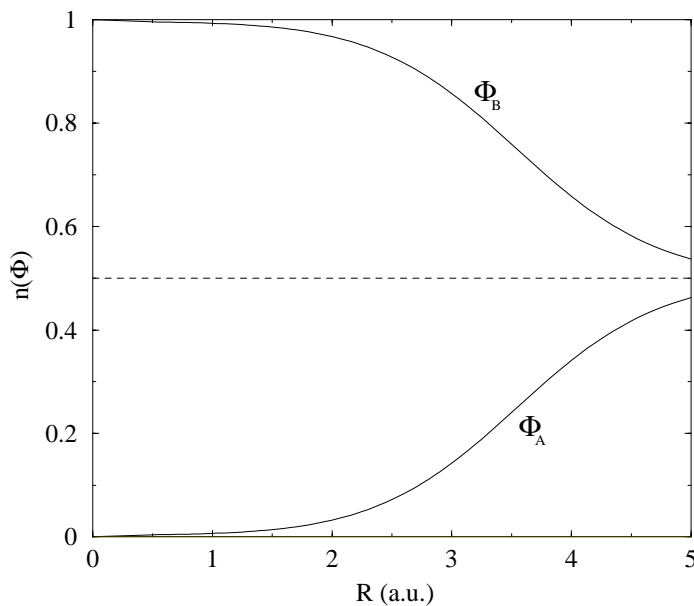


Fig. 11.5 Composition of the  $H_2$  ground state. In order to guide the eye, the 50% curve is indicated by the dashed line.

Also shown in Fig. 11.4 is the RHF dissociation curve,

$$D^{RHF}(R) = E_B(R) + \frac{1}{R} - 2E(\text{H-atom}), \quad (11.156)$$

obtained in the present model. Since  $D^{RHF}(R)$  does not vanish for large  $R$ , RHF has an incorrect dissociation limit. This can be traced back to the fact that, in the  $R \rightarrow \infty$  limit,  $E_B(R)$  reduces the energy of the  $H^-$  ion. Near the equilibrium distance  $R_e$ , however, the RHF curve provides a good approximation to the full  $D(R)$ . This is also seen in Fig. 11.5, where the occupation of the  $\Phi_B$  and  $\Phi_A$  configurations in the ground state are plotted. Up to  $R = 2.5$  the true ground state is for more than 90% the RHF configuration  $\Phi_B$ . For large  $R$ , the ground state goes to  $\Phi_{II}$ , which is an equal mixture of  $\Phi_A$  and  $\Phi_B$  and cannot be described in RHF.