Chapter 9

The calculation of electronic structure

Exercises

9.1 $\Psi^0 = \psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e)$

$$H^0 = \sum_{i=1}^{N_e} h_i$$

$$H^0\Psi^0 = \sum_{i=1}^{N_e} h_i\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e)$$

$$= (h_1 + h_2 + \cdots + h_{N_e})(\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e))$$

$$= [h_1\psi_a^0(1)]\psi_b^0(2)\ldots\psi_z^0(N_e) + \psi_a^0(1)[h_2\psi_b^0(2)]\ldots\psi_z^0(N_e)$$

$$+\cdots+\psi_a^0(1)\psi_b^0(2)\ldots[h_{N_e}\psi_z^0(N_e)]$$

$$= E_a^0\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e) + E_b^0\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e)$$

$$+\cdots+E_z^0\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e)$$

$$= [E_a^0 + E_b^0 + \cdots + E_z^0]\psi^0$$

Eigenvalue = $\underline{E_a^0 + E_b^0 + \cdots + E_z^0}$

Exercise: Confirm that $\det|\psi_a^0(1)\psi_b^0(2)\ldots\psi_z^0(N_e)|$ is an eigenfunction of H^0 and determine its corresponding eigenvalue.

9.2 $\Psi = (6)^{-1/2}\det|\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3)|$

$$= (6)^{-1/2}\begin{vmatrix} \psi_{1s}^{\alpha}(1) & \psi_{1s}^{\beta}(1) & \psi_{1s}^{\alpha}(1) \\ \psi_{1s}^{\alpha}(2) & \psi_{1s}^{\beta}(2) & \psi_{1s}^{\alpha}(2) \\ \psi_{1s}^{\alpha}(3) & \psi_{1s}^{\beta}(3) & \psi_{1s}^{\alpha}(3) \end{vmatrix}$$

$$= (6)^{-1/2}\left\{\begin{matrix} \psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3) \\ +\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(3)\psi_{1s}^{\alpha}(1) \\ +\psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(2)\psi_{1s}^{\alpha}(3) \\ -\psi_{1s}^{\alpha}(1)\psi_{1s}^{\beta}(2)\psi_{1s}^{\alpha}(3) \\ -\psi_{1s}^{\alpha}(2)\psi_{1s}^{\beta}(3)\psi_{1s}^{\alpha}(1) \\ -\psi_{1s}^{\beta}(1)\psi_{1s}^{\alpha}(2)\psi_{1s}^{\alpha}(3) \end{matrix}\right\} = (6)^{-1/2}\times 0 = \underline{0}$$

Exercise: Write the HF ground-state wavefunction Ψ_0 for the He^{-} ion and give examples of singly excited, doubly excited, and triply excited Slater determinants.

9.3 In the first *brief illustration* in Section 9.3, the Roothaan equations are presented in matrix form and one line of the resulting expansion is given. The remaining three lines of the expansion are

$$F_{AA}c_{A\sigma'} + F_{AB}c_{B\sigma'} = \varepsilon_{\sigma}S_{AA}c_{A\sigma'} + \varepsilon_{\sigma}S_{AB}c_{B\sigma'}$$

$$F_{BA}c_{A\sigma} + F_{BB}c_{B\sigma} = \varepsilon_{\sigma'}S_{BA}c_{A\sigma} + \varepsilon_{\sigma'}S_{BB}c_{B\sigma}$$

$$F_{BA}c_{A\sigma'} + F_{BB}c_{B\sigma'} = \varepsilon_{\sigma'}S_{BA}c_{A\sigma'} + \varepsilon_{\sigma'}S_{BB}c_{B\sigma'}$$

9.4 Proceed as in the *brief illustration* development for F_{AB}.

$$\begin{aligned} F_{AA} = h_{AA} + P_{AA}\left\{(AA|AA) - \tfrac{1}{2}(AA|AA)\right\} + P_{AB}\left\{(AA|AB) - \tfrac{1}{2}(AA|BA)\right\} \\ + P_{BA}\left\{(AB|AA) - \tfrac{1}{2}(AB|AA)\right\} + P_{BB}\left\{(AB|AB) - \tfrac{1}{2}(AB|BA)\right\} \\ = h_{AA} + P_{AA}\left\{\tfrac{1}{2}(AA|AA) + \tfrac{1}{2}(AB|AB)\right\} + P_{AB}\left\{\tfrac{1}{2}(AA|AB) + \tfrac{1}{2}(AB|AA)\right\} \end{aligned}$$

$$\begin{aligned} F_{BA} = h_{BA} + P_{AA}\left\{(BA|AA) - \tfrac{1}{2}(BA|AA)\right\} + P_{AB}\left\{(BA|AB) - \tfrac{1}{2}(BA|BA)\right\} \\ + P_{BA}\left\{(BB|AA) - \tfrac{1}{2}(BB|AA)\right\} + P_{BB}\left\{(BB|AB) - \tfrac{1}{2}(BB|BA)\right\} \\ = h_{BA} + P_{AA}\{(BA|AA)\} + P_{AB}\{(BB|AA)\} \end{aligned}$$

$$\begin{aligned}F_{\mathrm{BB}} = h_{\mathrm{BB}} &+ P_{\mathrm{AA}}\left\{(\mathrm{BA}|\mathrm{BA}) - \tfrac{1}{2}(\mathrm{BA}|\mathrm{AB})\right\} + P_{\mathrm{AB}}\left\{(\mathrm{BA}|\mathrm{BB}) - \tfrac{1}{2}(\mathrm{BA}|\mathrm{BB})\right\}\\ &+ P_{\mathrm{BA}}\left\{(\mathrm{BB}|\mathrm{BA}) - \tfrac{1}{2}(\mathrm{BB}|\mathrm{AB})\right\} + P_{\mathrm{BB}}\left\{(\mathrm{BB}|\mathrm{BB}) - \tfrac{1}{2}(\mathrm{BB}|\mathrm{BB})\right\}\\ &= h_{\mathrm{BB}} + P_{\mathrm{AA}}\left\{\tfrac{1}{2}(\mathrm{BA}|\mathrm{BA}) + \tfrac{1}{2}(\mathrm{BB}|\mathrm{BB})\right\} + P_{\mathrm{AB}}\left\{\tfrac{1}{2}(\mathrm{BA}|\mathrm{BB}) + \tfrac{1}{2}(\mathrm{BB}|\mathrm{BA})\right\}\end{aligned}$$

9.5 An Al atom has 13 electrons, so the normalization factor

$$N = (13!)^{-1/2} = 1.267\ldots \times 10^{-5}$$

A restricted HF wave function is

$$N\det\left|\psi_{1\mathrm{s}}^{\alpha}(1)\psi_{1\mathrm{s}}^{\beta}(2)\psi_{2\mathrm{s}}^{\alpha}(3)\psi_{2\mathrm{s}}^{\beta}(4)\psi_{2\mathrm{p}_{+1}}^{\alpha}(5)\psi_{2\mathrm{p}_{+1}}^{\beta}(6)\psi_{2\mathrm{p}_{0}}^{\alpha}(7)\right.$$

$$\left.\psi_{2\mathrm{p}_{0}}^{\beta}(8)\psi_{2\mathrm{p}_{-1}}^{\alpha}(9)\psi_{2\mathrm{p}_{-1}}^{\beta}(10)\psi_{3\mathrm{s}}^{\alpha}(11)\psi_{3\mathrm{s}}^{\beta}(12)\psi_{3\mathrm{p}_{+1}}^{\alpha}(13)\right|$$

An unrestricted HF wavefunction is

$$N\det\left|\psi_{1\mathrm{s}}^{\alpha}(1)\psi_{1\mathrm{s}}^{\beta}(2)\psi_{2\mathrm{s}}^{\alpha}(3)\psi_{2\mathrm{s}}^{\beta}(4)\psi_{2\mathrm{p}_{+1}}^{\alpha}(5)\psi_{2\mathrm{p}_{+1}}^{\beta}(6)\psi_{2\mathrm{p}_{0}}^{\alpha}(7)\right.$$

$$\left.\psi_{2\mathrm{p}_{0}}^{\beta}(8)\psi_{2\mathrm{p}_{-1}}^{\alpha}(9)\psi_{2\mathrm{p}_{-1}}^{\beta}(10)\psi_{3\mathrm{s}}^{\alpha}(11)\psi_{3\mathrm{s}}^{\beta}(12)\psi_{3\mathrm{p}_{+1}}^{\alpha}(13)\right|$$

Exercise: Give an example of a restricted and an unrestricted Hartree–Fock wavefunction for a sodium atom. Show that the RHF wavefunction is an eigenfunction of S^2 and evaluate its eigenvalue.

9.6 A calculation using 20 (spatial) basis functions yields 40 different Hartree–Fock SCF spinorbitals. As a chlorine atom has 17 electrons, there will be 17 occupied and 23 virtual orbitals.

Exercise: In a Hartree–Fock SCF calculation on the chloride ion Cl^{-} using 25 (spatial) basis functions, how many virtual orbitals are determined?

9.7 An f-type Gaussian orbital is one for which $i + j + k = 3$ for the integers (i, j, k) of eqn

9.20. There are therefore 10 f-type Gaussian orbitals with possibilities (0,0,3), (0,3,0), (3,0,0), (2,1,0), (2,0,1), (0,2,1), (1,2,0), (1,0,2), (0,1,2), (1,1,1).

9.8 Using the notation of eqn (9.17) for the two-electron integral for the basis functions, we have

$$(\mathrm{AA}|\mathrm{BB}) = j_0 \int \mathrm{A}^*(1)\mathrm{A}^*(2)\frac{1}{r_{12}}\mathrm{B}(1)\mathrm{B}(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

With an s-type Gaussian orbital of the form

$$g(\boldsymbol{r}_i) = N\mathrm{e}^{-\alpha r_{\mathrm{A}i}^2}$$

for electron *i* on atomic nucleus A and a similar expression for atomic nucleus B, we then have

$$(\mathrm{AA}|\mathrm{BB}) = j_0 N^4 \int \mathrm{e}^{-\alpha r_{\mathrm{A}1}^2}\mathrm{e}^{-\alpha r_{\mathrm{A}2}^2}\frac{1}{r_{12}}\mathrm{e}^{-\alpha r_{\mathrm{B}1}^2}\mathrm{e}^{-\alpha r_{\mathrm{B}2}^2}\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

9.9 **(a)** For NH_3:

A minimal basis set uses one basis function to represent each hydrogen 1s-orbital, and one basis function each for the nitrogen 1s, 2s, $2p_x$, $2p_y$, $2p_z$. The total number of basis functions is $\underline{8}$.

(b) For CH_3Cl:

A minimal basis set uses one basis function to represent each hydrogen 1s-orbital, one basis function for carbon 1s, one basis function for carbon 2s, three basis functions for the three carbon 2p-orbitals, one basis function for chlorine 1s, one basis function for chlorine 2s, three basis functions for chlorine 2p, one basis function for chlorine 3s, and three basis functions for chlorine 3p. The total number of basis functions is $3 \times 1 + 5 + 9 = \underline{17}$.

9.10 **(a)** A split-valence basis set uses two basis functions for each valence atomic orbital and one basis function for each inner-shell atomic orbital. Therefore the total number of basis functions is 6 (for the three H 1s) + 1 (for the N 1s) + 2 (for the N 2s) + 6 (for the three N 2p) = 15.

(b) A double-zeta (DZ) basis set replaces each basis set function in the minimal basis set by two basis function. Therefore, 8 (see Exercise 9.9a) is replaced by 16. In addition, for a DZP basis set, a set of three 2p-functions is added to each H atom (giving 9 more basis functions) and a set of six 3d-functions is added to the N atom. Therefore the total number of DZP basis set functions is 16 + 9 + 6 = 31.

9.11 Ethanol has two carbon, six hydrogen and one oxygen atom. We draw up the following tables showing the number of primitives comprising each contracted Gaussian function and the atomic orbital being represented.

(i) 6-31G

Number of primitives comprising contracted Gaussian function	Atomic orbital
3	H1s
1	H1s
6	C1s
3	C2s
1	C2s
3 × 3	3 C2p
3 × 1	3 C2p
6	O1s
3	O2s
1	O2s
3 × 3	3 O2p

3×1	3 O2p

The total number of basis functions (contracted Gaussians) is

$$6(1 + 1) + 2(1 + 1 + 1 + 3 + 3) + 1(1 + 1 + 1 + 3 + 3) = \underline{39}$$

The total number of primitives is

$$6(3 + 1) + 2(6 + 3 + 1 + 3 \times 3 + 3 \times 1) + 1(6 + 3 + 1 + 3 \times 3 + 3 \times 1) = \underline{90}$$

(ii) 6-31G*

To the 6-31G basis, we add six d-type polarization functions to each of the three non-hydrogen atoms.

Total number of basis functions $= 39 + 3 \times 6 = \underline{57}$

Total number of primitives $= 90 + 3 \times 6 = \underline{108}$

(iii) 6-31G**

To the 6-31G* basis, we add three p-type polarization functions to each of the six hydrogen atoms.

Total number of basis functions $= 57 + 6 \times 3 = \underline{75}$

Total number of primitives $= 108 + 6 \times 3 = \underline{126}$

Exercise: Repeat the determination of the number of basis set functions in electronic structure calculations on 1,4-dibromobenzene, $C_6H_4Br_2$.

9.12 In a 6-31G** calculation on ethanol, we see from Problem 9.11 that there are 75 basis set functions. In addition, there are $N_e = 6 \times 1 + 2 \times 6 + 1 \times 8 = 26$ electrons. The total number of different Slater determinants is therefore

$$\binom{2M}{N_e} = \binom{150}{26} = \frac{150!}{26!1224!} = \underline{9.406\ldots \times 10^{28}}$$

Exercise: Determine the total number of different Slater determinants that can be formed in a 6-31G** calculation on 1,4-dibromobenzene, $C_6H_4Br_2$.

9.13 Slater determinants **(a)**, **(b)**, **(d)**, and **(e)** can all contribute to a wavefunction of ^{2}S symmetry. Determinant (c) is of P symmetry and determinant (f) is of ^{4}S symmetry.

Exercise: Give examples of Slater determinants that can contribute to the ground-state wavefunction of magnesium. Be sure to include determinants that use 3p- and 3d-orbitals.

9.14 Slater determinants **(a)**, **(d)**, and **(e)** can contribute. Determinants (b) and (c) are of Π symmetry and (f) is of gerade symmetry.

Exercise: Give examples of Slater determinants that can contribute to the $^3\Sigma_g^-$ ground-state wavefunction of molecular oxygen. Include determinants that involve 3p- and 3d-orbitals.

9.15 The unwritten integrals arise from expansion of the integrand (the *brief illustration in Section* 9.9) [A(1) – B(1)][A(2) – B(2)]1/r_{12}) [A(1) + B(1)][A(2) + B(2)] and therefore the complete set of two-electron integrals is

(AA|AA) **+** (AA|AB) + (AA|BA) + (AA|BB) – (AB|BA) – (AB|AA) – (AB|AB) – (AB|BB) – (BA|BA) – (BA|AB) – (BA|AA) – (BA|BB) + (BB|AA) **+** (BB|AB) + (BB|BA) + (BB|BB).

9.16 In the *brief illustration* in Section 9.9, we showed that when MP2 is applied to molecular hydrogen in the minimal basis of two H1s orbitals, the (second-order) estimate of the correlation energy is

$$E_0^{(2)} = \frac{\{(\mathrm{AA}|\mathrm{AA}) - (\mathrm{AB}|\mathrm{AB})\}^2}{4\{E(1\sigma_g 1\sigma_g) - E(1\sigma_u 1\sigma_u)\}}$$

If we define Q and ΔE as in the *brief illustration* in Section 9.10, we can write the above as

$$E_0^{(2)} = -\frac{Q^2}{\Delta E}$$

It should also be noted that in MPPT as discussed in Section 9.9, the HF energy is the sum of the zero-order energy and first order correction. As a result,

$$E_0^{(2)} = E - \left(E_0^{(0)} + E_0^{(1)}\right) = E - \ E_{\mathrm{HF}}$$

In the coupled-cluster CCD method (see eqn 9.33),

$$E - E_{\mathrm{HF}} = \ \langle\Psi_0|HC_2|\Psi_0\rangle = \left\langle\Psi_0\middle|H\middle|\Psi_{1\sigma_\mathrm{g}1\sigma_\mathrm{g}}^{1\sigma_\mathrm{u}1\sigma_\mathrm{u}}\right\rangle t = Qt$$

The equation for *t* is

$$Qt^2 - \Delta Et - Q = 0$$

with roots of

$$t = \frac{\Delta E \pm \sqrt{(\Delta E)^2 + 4Q^2}}{2\mathrm{Q}} = \frac{\Delta E \pm \Delta E\sqrt{1 + 4(Q/\Delta E)^2}}{2\mathrm{Q}}$$

If $Q << \Delta E$, we can use the approximation $(1 + x)^{1/2} = 1 + x/2$ which yields, taking the negative choice of the plus/minus,

$$t = \frac{\Delta E - \Delta E\left(1 + \frac{2Q^2}{\{\Delta E\}^2}\right)}{2Q} = -\frac{Q}{\Delta E}$$

and therefore

$$E - E_{HF} = Qt = -Q^2/\Delta E$$

This matches the result from MP2.

9.17 Equation 7.65 gives the expression for the 'one-point' electron density:

$$\rho(\boldsymbol{r}) = 2\sum_m \psi_m^*(\boldsymbol{r})\psi_m(\boldsymbol{r})$$

If we use the molecular orbital $\psi_A + \psi_B$ for ψ_m, then the density is given by

$$\begin{aligned}\rho(\boldsymbol{r}) &= 2\{\psi_A^*(\boldsymbol{r}) + \psi_B^*(\boldsymbol{r})\}\{\psi_A(\boldsymbol{r}) + \psi_B(\boldsymbol{r})\}\\ &= 2\{|\psi_A(\boldsymbol{r})|^2 + |\psi_B(\boldsymbol{r})|^2 + \psi_A^*(\boldsymbol{r})\psi_B(\boldsymbol{r}) + \psi_A(\boldsymbol{r})\psi_B^*(\boldsymbol{r})\}\end{aligned}$$

If the basis set functions are real, this becomes

$$\rho(\boldsymbol{r}) = 2\{\psi_A^2(\boldsymbol{r}) + \psi_B^2(\boldsymbol{r}) + 2\psi_A(\boldsymbol{r})\psi_B(\boldsymbol{r})\}$$

9.18 To compute the Hessian matrix, we need the second derivatives of the function.

$$f = \sin ax \cos by$$

$$\frac{\partial f}{\partial x} = a\cos ax \cos by$$

$$\frac{\partial^2 f}{\partial x^2} = -a^2 \sin ax \cos by$$

$$\frac{\partial^2 f}{\partial x \partial y} = -ab\cos ax \sin by = \frac{\partial^2 f}{\partial y \partial x}$$

$$\frac{\partial f}{\partial y} = -b\sin ax \sin by$$

$$\frac{\partial^2 f}{\partial y^2} = -b^2 \sin ax \cos by$$

Therefore, the Hessian matrix is

$$\boldsymbol{H} = \begin{pmatrix} -a^2\sin ax\cos by & -ab\cos ax\sin by \\ -ab\cos ax\sin by & -b^2\sin ax\cos by \end{pmatrix}$$

9.19 **(a)** MPPT and CC are not variational so (iv), (v) and (vi) can yield energies below the exact ground-state energy.

(b) Of the methods discussed in Chapter 9, full CI, MPPT, and CC are size-consistent. Therefore, (i), (iii), and (vii) are not assured of being size-consistent.

Exercise: Discuss which of the two features, being variational or being size-consistent, is a more important characteristic of an electronic structure calculation.

9.20 A p-type GTO is given by

$$g_{100} = Nx\mathrm{e}^{-\alpha r^2}$$

$$\frac{\partial g_{100}}{\partial x} = N\mathrm{e}^{-\alpha r^2} - 2\alpha N x^2 \mathrm{e}^{-\alpha r^2}$$

$$= \underline{g_{000} - 2\alpha g_{200}}$$

Exercise: Consider a general Cartesian Gaussian g_{ijk}. Find expressions for both the first and second derivatives of g_{ijk} with respect to x in terms of other Gaussian functions.

9.21 In the ZDO approximation, all two-electron integrals (ab|cd) vanish except those for which a = c and b = d. Therefore, the following integrals that appear in the solution of Exercise 9.4 vanish in the ZDO approximation:

(AA|BB) = (AA|AB) = (AB|AA) = (BA|AA) = (BB|AA) = (BA|BB) = (BB|BA) = 0

9.22 We begin with equation 9.58c and specifically consider a *cis* conformation of the quartet of atoms, for which the convention is the dihedral angle $\tau = 0$. For small torsional displacements φ, $\cos(-\varphi) = \cos\varphi = 1 - \varphi^2/2$. Therefore,

$$E_{\text{tor}} = \sum A[1+\cos(n\tau-\varphi)] = \sum A[1+\cos(-\varphi)] = \sum A[1+\cos(\varphi)]$$
$$= \sum A[1+1-\tfrac{1}{2}\varphi^2] = \sum 2A - \sum \tfrac{1}{2}A\varphi^2$$

The presence of the term of the form ½ $A\varphi^2$ indicates harmonic oscillation.

Problems

9.1 We write the single Slater determinant as

$$N \det |\phi_a(1)\phi_b(2)\ldots\phi_z(N_\mathrm{e})|$$

and show that $N = (N_e!)^{-1/2}$ is the normalization factor.

When we expand the Slater determinant, we get

$$N\begin{vmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_z(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_z(2) \\ \vdots & \vdots & & \vdots \\ \phi_a(N_e) & \phi_b(N_e) & \dots & \phi_z(N_e) \end{vmatrix} = N\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)$$

where P allows for all permutations of electrons among the spinorbitals and ε_P is either +1 or −1, depending on whether the number of electron interchanges is even or odd.

We require a normalized Slater determinant, so

$$1 = \int |N|^2 \left[\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)\right]^*$$

$$\times \left[\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)\right]\mathrm{d}\tau$$

$$= |N|^2 \int \left[\sum_P \varepsilon_P P\phi_a^*(1)\phi_b^*(2)\dots\phi_z^*(N_e)\right]$$

$$\times \left[\sum_P \varepsilon_P P\phi_a(1)\phi_b(2)\dots\phi_z(N_e)\right]\mathrm{d}\tau$$

Each permutation operator P will give rise to a sum of N_e ! products of spinorbitals. However, because the spinorbitals are orthonormal, we only have contributions to the integral when the permutation arising from $[\Sigma_P\ \varepsilon_P P\phi_a(1)\phi_b(2)\ \dots\ \phi_z(N_e)]^*$ is exactly the same permutation that arises from $[\Sigma_P\ \varepsilon_P P\phi_a(1)\phi_b(2)\ \dots\ \phi_z(N_e)]$. Therefore, there are N_e! contributions to the integral. In addition, because the spinorbitals are normalized, each of the N_e! contributions is exactly 1. (Note that $\varepsilon_P^2 = 1$.) For example, one of the N_e! contributions is

$$\int \phi_a^*(1)\phi_b^*(2)\ldots\phi_z^*(N_\mathrm{e})\phi_a(1)\phi_b(2)\ldots\phi_z(N_\mathrm{e})\mathrm{d}\tau$$

$$= \int \phi_a^*(1)\phi_a(1)\mathrm{d}\tau_1 \int \phi_b^*(2)\phi_b(2)\mathrm{d}\tau_2 \ldots \int \phi_z^*(N_\mathrm{e})\phi_z(N_\mathrm{e})\mathrm{d}\tau_n$$

$$= 1 \times 1 \times \cdots \times 1 = 1$$

Thus,

$$1 = |N|^2 \times N_\mathrm{e}!$$

Choosing N as positive and real, we have

$$\underline{N = (N_\mathrm{e}!)^{-1/2}}$$

Exercise: Show that the HF wavefunction Ψ_0 and a singly excited Slater determinant are orthonormal.

9.4 In a (4s)/[2s] contraction scheme, the most diffuse s-type primitive is left uncontracted. Therefore, the s-type Gaussian with exponent $\alpha = 0.123\,317$ is a single basis function. The remaining three primitives are used to form a single contracted Gaussian basis function of the form

$$\chi = N\begin{Bmatrix} 0.474\,49\; g\;(\alpha = 0.453\,757) + \\ 0.134\,24\; g\;(\alpha = 2.013\,30) + \\ 0.019\,06\; g\;(\alpha = 13.3615) \end{Bmatrix}$$

where N is a constant so that χ is properly normalized.

Exercise: Determine the constant N such that the contracted basis function χ is normalized.

9.7 We need to show that

$$\langle \Phi_0 |H| \Phi_a^p \rangle = 0$$

where Φ_0 is the HF ground-state wavefunction

$$\Phi_0 = (N_e!)^{-1/2} \det |\phi_1\phi_2 \dots \phi_a\phi_b \dots \phi_{N_e}|$$

and Φ_a^p is a singly excited determinant

$$\Phi_a^p = (N_e!)^{-1/2} \det |\phi_1\phi_2 \dots \phi_p\phi_b \dots \phi_{N_e}|$$

Using the Slater–Condon rule for two Slater determinants differing by only one spinorbital (see Problem 9.8), we have

$$\langle \Phi_0 |H| \Phi_a^p \rangle = \langle \phi_a(1) |h_1| \phi_p(1) \rangle + \sum_i \{[\phi_a\phi_i][\phi_p\phi_i] - [\phi_a\phi_i][\phi_i\phi_p]\}$$

We now show that $\langle \phi_a(1)|f_1|\phi_p(1)\rangle$ and $\langle \Phi_0|H|\Phi_a^p\rangle$ are equal, and we subsequently show that $\langle \phi_a(1)|f_1|\phi_p(1)\rangle = 0$.

$$f_1\phi_p(1) = \varepsilon_p\phi_p(1) \quad \text{[eqn 7.89]}$$

$$= h_1\phi_p(1) + \sum_i \{J_i(1) - K_i(1)\}\phi_p(1) \quad \text{[eqn 7.88b]}$$

$$= h_1\phi_p(1) + \sum_i \left\{\int \phi_i^*(2)\left(\frac{j_0}{r_{12}}\right)\phi_i(2)\mathrm{d}\boldsymbol{x}_2\right\}\phi_p(1)$$

$$- \sum_i \left\{\int \phi_i^*(2)\left(\frac{j_0}{r_{12}}\right)\phi_p(2)\mathrm{d}\boldsymbol{x}_2\right\}\phi_i(1)$$

Multiplication by $\phi_a^*(1)$ and integration over $\boldsymbol{x}_1$ yields

$$\langle \phi_a(1)|f_1|\phi_p(1)\rangle = \langle \phi_a(1)|h_1|\phi_p(1)\rangle + \sum_i \{[\phi_a\phi_i|\phi_p\phi_i] - [\phi_a\phi_i|\phi_i\phi_p]\}$$

where we have used the notation of *Further information* 7.1 and Problem 9.8. We therefore have shown

$$\langle \Phi_0 | H | \Phi_a^p \rangle = \langle \phi_a(1) | f_1 | \phi_p(1) \rangle$$

In addition since

$$f_1 \phi_p(1) = \varepsilon_p \phi_p(1)$$

we see that

$$\begin{aligned} \langle \phi_a(1) | f_1 | \phi_p(1) \rangle &= \langle \phi_a(1) | \varepsilon_p | \phi_p(1) \rangle \\ &= \varepsilon_p \langle \phi_a(1) | \phi_p(1) \rangle \\ &= 0 \end{aligned}$$

because the spinorbitals are orthogonal. Therefore

$$\underline{\langle \Phi_0 | H | \Phi_a^p \rangle = 0}$$

as was to be proved.

Exercise: Show that hamiltonian matrix elements between Φ_0 and triply excited determinants are identically zero.

9.10 **(a)** The ground-state electron configuration of the diatomic molecule C_2 is (Section 8.6)

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4$$

where $1\sigma_g$ and $1\sigma_u$ arise from carbon 1s atomic orbitals and $2\sigma_g$, $2\sigma_u$, and $1\pi_u$ arise from valence shell atomic orbitals. (In Chapter 8, only valence electrons are considered and the numbering of the molecular orbitals is different.)

Inactive orbitals:	$1\sigma_g$ and $1\sigma_u$
Active orbitals:	$2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$, $3\sigma_u$, and $1\pi_g$
Virtual orbitals:	$4\sigma_g$, $4\sigma_u$ . . . arising from $n = 3$, . . . atomic orbitals

(b) There are 4 inactive electrons (in inactive orbitals) and 8 active electrons (in active orbitals).

(c) In a restricted active-space (RAS) SCF calculation, the set of active orbitals is further divided into orbital subsets I, II, and III. Subset I could consist of the $2\sigma_g$ and $2\sigma_u$ orbitals, with a minimum of two electrons in the subset. Subset II could consist of the $1\pi_u$, $3\sigma_g$ and $1\pi_g$ orbitals. Subset III could consist of the $3\sigma_u$ orbital with a maximum of two electrons. The total number of electrons in the three subsets is held fixed at 8.

Exercise: With the above distribution of σ and π molecular orbitals into active, inactive, and virtual orbitals, what is the number of Slater determinants that would be used in the CASSCF calculation?

9.13 In the meta-generalized gradient approximation of DFT,

$$\tau(\boldsymbol{r}) = \frac{\hbar^2}{2m_e}\sum_i \nabla\psi_i^*(\boldsymbol{r}) \cdot \nabla\psi_i(\boldsymbol{r})$$

where the sum is over occupied orbitals. That such an expression represents a kinetic energy density follows from its integration by parts ($\int u \, dv = uv - \int v \, du$):

$$\begin{aligned}\int \tau(\boldsymbol{r})\mathrm{d}\boldsymbol{r} &= \frac{\hbar^2}{2m_\mathrm{e}}\sum_i \int \nabla\psi_i^*(\boldsymbol{r})\cdot\nabla\psi_i(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} \\ &= \frac{\hbar^2}{2m_\mathrm{e}}\sum_i \left\{\psi_i^*(\boldsymbol{r})\nabla\psi_i(\boldsymbol{r}) - \int \psi_i^*(\boldsymbol{r})\nabla^2\psi_i(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\right\} \\ &= -\frac{\hbar^2}{2m_\mathrm{e}}\sum_i \int \psi_i^*(\boldsymbol{r})\nabla^2\psi_i(\boldsymbol{r})\mathrm{d}\boldsymbol{r}\end{aligned}$$

where we have used the fact that ψ vanishes at the boundaries so the first term in the middle line above vanishes when evaluated at the limits of integration.

9.16 For this problem and the next three problems in this chapter, all electronic structure computations were performed using the software package GAMESS. All ground-state energies are reported in hartrees and all internuclear distances in ångströms (1 ångström = 10^{-10} m).

(a) H_2 RHF/6-31G: energy = –1.1268 bond length = 0.7299

F_2 RHF/6-31G: energy = –198.6461 bond length = 1.4125

(b) H_2 RHF/6-31G**: energy = –1.1313 bond length = 0.7326

F_2 RHF/6-31G**: energy = –198.6778 bond length = 1.3449

Exercise: Use electronic structure software to compute the energies of the separated atom limits (H + H and F + F) and, using these values and the above results, calculate the bond dissociation energies of H_2 and F_2. Compare the computed dissociation energies and equilibrium bond distances to the experimental values.

9.19 Electronic structure computations were performed using the software package GAMESS. All enthalpies of formation are reported in kcal mol^{-1} (1 kcal = 4.184 kJ) and all equilibrium bond lengths are in ångströms (1 ångström = 10^{-10} m).

(a)(i) ethanol: AM1

C–C distance = 1.5116

C–O distance = 1.4195

O–H distance = 0.9637

(methyl group) C–H distances = 1.1161, 1.1161, 1.1153

(methylene group) C–H distances = 1.1237, 1.1237

Enthalpy of formation = –62.6632

(a)(ii) ethanol: PM3

C–C distance = 1.5179

C–O distance = 1.4095

O–H distance = 0.9472

(methyl group) C–H distances = 1.0978, 1.0979, 1.0971

(methylene group) C–H distances = 1.1080, 1.1079

Ethalpy of formation = –56.8549

(b)(i) 1,4-dichlorobenzene: AM1

C–C distance = 1.3899

C–Cl distance = 3.0890

C–H distance = 2.5011

Enthalpy of formation = 7.9737

(b)(ii) 1,4-dichlorobenzene: PM3

C–C distance = 1.3799

C–Cl distance = 3.0648

C–H distance = 2.4938

Enthalpy of formation = 10.1113

Exercise: Compare the computed enthalpies of formation and equilibrium bond distances to the experimental values.