CHAPTER

TWO

MANY-ELECTRON WAVE FUNCTIONS AND OPERATORS

This chapter introduces the basic concepts, techniques, and notations of quantum chemistry. We consider the structure of many-electron operators (e.g., the Hamiltonian) and discuss the form of many-electron wave functions (Slater determinants and linear combinations of these determinants). We describe the procedure for evaluating matrix elements of operators between Slater determinants. We introduce the basic ideas of the Hartree-Fock approximation. This allows us to develop the material of this chapter in a form most useful for subsequent chapters where the Hartree-Fock approximation and a variety of more sophisticated approaches, which use the Hartree-Fock method as a starting point, are considered in detail.

In Section 2.1, the electronic problem is formulated, i.e., the problem of describing the motion of electrons in the field of fixed nuclear point charges. This is one of the central problems of quantum chemistry and our sole concern in this book. We begin with the full nonrelativistic time-independent Schrödinger equation and introduce the Born-Oppenheimer approximation. We then discuss a general statement of the Pauli exclusion principle called the *antisymmetry principle*, which requires that many-electron wave functions must be antisymmetric with respect to the interchange of any two electrons.

In Section 2.2, we describe one-electron functions (spatial and spin orbitals) and then construct many-electron functions (Hartree products and

Slater determinants) in terms of these one-electron functions. We then consider the Hartree-Fock approximation in which the exact wave function of the system is approximated by a single Slater determinant and describe its qualitative features. At this point, we introduce a simple system, the minimal basis (1*s* orbital on each atom) *ab initio* model of the hydrogen molecule. We shall use this model throughout the book as a pedagogical tool to illustrate and illuminate the essential features of a variety of formalisms that at first glance appear to be rather formidable. Finally, we discuss the multideterminantal expansion of the exact wave function of an N-electron system.

Section 2.3 is concerned with the form of the one- and two-electron operators of quantum chemistry and the rules for evaluating matrix elements of these operators between Slater determinants. The conversion of expressions for matrix elements involving spin orbitals to expressions involving spatial orbitals is discussed. Finally, we describe a mnemonic device for obtaining the expression for the energy of any single determinant.

Section 2.4 introduces creation and annihilation operators and the formalism of second quantization. Second quantization is an approach to dealing with many-electron systems, which incorporates the Pauli exclusion principle but avoids the explicit use of Slater determinants. This formalism is widely used in the literature of many-body theory. It is, however, not required for a comprehension of most of the rest of this book, and thus this section can be skipped without loss of continuity.

Section 2.5 discusses electron spin and spin operators in many-electron systems and contains a description of restricted and unrestricted spin orbitals and spin-adapted configurations. Spin-adapted configurations, unlike many single determinants derived from restricted spin orbitals, are correct eigenfunctions of the total electron spin operator. Singlet, doublet, and triplet spin-adapted configurations as well as unrestricted wave functions, which are not eigenfunctions of the total electron spin operator, are described.

2.1 THE ELECTRONIC PROBLEM

Our main interest in this book is finding approximate solutions of the nonrelativistic time-independent Schrödinger equation

$$\mathscr{H}|\Phi\rangle = \mathscr{E}|\Phi\rangle \tag{2.1}$$

where $\mathscr{H}$ is the Hamiltonian operator for a system of nuclei and electrons described by position vectors $\mathbf{R}_A$ and $\mathbf{r}_i$, respectively. A molecular coordinate system is shown in Fig. 2.1. The distance between the ith electron and Ath nucleus is $r_{iA} = |\mathbf{r}_{iA}| = |\mathbf{r}_i - \mathbf{R}_A|$; the distance between the ith and jth electron is $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and the distance between the Ath nucleus and the Bth nucleus is $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$. In atomic units, the Hamiltonian for N electrons

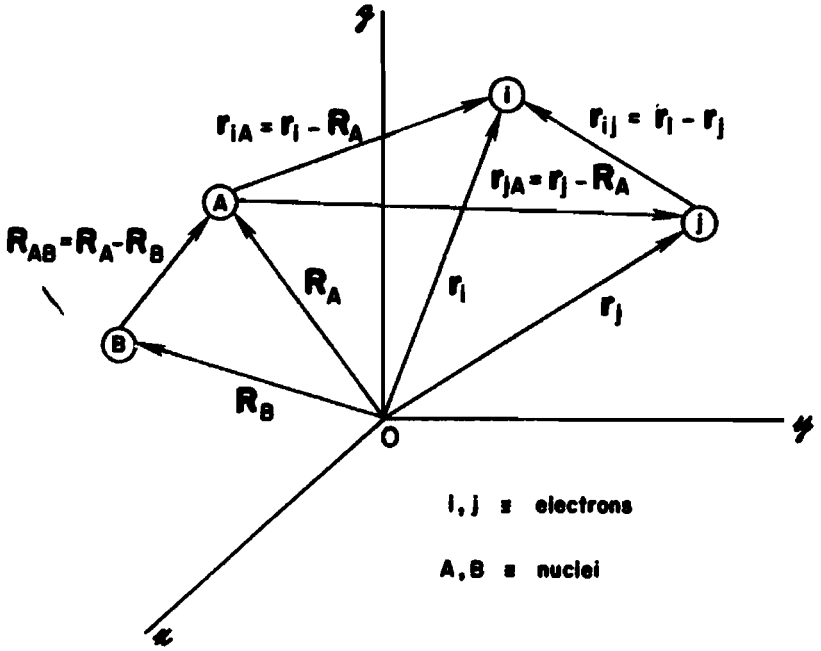


Figure 2.1 A molecular coordinate system: i, j = electrons; A, B = nuclei.

and M nuclei is

$$\mathscr{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{1}{2M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{2.2}$$

In the above equation, M_A is the ratio of the mass of nucleus A to the mass of an electron, and Z_A is the atomic number of nucleus A. The Laplacian operators ∇_i^2 and ∇_A^2 involve differentiation with respect to the coordinates of the ith electron and the Ath nucleus. The first term in Eq. (2.2) is the operator for the kinetic energy of the electrons; the second term is the operator for the kinetic energy of the nuclei; the third term represents the coulomb attraction between electrons and nuclei; the fourth and fifth terms represent the repulsion between electrons and between nuclei, respectively.

2.1.1 Atomic Units

The units we use throughout this book are called atomic units. To see how these units arise naturally let us consider the Schrödinger equation for the hydrogen atom. In SI units, we have

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\phi = \mathscr{E}\phi \tag{2.3}$$

where $\hbar$ is Planck's constant divided by 2π, m_e is the mass of the electron, and $-e$ is the charge on the electron. To cast this equation into dimensionless form we let $x, y, z \rightarrow \lambda x', \lambda y', \lambda z'$ and obtain

$$\left[-\frac{\hbar^2}{2m_e\lambda^2}\nabla'^2 - \frac{e^2}{4\pi\varepsilon_0\lambda r'}\right]\phi' = \mathscr{E}\phi' \tag{2.4}$$

The constants in front of the kinetic and potential energy operators can then be factored, provided we choose λ such that

$$\frac{\hbar^2}{m_e\lambda^2} = \frac{e^2}{4\pi\varepsilon_0\lambda} = \mathscr{E}_a \tag{2.5}$$

where $\mathscr{E}_a$ is the atomic unit of energy called the *Hartree*. Solving Eq. (2.5) for λ we find

$$\lambda = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2} = a_0 \tag{2.6}$$

Thus λ is just the Bohr radius a_0 which is the atomic unit of length called a *Bohr*. Finally, since

$$\mathscr{E}_a\left[-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right]\phi' = \mathscr{E}\phi' \tag{2.7}$$

if we let $\mathscr{E}' = \mathscr{E}/\mathscr{E}_a$, we obtain the dimensionless equation

$$\left(-\frac{1}{2}\nabla'^2 - \frac{1}{r'}\right)\phi' = \mathscr{E}'\phi' \tag{2.8}$$

which is the Schrödinger equation in atomic units. The solution of this equation for the ground state of the hydrogen atom yields an energy $\mathscr{E}'$ equal to -0.5 atomic units $\equiv -0.5$ Hartrees. Table 2.1 gives the conversion factors X between atomic units and SI units, such that the SI value of any

Table 2.1 Conversion of atomic units to SI units

Physical quantity	Conversion factor X	Value of X (SI)
Length	a_0	5.2918×10^{-11} m
Mass	m_e	9.1095×10^{-31} kg
Charge	e	1.6022×10^{-19} C
Energy	$\mathscr{E}_a$	4.3598×10^{-18} J
Angular momentum	$\hbar$	1.0546×10^{-34} J s
Electric dipole moment	ea_0	8.4784×10^{-30} Cm
Electric polarizability	$e^2a_0^2\mathscr{E}_a^{-1}$	1.6488×10^{-41} $C^2m^2J^{-1}$
Electric field	$\mathscr{E}_a e^{-1}a_0^{-1}$	5.1423×10^{11} V m^{-1}
Wave function	$a_0^{-3/2}$	2.5978×10^{15} $m^{-3/2}$

quantity Q is related to its value in atomic units Q' by

$$Q = XQ' \tag{2.9}$$

Conversion factors for a few other units, which are not related to SI but which are necessary to read the existing literature, are as follows. One atomic unit of length equals 0.52918 Angströms (Å). One atomic unit of dipole moment (two unit charges separated by a_0) equals 2.5418 Debyes (D), and one atomic unit of energy equals 27.211 electron volts (eV) or 627.51 kcal/mole.

From now on we drop the primes and all our quantities will be in atomic units.

2.1.2 The Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is central to quantum chemistry. Our discussion of this approximation is qualitative. The quantitative aspects of this approximation, including the problem of deriving corrections to it, are clearly discussed by Sutcliffe.[1] Since nuclei are much heavier than electrons, they move more slowly. Hence, to a good approximation, one can consider the electrons in a molecule to be moving in the field of fixed nuclei. Within this approximation, the second term of (2.2), the kinetic energy of the nuclei, can be neglected and the last term of (2.2), the repulsion between the nuclei, can be considered to be constant. Any constant added to an operator only adds to the operator eigenvalues and has no effect on the operator eigenfunctions. The remaining terms in (2.2) are called the electronic Hamiltonian or Hamiltonian describing the motion of N electrons in the field of M point charges,

$$\mathscr{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} \tag{2.10}$$

The solution to a Schrödinger equation involving the electronic Hamiltonian,

$$\mathscr{H}_{\text{elec}}\Phi_{\text{elec}} = \mathscr{E}_{\text{elec}}\Phi_{\text{elec}} \tag{2.11}$$

is the electronic wave function,

$$\Phi_{\text{elec}} = \Phi_{\text{elec}}(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) \tag{2.12}$$

which describes the motion of the electrons and *explicitly* depends on the electronic coordinates but depends *parametrically* on the nuclear coordinates, as does the electronic energy,

$$\mathscr{E}_{\text{elec}} = \mathscr{E}_{\text{elec}}(\{\mathbf{R}_A\}) \tag{2.13}$$

By a parametric dependence we mean that, for different arrangements of the nuclei, Φ_{elec} is a different function of the electronic coordinates. The nuclear

coordinates do not appear explicitly in Φ_{elec}. The total energy for fixed nuclei must also include the constant nuclear repulsion.

$$\mathscr{E}_{\text{tot}} = \mathscr{E}_{\text{elec}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{2.14}$$

Equations (2.10) to (2.14) constitute the electronic problem, which is our interest in this book.

If one has solved the electronic problem, it is subsequently possible to solve for the motion of the nuclei under the same assumptions as used to formulate the electronic problem. As the electrons move much faster than the nuclei, it is a reasonable approximation in (2.2) to replace the electronic coordinates by their average values, averaged over the electronic wave function. This then generates a nuclear Hamiltonian for the motion of the nuclei in the average field of the electrons,

$$\begin{aligned}
\mathscr{H}_{\text{nucl}} &= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \left\langle -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \right\rangle \\
&\quad + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \\
&= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \mathscr{E}_{\text{elec}}(\{\mathbf{R}_A\}) + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \\
&= -\sum_{A=1}^{M} \frac{1}{2M_A} \nabla_A^2 + \mathscr{E}_{\text{tot}}(\{\mathbf{R}_A\})
\end{aligned} \tag{2.15}$$

The total energy $\mathscr{E}_{\text{tot}}(\{\mathbf{R}_A\})$ provides a potential for nuclear motion. This function constitutes a potential energy surface as shown schematically in Fig. 2.2. Thus the nuclei in the Born-Oppenheimer approximation move on a potential energy surface obtained by solving the electronic problem. Solu-

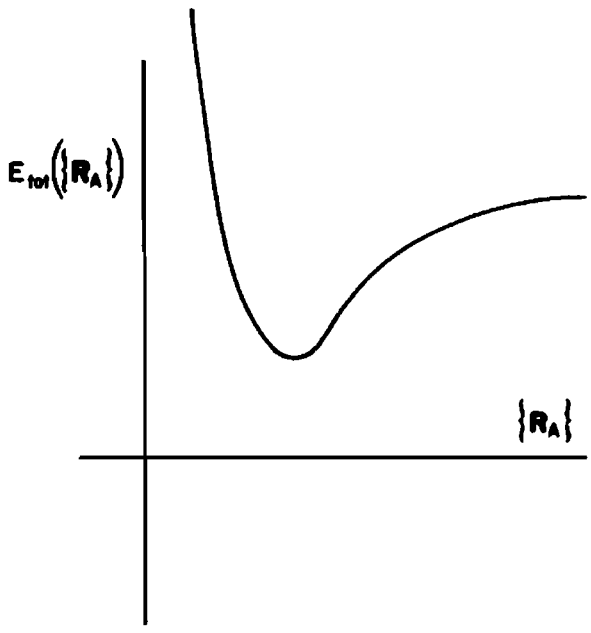


Figure 2.2 Schematic illustration of a potential surface.

tions to a nuclear Schrödinger equation,

$$\mathscr{H}_{\text{nucl}}\Phi_{\text{nucl}} = \mathscr{E}\Phi_{\text{nucl}} \tag{2.16}$$

describe the vibration, rotation, and translation of a molecule,

$$\Phi_{\text{nucl}} = \Phi_{\text{nucl}}(\{\mathbf{R}_A\}) \tag{2.17}$$

and $\mathscr{E}$, which is the Born-Oppenheimer approximation to the total energy of (2.1), includes electronic, vibrational, rotational, and translational energy. The corresponding approximation to the total wave function of (2.1) is,

$$\Phi(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) = \Phi_{\text{elec}}(\{\mathbf{r}_i\}; \{\mathbf{R}_A\})\Phi_{\text{nucl}}(\{\mathbf{R}_A\}) \tag{2.18}$$

From now on, we will not consider the vibrational-rotational problem but concentrate solely on the electronic problem of (2.11) to (2.14). We thus drop the subscript "elec" and only consider electronic Hamiltonians and electronic wave functions. Where it is convenient or necessary, we will distinguish between the electronic energy of (2.13) and the total energy of (2.14), which includes nuclear-nuclear repulsion.

2.1.3 The Antisymmetry or Pauli Exclusion Principle

The electronic Hamiltonian in Eq. (2.10) depends only on the spatial coordinates of the electrons. To completely describe an electron it is necessary, however, to specify its *spin*. We do this in the context of our nonrelativistic theory by introducing two spin functions $\alpha(\omega)$ and $\beta(\omega)$, corresponding to spin up and down, respectively. These are functions of an unspecified spin variable ω; from the operational point of view we need only specify that the two spin functions are complete and that they are orthonormal,

$$\int d\omega\, \alpha^*(\omega)\alpha(\omega) = \int d\omega\, \beta^*(\omega)\beta(\omega) = 1 \tag{2.19a}$$

$$\langle\alpha|\alpha\rangle = \quad \langle\beta|\beta\rangle \quad = 1 \tag{2.19b}$$

and

$$\int d\omega\, \alpha^*(\omega)\beta(\omega) = \int d\omega\, \beta^*(\omega)\alpha(\omega) = 0 \tag{2.20a}$$

$$\langle\alpha|\beta\rangle = \quad \langle\beta|\alpha\rangle \quad = 0 \tag{2.20b}$$

where the integration has been used in a formal way. In this formalism an electron is described not only by the three spatial coordinates $\mathbf{r}$ but also by one spin coordinate ω. We denote these four coordinates collectively by $\mathbf{x}$,

$$\mathbf{x} = \{\mathbf{r}, \omega\} \tag{2.21}$$

The wave function for an N-electron system is then a function of $\mathbf{x}_1$, $\mathbf{x}_2, \ldots, \mathbf{x}_N$. That is, we write $\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$.

Because the Hamiltonian operator makes no reference to spin, simply making the wave function depend on spin (in the way just described) does

not lead anywhere. A satisfactory theory can be obtained, however, if we make the following additional requirement on a wave function: *A many-electron wave function must be antisymmetric with respect to the interchange of the coordinate* **x** *(both space and spin) of any two electrons,*

$$\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = -\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \quad (2.22)$$

This requirement, sometimes called the *antisymmetry principle*, is a very general statement of the familiar Pauli exclusion principle. It is an independent postulate of quantum mechanics. Thus the exact wave function not only has to satisfy the Schrödinger equation, it also must be antisymmetric in the sense of Eq. (2.22). As we shall see, the requirement of antisymmetry is easily enforced by using Slater determinants.

2.2 ORBITALS, SLATER DETERMINANTS, AND BASIS FUNCTIONS

In this section we are concerned with the nomenclature, the conventions, and the procedure for writing down the wave functions that we use to describe many-electron systems. We will only consider many-electron wave functions that are either a single Slater determinant or a linear combination of Slater determinants. Sometimes, for very small systems, special functional forms are used for the wave function, but in most cases quantum chemists use Slater determinants. Before considering wave functions for many electrons, however, it is necessary to discuss wave functions for a single electron.

2.2.1 Spin Orbitals and Spatial Orbitals

We define an *orbital* as a wave function for a single particle, an electron. Because we are concerned with molecular electronic structure, we will be using *molecular orbitals* for the wave functions of the electrons in a molecule. A *spatial orbital* $\psi_i(\mathbf{r})$, is a function of the position vector $\mathbf{r}$ and describes the spatial distribution of an electron such that $|\psi_i(\mathbf{r})|^2\, d\mathbf{r}$ is the probability of finding the electron in the small volume element $d\mathbf{r}$ surrounding $\mathbf{r}$. Spatial molecular orbitals will usually be assumed to form an orthonormal set

$$\int d\mathbf{r}\, \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) = \delta_{ij} \quad (2.23)$$

If the set of spatial orbitals $\{\psi_i\}$ were complete, then any arbitrary function $f(\mathbf{r})$ could be exactly expanded as

$$f(\mathbf{r}) = \sum_{i=1}^{\infty} a_i \psi_i(\mathbf{r}) \quad (2.24)$$

where the a_i are constant coefficients. In general, the set would have to be infinite to be complete; however, in practice we will never have available a

complete set, but only a finite set $\{\psi_i | i = 1, 2, \ldots, K\}$ of K such orbitals. This finite set will only span a certain region of the complete space, but we can, however, describe results as being "exact" within the subspace spanned by the finite set of orbitals.

To completely describe an electron, it is necessary to specify its spin. A complete set for describing the spin of an electron consists of the two orthonormal functions $\alpha(\omega)$ and $\beta(\omega)$, i.e., spin up ($\uparrow$) and spin down ($\downarrow$). The wave function for an electron that describes both its spatial distribution and its spin is a *spin orbital*, $\chi(\mathbf{x})$, where $\mathbf{x}$ indicates both space and spin coordinates (see Eq. (2.21)). From each spatial orbital, $\psi(\mathbf{r})$, one can form two different spin orbitals—one corresponding to spin up and the other to spin down—by multiplying the spatial orbital by the α or β spin function, respectively, i.e.,

$$\chi(\mathbf{x}) = \begin{cases} \psi(\mathbf{r})\alpha(\omega) \\ \quad \text{or} \\ \psi(\mathbf{r})\beta(\omega) \end{cases} \tag{2.25}$$

Given a set of K spatial orbitals $\{\psi_i | i = 1, 2, \ldots, K\}$, one can thus form a set of $2K$ spin orbitals $\{\chi_i | i = 1, 2, \ldots, 2K\}$ as

$$\left.\begin{aligned} \chi_{2i-1}(\mathbf{x}) &= \psi_i(\mathbf{r})\alpha(\omega) \\ \chi_{2i}(\mathbf{x}) &= \psi_i(\mathbf{r})\beta(\omega) \end{aligned}\right\} i = 1, 2, \ldots, K \tag{2.26}$$

If the spatial orbitals are orthonormal, so are the spin orbitals

$$\int d\mathbf{x}\, \chi_i^*(\mathbf{x})\chi_j(\mathbf{x}) = \langle \chi_i | \chi_j \rangle = \delta_{ij} \tag{2.27}$$

Exercise 2.1 Given a set of K orthonormal spatial functions, $\{\psi_i^\alpha(\mathbf{r})\}$, and another set of K orthonormal functions, $\{\psi_i^\beta(\mathbf{r})\}$, such that the first set is not orthogonal to the second set, i.e.,

$$\int d\mathbf{r}\, \psi_i^{\alpha *}(\mathbf{r})\psi_j^\beta(\mathbf{r}) = S_{ij}$$

where $\mathbf{S}$ is an overlap matrix, show that the set $\{\chi_i\}$ of $2K$ spin orbitals, formed by multiplying $\psi_i^\alpha(\mathbf{r})$ by the α spin function and $\psi_i^\beta(\mathbf{r})$ by the β spin function, i.e.,

$$\left.\begin{aligned} \chi_{2i-1}(\mathbf{x}) &= \psi_i^\alpha(\mathbf{r})\alpha(\omega) \\ \chi_{2i}(\mathbf{x}) &= \psi_i^\beta(\mathbf{r})\beta(\omega) \end{aligned}\right\} i = 1, 2, \ldots, k$$

is an orthonormal set.

2.2.2 Hartree Products

Having seen that the appropriate wave function describing a single electron is a spin orbital, we now consider wave functions for a collection of electrons,

i.e., N-electron wave functions. Before considering the form of the exact wave function for a fully interacting system, let us first consider a simpler system containing noninteracting electrons having a Hamiltonian of the form

$$\mathscr{H} = \sum_{i=1}^{N} h(i) \tag{2.28}$$

where $h(i)$ is the operator describing the kinetic energy and potential energy of electron i. If we neglect electron-electron repulsion, then the full electronic Hamiltonian has this form. Alternatively, $h(i)$ might be an effective one-electron Hamiltonian that includes the effects of electron-electron repulsion in some average way.

Now, the operator $h(i)$ will have a set of eigenfunctions that we can take to be a set of spin orbitals $\{\chi_j\}$,

$$h(i)\chi_j(\mathbf{x}_i) = \varepsilon_j\chi_j(\mathbf{x}_i) \tag{2.29}$$

We now ask, "What are the corresponding eigenfunctions of $\mathscr{H}$?" Because $\mathscr{H}$ is a sum of one-electron Hamiltonians, a wave function which is a simple product of spin orbital wave functions for each electron,

$$\Psi^{\mathrm{HP}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N) \tag{2.30}$$

is an eigenfunction of $\mathscr{H}$,

$$\mathscr{H}\Psi^{\mathrm{HP}} = E\Psi^{\mathrm{HP}} \tag{2.31}$$

with eigenvalue E, which is just the sum of the spin orbital energies of each of the spin orbitals appearing in Ψ^{HP},

$$E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k \tag{2.32}$$

Such a many-electron wave function is termed a *Hartree product*, with electron-one being described by the spin orbital χ_i, electron-two being described by the spin orbital χ_j, etc.

Exercise 2.2 Show that the Hartree product of (2.30) is an eigenfunction of $\mathscr{H} = \sum_{i=1}^{N} h(i)$ with an eigenvalue given by (2.32).

The Hartree product is an uncorrelated or independent-electron wave function because

$$|\Psi^{\mathrm{HP}}(\mathbf{x}_1, \ldots, \mathbf{x}_N)|^2 \, d\mathbf{x}_1 \cdots d\mathbf{x}_N$$

which is the simultaneous probability of finding electron-one in the volume element $d\mathbf{x}_1$, centered at $\mathbf{x}_1$, electron-two in $d\mathbf{x}_2$, etc., is just equal, from (2.30), to the product of probabilities

$$|\chi_i(\mathbf{x}_1)|^2 \, d\mathbf{x}_1 \, |\chi_j(\mathbf{x}_2)|^2 \, d\mathbf{x}_2 \cdots |\chi_k(\mathbf{x}_N)|^2 \, d\mathbf{x}_N$$

that electron-one is in dx_1, times the probability that electron-two is in dx_2, etc. The situation is analogous to the probability of drawing an ace of hearts (1/52) being equal to the probability of drawing an ace (1/13) times the probability of drawing a heart (1/4), since the probability of a particular card being an ace is independent or uncorrelated with the probability that the given card is a heart. The probability of finding electron-one at a given point in space is independent of the position of electron-two when a Hartree product wave function is used. In reality, electron-one and electron-two will be instantaneously repelled by the two-electron coulomb interaction, and electron-one will "avoid" regions of space occupied by electron-two so that the motion of the two electrons will be explicitly correlated. An example of correlated probabilities is provided by 2 hot potatoes and 2 cold apples in a bucket. The probability of obtaining a hot potato upon randomly withdrawing an object from the bucket (1/2) is not equal to the product of the probability of getting a hot object (1/2) times the probability of getting a potato (1/2), since whether the object is hot is perfectly correlated with whether the object is a potato.

Assuming independent electrons and a Hamiltonian of the form of Eq. (2.28), there is still a basic deficiency in the Hartree product; it takes no account of the indistinguishability of electrons, but specifically distinguishes electron-one as occupying spin orbital χ_i, electron-two as occupying χ_j, etc. The antisymmetry principle does not distinguish between identical electrons and requires that electronic wave functions be antisymmetric (change sign) with respect to the interchange of the space *and* spin coordinates of any two electrons.

2.2.3 Slater Determinants

The Hartree product does not satisfy the antisymmetry principle. However, we can obtain correctly antisymmetrized wave functions as follows. Consider a two-electron case in which we occupy the spin orbitals χ_i and χ_j. If we put electron-one in χ_i and electron-two in χ_j, we have

$$\Psi_{12}^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) \tag{2.33a}$$

On the other hand, if we put electron-one in χ_j and electron-two in χ_i, we have

$$\Psi_{21}^{HP}(\mathbf{x}_1, \mathbf{x}_2) = \chi_i(\mathbf{x}_2)\chi_j(\mathbf{x}_1) \tag{2.33b}$$

Each of these Hartree products clearly distinguishes between electrons; however, we can obtain a wave function which does not, and which satisfies the requirement of the antisymmetry principle by taking the appropriate linear combination of these two Hartree products,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2}(\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1)\chi_i(\mathbf{x}_2)) \tag{2.34}$$

The factor $2^{-1/2}$ is a normalization factor. The minus sign insures that $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ is antisymmetric with respect to the interchange of the coordinates

of electrons one and two. Clearly,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = -\Psi(\mathbf{x}_2, \mathbf{x}_1) \tag{2.35}$$

From the form of Eq. (2.34), it is evident that the wave function vanishes if both electrons occupy the same spin orbital (i.e., if $i = j$). Thus the antisymmetry requirement immediately leads to the usual statement of the Pauli exclusion principle namely, that no more than one electron can occupy a spin orbital.

Exercise 2.3 Show that $\Psi(\mathbf{x}_1, \mathbf{x}_2)$ of Eq. (2.34) is normalized.

Exercise 2.4 Suppose the spin orbitals χ_i and χ_j are eigenfunctions of a one-electron operator h with eigenvalues ε_i and ε_j as in Eq. (2.29). Show that the Hartree products in Eqs. (2.33a, b) and the antisymmetrized wave function in Eq. (2.34) are eigenfunctions of the independent-particle Hamiltonian $\mathscr{H} = h(1) + h(2)$ (c.f. Eq. (2.28)) and have the same eigenvalue namely, $\varepsilon_i + \varepsilon_j$.

The antisymmetric wave function of Eq. (2.34) can be rewritten as a determinant (see Eq. (1.39))

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = 2^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) \end{vmatrix} \tag{2.36}$$

and is called a *Slater determinant*. For an N-electron system the generalization of Eq. (2.36) is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\mathbf{x}_1) & \chi_j(\mathbf{x}_1) & \cdots & \chi_k(\mathbf{x}_1) \\ \chi_i(\mathbf{x}_2) & \chi_j(\mathbf{x}_2) & \cdots & \chi_k(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(\mathbf{x}_N) & \chi_j(\mathbf{x}_N) & \cdots & \chi_k(\mathbf{x}_N) \end{vmatrix} \tag{2.37}$$

The factor $(N!)^{-1/2}$ is a normalization factor. This Slater determinant has N electrons occupying N spin orbitals $(\chi_i, \chi_j, \ldots, \chi_k)$ without specifying which electron is in which orbital. Note that the rows of an N-electron Slater determinant are labeled by electrons: first row $(\mathbf{x}_1)$, second row $(\mathbf{x}_2)$, etc., and the columns are labeled by spin orbitals: first column (χ_i), second column (χ_j), etc. Interchanging the coordinates of two electrons corresponds to interchanging two rows of the Slater determinant, which changes the sign of the determinant. Thus Slater determinants meet the requirement of the antisymmetry principle. Having two electrons occupying the same spin orbital corresponds to having two columns of the determinant equal, which makes the determinant zero. Thus no more than one electron can occupy a spin orbital (Pauli exclusion principle). It is convenient to introduce a short-hand notation for a normalized Slater determinant, which *includes the normaliza-*

tion constant and only shows the diagonal elements of the determinant,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_i(\mathbf{x}_1)\chi_j(\mathbf{x}_2)\cdots\chi_k(\mathbf{x}_N)\rangle \tag{2.38}$$

If we always choose the electron labels to be in the order $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$, then Eq. (2.38) can be further shortened to

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = |\chi_i\chi_j\cdots\chi_k\rangle \tag{2.39}$$

Because the interchange of any two columns changes the sign of a determinant, the ordering of spin orbital labels in Eq. (2.39) is important. In our short-hand notation, the antisymmetry property of Slater determinants is

$$|\cdots\chi_m\cdots\chi_n\cdots\rangle = -|\cdots\chi_n\cdots\chi_m\cdots\rangle \tag{2.40}$$

To within a sign, a Slater determinant is completely specified by the spin orbitals from which it is formed (i.e., the spin orbitals that are occupied). Slater determinants formed from orthonormal spin orbitals are normalized. N-electron Slater determinants that have different orthonormal spin orbitals occupied are orthogonal.

Exercise 2.5 Consider the Slater determinants

$$|K\rangle = |\chi_i\chi_j\rangle$$
$$|L\rangle = |\chi_k\chi_l\rangle$$

Show that

$$\langle K|L\rangle = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

Note that the overlap is zero unless: 1) $k = i$ and $l = j$, in which case $|L\rangle = |K\rangle$ and the overlap is unity and 2) $k = j$ and $l = i$ in which case $|L\rangle = |\chi_j\chi_i\rangle = -|K\rangle$ and the overlap is minus one.

We have seen that a Hartree product is truly an independent-electron wave function since the simultaneous probability of finding electron-one in $d\mathbf{x}_1$ at $\mathbf{x}_1$, electron-two in $d\mathbf{x}_2$ at $\mathbf{x}_2$, etc. is simply equal to the product of the probabilities that electron-one is in $d\mathbf{x}_1$, electron-two is in $d\mathbf{x}_2$, etc. Antisymmetrizing a Hartree product to obtain a Slater determinant introduces *exchange* effects, so-called because they arise from the requirement that $|\Psi|^2$ be invariant to the exchange of the space and spin coordinates of any two electrons. In particular, a Slater determinant incorporates *exchange correlation*, which means that the motion of two electrons with parallel spins is correlated. Since the motion of electrons with opposite spins remains uncorrelated, it is customary to refer to a single determinantal wave function as an uncorrelated wave function.

To see how exchange correlation arises, we now investigate the effect of antisymmetrizing a Hartree product on the electron density. Consider a

two-electron Slater determinant in which spin orbitals χ_1 and χ_2 are occupied

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\rangle \tag{2.41}$$

If the two electrons have opposite spins and occupy different spatial orbitals,

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\alpha(\omega_1) \tag{2.42}$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(\omega_2) \tag{2.43}$$

then by expanding the determinant, one obtains

$$|\Psi|^2 \, d\mathbf{x}_1 \, d\mathbf{x}_2 = \tfrac{1}{2}|\psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2) - \psi_1(\mathbf{r}_2)\alpha(\omega_2)\psi_2(\mathbf{r}_1)\beta(\omega_1)|^2 \, d\mathbf{x}_1 \, d\mathbf{x}_2 \tag{2.44}$$

for the simultaneous probability of electron-one being in $d\mathbf{x}_1$ and electron-two being in $d\mathbf{x}_2$. Let $P(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1 d\mathbf{r}_2$ be the probability of finding electron-one in $d\mathbf{r}_1$ at $\mathbf{r}_1$ and simultaneously electron-two in $d\mathbf{r}_2$ at $\mathbf{r}_2$, as shown in Fig. 2.3. This probability is obtained by integrating (averaging) Eq. (2.44) over the spins of the two electrons,

$$\begin{aligned} P(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1 \, d\mathbf{r}_2 &= \int d\omega_1 \, d\omega_2 \, |\Psi|^2 \, d\mathbf{r}_1 \, d\mathbf{r}_2 \\ &= \tfrac{1}{2}[|\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2|\psi_2(\mathbf{r}_1)|^2] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \end{aligned} \tag{2.45}$$

The first term in (2.45) is the product of the probability of finding electron-one in $d\mathbf{r}_1$ at $\mathbf{r}_1$ times the probability of finding electron-two in $d\mathbf{r}_2$ at $\mathbf{r}_2$, *if* electron-one occupies ψ_1 and electron-two occupies ψ_2. The second term has electron-one occupying ψ_2 and electron-two occupying ψ_1. Since electrons are indistinguishable, the correct probability is the average of the two

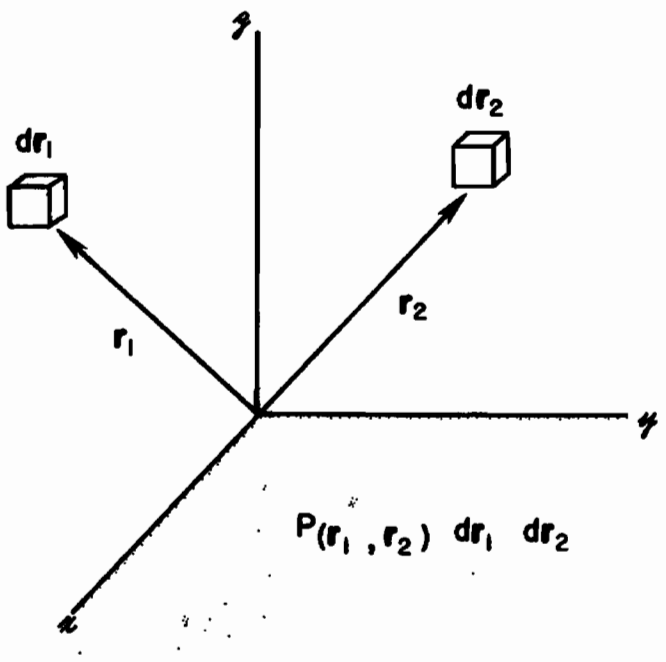


Figure 2.3 Probability of electron-one being in $d\mathbf{r}_1$ and electron-two being in $d\mathbf{r}_2$.

terms as shown. Thus the motion of the two electrons is uncorrelated. This is particularily obvious if $\psi_1 = \psi_2$, for in that case

$$P(\mathbf{r}_1, \mathbf{r}_2) = |\psi_1(\mathbf{r}_1)|^2 |\psi_1(\mathbf{r}_2)|^2 \tag{2.46}$$

Note that $P(\mathbf{r}_1, \mathbf{r}_1) \neq 0$ so that there is a finite probability of finding two electrons with opposite spins at the same point in space.

If the two electrons have the same spin (say β), we have

$$\chi_1(\mathbf{x}_1) = \psi_1(\mathbf{r}_1)\beta(\omega_1) \tag{2.47}$$

$$\chi_2(\mathbf{x}_2) = \psi_2(\mathbf{r}_2)\beta(\omega_2) \tag{2.48}$$

then, by steps identical to the above, we obtain

$$P(\mathbf{r}_1, \mathbf{r}_2) = \tfrac{1}{2}\{|\psi_1(\mathbf{r}_1)|^2|\psi_2(\mathbf{r}_2)|^2 + |\psi_1(\mathbf{r}_2)|^2|\psi_2(\mathbf{r}_1)|^2 - [\psi_1^*(\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_2^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2) + \psi_1(\mathbf{r}_1)\psi_2^*(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_1^*(\mathbf{r}_2)]\} \tag{2.49}$$

where we now have an extra cross term, making the probabilities correlated. This is exchange correlation between electrons of parallel spin. Note that $P(\mathbf{r}_1, \mathbf{r}_1) = 0$, and thus the probability of finding two electrons with parallel spins at the same point in space is zero. A *Fermi hole* is said to exist around an electron. In summary, within the single Slater determinantal description, the motion of electrons with parallel spins is correlated but the motion of electrons with opposite spins is not.

2.2.4 The Hartree-Fock Approximation

Finding and describing approximate solutions to the electronic Schrödinger equation has been a major preoccupation of quantum chemists since the birth of quantum mechanics. Except for the very simplest cases like H_2^+, quantum chemists are faced with many-electron problems. Central to attempts at solving such problems, and central to this book, is the Hartree-Fock approximation. It has played an important role in elucidating modern chemistry. In addition, it usually constitutes the first step towards more accurate approximations. We are now in a position to consider some of the basic ideas which underlie this approximation. A detailed description of the Hartree-Fock method is given in Chapter 3.

The simplest antisymmetric wave function, which can be used to describe the ground state of an N-electron system, is a single Slater determinant,

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_N\rangle \tag{2.50}$$

The variation principle states that the best wave function of this functional form is the one which gives the lowest possible energy

$$E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle \tag{2.51}$$

where $\mathscr{H}$ is the full electronic Hamiltonian. The variational flexibility in the wave function (2.50) is in the choice of spin orbitals. By minimizing E_0 with respect to the choice of spin orbitals, one can derive an equation, called the Hartree-Fock equation, which determines the optimal spin orbitals. We shall show in Chapter 3 that the Hartree-Fock equation is an eigenvalue equation of the form

$$f(i)\chi(\mathbf{x}_i) = \varepsilon\chi(\mathbf{x}_i) \tag{2.52}$$

where $f(i)$ is an effective one-electron operator, called the *Fock* operator, of the form

$$f(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + v^{\mathrm{HF}}(i) \tag{2.53}$$

where $v^{\mathrm{HF}}(i)$, which will be explicitly defined in Chapter 3, is the *average* potential experienced by the ith electron due to the presence of the other electrons. The essence of the Hartree-Fock approximation is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way.

The Hartree-Fock potential $v^{\mathrm{HF}}(i)$, or equivalently the "field" seen by the ith electron, depends on the spin orbitals of the other electrons (i.e., the Fock operator depends on its eigenfunctions). Thus the Hartree-Fock equation (2.52) is nonlinear and must be solved iteratively. The procedure for solving the Hartree-Fock equation is called the self-consistent-field (SCF) method.

The basic idea of the SCF method is simple. By making an initial guess at the spin orbitals, one can calculate the average field (i.e., v^{HF}) seen by each electron and then solve the eigenvalue equation (2.52) for a new set of spin orbitals. Using these new spin orbitals, one can obtain new fields and repeat the procedure until self-consistency is reached (i.e., until the fields no longer change and the spin orbitals used to construct the Fock operator are the same as its eigenfunctions).

The solution of the Hartree-Fock eigenvalue problem (2.52) yields a set $\{\chi_k\}$ of orthonormal Hartree-Fock spin orbitals with orbital energies $\{\varepsilon_k\}$. The N spin orbitals with the lowest energies are called the *occupied* or *hole* spin orbitals. The Slater determinant formed from these orbitals is the Hartree-Fock ground state wave function and is the best variational approximation to the ground state of the system, of the single determinant form. We shall label occupied spin orbitals by the indices $a, b, c, \ldots$ (i.e., $\chi_a, \chi_b, \ldots$). The remaining members of the set $\{\chi_k\}$ are called *virtual*, *unoccupied*, or *particle* spin orbitals. We shall label virtual spin orbitals by the indices $r, s, t, \ldots$ (i.e., $\chi_r, \chi_s, \ldots$).

In principle, there are an infinite number of solutions to the Hartree-Fock equation (2.52) and an infinite number of virtual spin orbitals. In practice, the Hartree-Fock equation is solved by introducing a finite set of

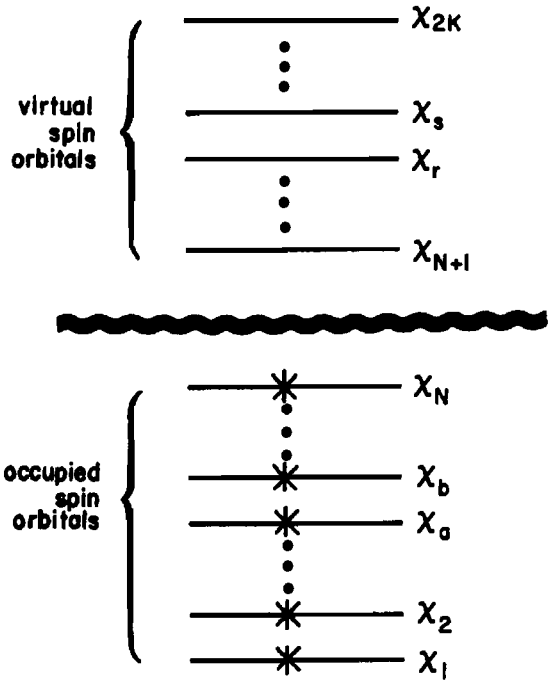


Figure 2.4 The Hartree-Fock ground state determinant, $|\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle$.

spatial basis functions $\{\phi_\mu(\mathbf{r}) | \mu = 1, 2, \ldots, K\}$. The spatial parts of the spin orbitals with the α spin function can then be expanded in terms of the known set of functions $\{\phi_\mu\}$. The spatial parts of the spin orbitals with the β spin can be expanded in the same way and both expansions substituted into the eigenvalue problem (2.52) to obtain matrix eigenvalue equations for the expansion coefficients. These matrix equations (e.g., the Roothaan equations) will be studied in some detail in Chapter 3. It is sufficient for this discussion to realize that using a basis set of K spatial functions $\{\phi_\mu\}$ leads to a set of $2K$ spin orbitals (K with α spin and K with β spin). This leads to a set of N occupied spin orbitals $\{\chi_a\}$ and a complementary set of $2K - N$ unoccupied or virtual spin orbitals $\{\chi_r\}$. A single Slater determinant formed from the set $\{\chi_a\}$ is the variational Hartree-Fock ground state, for which we will use the symbol Ψ_0 or $|\Psi_0\rangle$. A pictorial representation of $|\Psi_0\rangle$ is presented in Fig. 2.4. The $2K$ Hartree-Fock spin orbitals have been ordered according to their energy, and we have neglected possible degeneracies. The occupancy of the N lowest energy spin orbitals—one electron per spin orbital—is indicated by the asterisks.

The larger and more complete the set of basis functions $\{\phi_\mu\}$, the greater is the degree of flexibility in the expansion for the spin orbitals and the lower will be the expectation value $E_0 = \langle\Psi_0|\mathscr{H}|\Psi_0\rangle$. Larger and larger basis sets will keep lowering the Hartree-Fock energy E_0 until a limit is reached, called the *Hartree-Fock limit*. In practice, any finite value of K will lead to an energy somewhat above the Hartree-Fock limit.

2.2.5 The Minimal Basis H_2 Model

At this point we introduce a simple model system, which we will be using throughout this book to illustrate many of the methods and ideas of quantum

chemistry. The model we use is the familiar minimal basis MO-LCAO description of H_2.

In this model, each hydrogen atom has a $1s$ atomic orbital and, as the two atoms approach, molecular orbitals (MOs) are formed as a linear combination of atomic orbitals (LCAO). The coordinate system is shown in Fig. 2.5. The first atomic orbital, ϕ_1, is centered on atom 1 at $\mathbf{R}_1$. The value of ϕ_1 at a point in space $\mathbf{r}$ is $\phi_1(\mathbf{r})$ or, since its value depends on the distance from its origin, we sometimes write $\phi_1 \equiv \phi_1(\mathbf{r} - \mathbf{R}_1)$. The second atomic orbital is centered on atom 2 at $\mathbf{R}_2$, i.e., $\phi_2 \equiv \phi_2(\mathbf{r} - \mathbf{R}_2)$. The exact $1s$ orbital of a hydrogen atom centered at $\mathbf{R}$ has the form

$$\phi(\mathbf{r} - \mathbf{R}) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}|} \tag{2.54}$$

where ζ, the orbital exponent, has a value of 1.0. This is an example of a *Slater orbital.* In this book we will be concerned mostly with *Gaussian orbitals,* which lead to simpler integral evaluations than Slater orbitals. The $1s$ Gaussian orbital has the form

$$\phi(\mathbf{r} - \mathbf{R}) = (2\alpha/\pi)^{3/4} e^{-\alpha|\mathbf{r}-\mathbf{R}|^2} \tag{2.55}$$

where α is the Gaussian orbital exponent. For the present, we need not be concerned with the particular form of the $1s$ atomic orbitals. The two atomic orbitals ϕ_1 and ϕ_2 can be assumed to be normalized, but they will not be orthogonal. They will *overlap,* such that the overlap integral is

$$S_{12} = \int d\mathbf{r}\, \phi_1^*(\mathbf{r})\phi_2(\mathbf{r}) \tag{2.56}$$

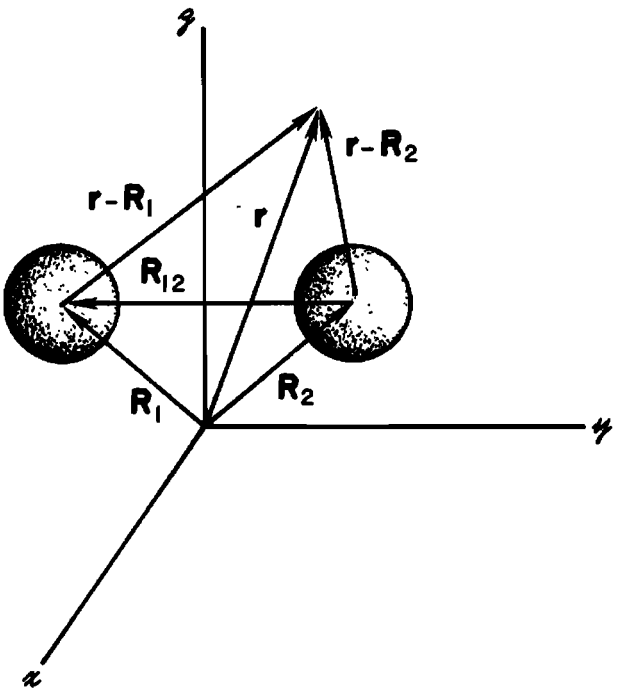


Figure 2.5 Coordinate system for minimal basis H_2.

The overlap will depend on the distance $R_{12} = |\mathbf{R}_1 - \mathbf{R}_2|$, such that $S_{12} = 1$ when $R_{12} = 0$ and $S_{12} = 0$ when $R_{12} = \infty$.

From the two localized atomic orbitals, ϕ_1 and ϕ_2, one can form, by linear combination, two delocalized molecular orbitals. The symmetric combination leads to a bonding molecular orbital of *gerade* symmetry (i.e., symmetric with respect to inversion about the point centered between the nuclei)

$$\psi_1 = [2(1 + S_{12})]^{-1/2}(\phi_1 + \phi_2) \tag{2.57}$$

whereas, the antisymmetric combination leads to an antibonding molecular orbital of *ungerade* symmetry (i.e., antisymmetric with respect to inversion about the point centered between the nuclei)

$$\psi_2 = [2(1 - S_{12})]^{-1/2}(\phi_1 - \phi_2) \tag{2.58}$$

Exercise 2.6 Show that ψ_1 and ψ_2 form an orthonormal set.

The above procedure is the simplest example of the general technique of expanding a set of spatial molecular orbitals in a set of known spatial basis functions

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^{K} C_{\mu i}\phi_\mu(\mathbf{r}) \tag{2.59}$$

To obtain the exact molecular orbitals of H_2 one would need an infinite number of terms in such an expansion. Using only two basis functions for H_2 is an example of a *minimal* basis set and an obvious choice for the two functions ϕ_1 and ϕ_2 is the 1*s* atomic orbitals of the atoms. The correct linear combinations for this simple choice are determined by symmetry, and one need not solve the Hartree-Fock equations; ψ_1 and ψ_2 of Eqs. (2.57) and (2.58) are the Hartree-Fock spatial orbitals in the space spanned by ϕ_1 and ϕ_2.

Given the two spatial orbitals ψ_1 and ψ_2, we can form four spin orbitals

$$\begin{aligned}
\chi_1(\mathbf{x}) &= \psi_1(\mathbf{r})\alpha(\omega) \\
\chi_2(\mathbf{x}) &= \psi_1(\mathbf{r})\beta(\omega) \\
\chi_3(\mathbf{x}) &= \psi_2(\mathbf{r})\alpha(\omega) \\
\chi_4(\mathbf{x}) &= \psi_2(\mathbf{r})\beta(\omega)
\end{aligned} \tag{2.60}$$

The orbital energies associated with these spin orbitals can be obtained only by explicitly considering the Hartree-Fock operator. But, as might be expected, χ_1 and χ_2 are degenerate and have the lower energy corresponding to a bonding situation, while χ_3 and χ_4 are also degenerate having a higher energy corresponding to an antibonding situation. The Hartree-Fock ground state in this model is the single determinant

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle \tag{2.61}$$

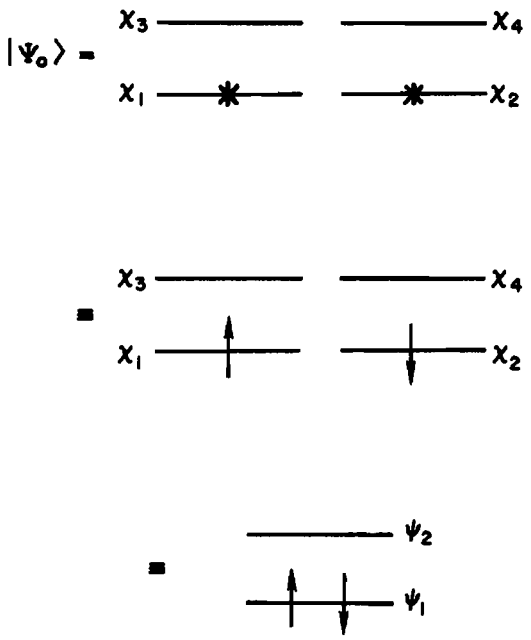


Figure 2.6 Three different representations of the Hartree-Fock ground state of minimal basis H_2.

shown pictorially in Fig. 2.6. Sometimes it is convenient to use a notation that indicates a spin orbital by its spatial part, using a bar or lack of a bar to denote whether it has the β or α spin function. Thus

$$\begin{aligned} \chi_1 &\equiv \psi_1 & \chi_2 &\equiv \bar{\psi}_1 \\ \chi_3 &\equiv \psi_2 & \chi_4 &\equiv \bar{\psi}_2 \end{aligned} \tag{2.62}$$

In this notation the Hartree-Fock ground state is

$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle \tag{2.63}$$

which indicates that both electrons occupy the same spatial orbital ψ_1, but one has an α spin and one has a β spin. It will be apparent from the context whether ψ_1 denotes a spatial orbital, or a spin orbital made up of the ψ_1 spatial orbital and the α spin function.

2.2.6 Excited Determinants

The Hartree-Fock procedure produces a set $\{\chi_i\}$ of $2K$ spin orbitals. The Hartree-Fock ground state,

$$|\Psi_0\rangle = |\chi_1\chi_2 \cdots \chi_a\chi_b \cdots \chi_N\rangle \tag{2.64}$$

is the best (in a variational sense) approximation to the ground state, of the single determinant form. However, it clearly is only one of many determinants that could be formed from the $2K > N$ spin orbitals. The number of combinations of $2K$ objects taken N at a time is the binomial coefficient

$$\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$$

This is the same as the number of different single determinants that one can form from N electrons and $2K$ spin orbitals; the Hartree-Fock ground state is just one of these. A convenient way of describing these other determinants is to consider the Hartree-Fock ground state (2.64) to be a reference state and to classify other possible determinants by how they differ from the reference state, i.e., by stating which occupied or hole spin orbitals of the set $\{\chi_a\}$ in (2.64), have been replaced by which virtual or particle spin orbitals of the set $\{\chi_r\}$. These other determinants can be taken to represent approximate excited states of the system or, as we shall see shortly, they can be used in linear combination with $|\Psi_0\rangle$ for a more accurate description of the ground state or any excited state of the system.

A singly excited determinant is one in which an electron, which occupied χ_a in the Hartree-Fock ground state (2.64), has been promoted to a virtual spin orbital χ_r, as shown in Fig. 2.7,

$$|\Psi_a^r\rangle = |\chi_1\chi_2 \cdots \chi_r\chi_b \cdots \chi_N\rangle \tag{2.65}$$

A doubly excited determinant, shown in Fig. 2.8, is one in which electrons have been excited from χ_a and χ_b to χ_r and χ_s,

$$|\Psi_{ab}^{rs}\rangle = |\chi_1\chi_2 \cdots \chi_r\chi_s \cdots \chi_N\rangle \tag{2.66}$$

All $\binom{2K}{N}$ determinants can thus be classified as either the Hartree-Fock ground state or singly, doubly, triply, quadruply, . . . , N-tuply excited states. The importance of these determinants as approximate representations of the true states of the system diminishes, in some sense, in the above order. While the excited determinants are not accurate representations of the

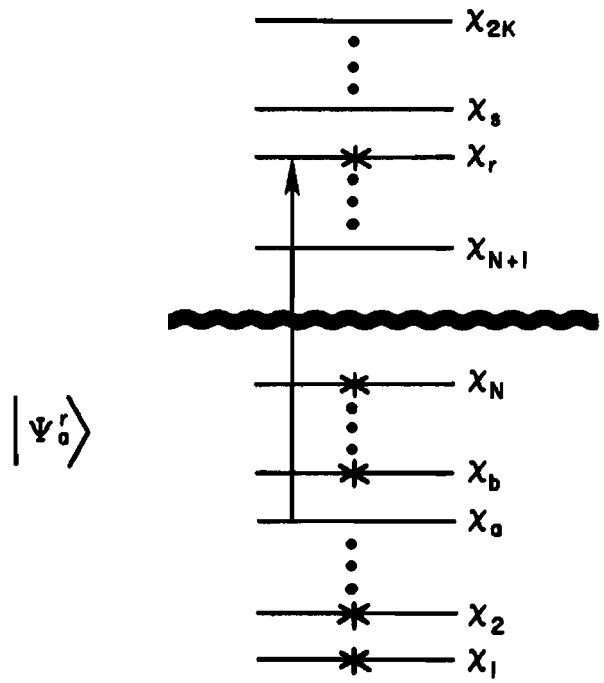


Figure 2.7 A singly excited determinant.

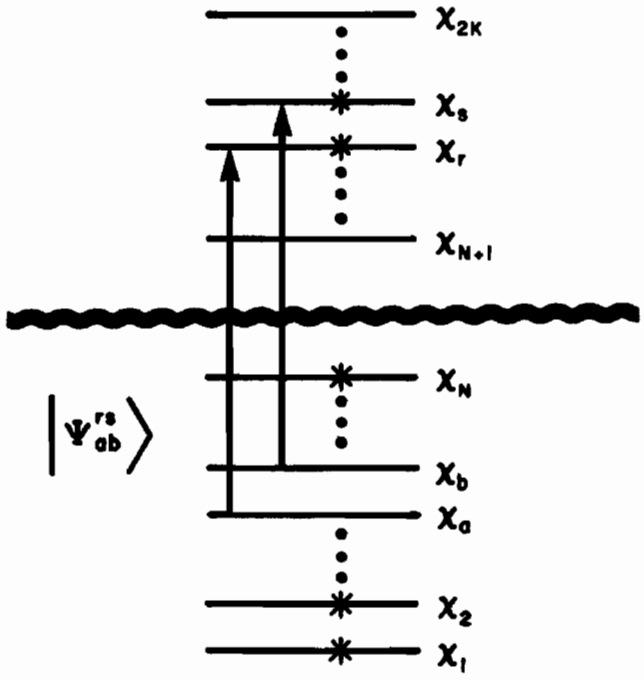


Figure 2.8 A doubly excited determinant.

excited states of the system, they are important as N-electron basis functions for an expansion of the exact N-electron states of the system.

2.2.7 Form of the Exact Wave Function and Configuration Interaction

We now consider the use of excited determinants as N-electron basis functions. Suppose we have a complete set of functions $\{\chi_i(x)\}$. Any function $\Phi(x_1)$ of a single variable can then be exactly expanded as

$$\Phi(x_1) = \sum_i a_i \chi_i(x_1) \tag{2.67}$$

where a_i is an expansion coefficient. How can we expand a function of two variables $\Phi(x_1, x_2)$ in an analogous way? If we think of x_2 as being held fixed, then we can expand $\Phi(x_1, x_2)$ as

$$\Phi(x_1, x_2) = \sum_i a_i(x_2)\chi_i(x_1) \tag{2.68}$$

where the expansion coefficients are now functions of x_2. Since $a_i(x_2)$ is a function of a single variable, it can be expanded in the complete set $\{\chi_i\}$ as

$$a_i(x_2) = \sum_j b_{ij}\chi_j(x_2) \tag{2.69}$$

Substituting this result in (2.68) gives

$$\Phi(x_1, x_2) = \sum_{ij} b_{ij}\chi_i(x_1)\chi_j(x_2) \tag{2.70}$$

If, however, we require Φ to be antisymmetric,

$$\Phi(x_1, x_2) = -\Phi(x_2, x_1) \tag{2.71}$$

then $b_{ij} = -b_{ji}$ and $b_{ii} = 0$, or

$$\begin{aligned}\Phi(x_1, x_2) &= \sum_i \sum_{j>i} b_{ij}[\chi_i(x_1)\chi_j(x_2) - \chi_j(x_1)\chi_i(x_2)] \\ &= \sum_{i<j} 2^{1/2} b_{ij}|\chi_i\chi_j\rangle\end{aligned} \tag{2.72}$$

Thus an arbitrary antisymmetric function of the two variables can be exactly expanded in terms of all unique determinants formed from a complete set of one-variable functions $\{\chi_i(x)\}$. This argument is readily extended to more than two variables, so that the exact wave function for the ground and excited states of our N-electron problem can be written as a linear combination of all possible N-electron Slater determinants formed from a complete set of spin orbitals $\{\chi_i\}$.

Since all possible determinants can be described by reference to the Hartree-Fock determinant, we can write the exact wave function for any state of the system as

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst}|\Psi_{abc}^{rst}\rangle + \cdots \tag{2.73}$$

By summing over $a < b$, we mean summing over all a *and* over all b greater than a (i.e., over all unique pairs of occupied spin orbitals). Similarly, summing over $r < s$ means summing over all unique pairs of virtual spin orbitals. Thus all unique doubly excited configurations are included in the expansion. The situation is analogous for triply and higher excited determinants. Thus the infinite set of N-electron determinants $\{|\Psi_i\rangle\} = \{|\Psi_0\rangle, |\Psi_a^r\rangle, |\Psi_{ab}^{rs}\rangle, \ldots\}$ is a complete set for the expansion of any N-electron wave function. The exact energies of the ground and excited states of the system are the eigenvalues of the Hamiltonian matrix (i.e., the matrix with elements $\langle\Psi_i|\mathscr{H}|\Psi_j\rangle$) formed from the complete set $\{|\Psi_i\rangle\}$. Since every $|\Psi_i\rangle$ can be defined by specifying a "configuration" of spin orbitals from which it is formed, this procedure is called *configuration interaction* (CI); CI will be considered in some detail in Chapter 4. The lowest eigenvalue of the Hamiltonian matrix, denoted by $\mathscr{E}_0$, is the exact nonrelativistic ground state energy of the system within the Born-Oppenheimer approximation. The difference between this exact energy, $\mathscr{E}_0$, and the Hartree-Fock-limit energy, E_0, is called the *correlation energy*

$$E_{\text{corr}} = \mathscr{E}_0 - E_0 \tag{2.74}$$

since the motion of electrons with opposite spins is not correlated within the Hartree-Fock approximation.

Unfortunately, the above procedure for the complete solution to the many-electron problem cannot be implemented in practice because one

cannot handle infinite basis sets. If we work with a finite set of spin orbitals $\{\chi_i | i = 1, 2, \ldots, 2K\}$, then the $\binom{2K}{N}$ determinants formed from these spin orbitals do not form a complete N-electron basis. Nevertheless, diagonalizing the finite Hamiltonian matrix formed from this set of determinants leads to solutions that are exact within the one-electron subspace spanned by the $2K$ spin orbitals or, equivalently, within the N-electron subspace spanned by the $\binom{2K}{N}$ determinants. This procedure is called *full* CI. Even for relatively small systems and minimal basis sets, the number of determinants that must be included in a full CI calculation is extremely large. Thus in practice one must truncate the full CI expansion and use only a small fraction of the $\binom{2K}{N}$ possible determinants. Figure 2.9 schematically shows how the exact nonrelativistic Born-Oppenheimer wave function is approached as the size of the one-electron and N-electron basis sets increases.

Exercise 2.7 A minimal basis set for benzene consists of 72 spin orbitals. Calculate the size of the full CI matrix if it would be formed from determinants. How many singly excited determinants are there? How many doubly excited determinants are there?

Let us illustrate the above ideas with our minimal basis H_2 model. Recall (see Eq. (2.60)) that there are four ($2K = 4$) spin orbitals χ_1, χ_2, χ_3,

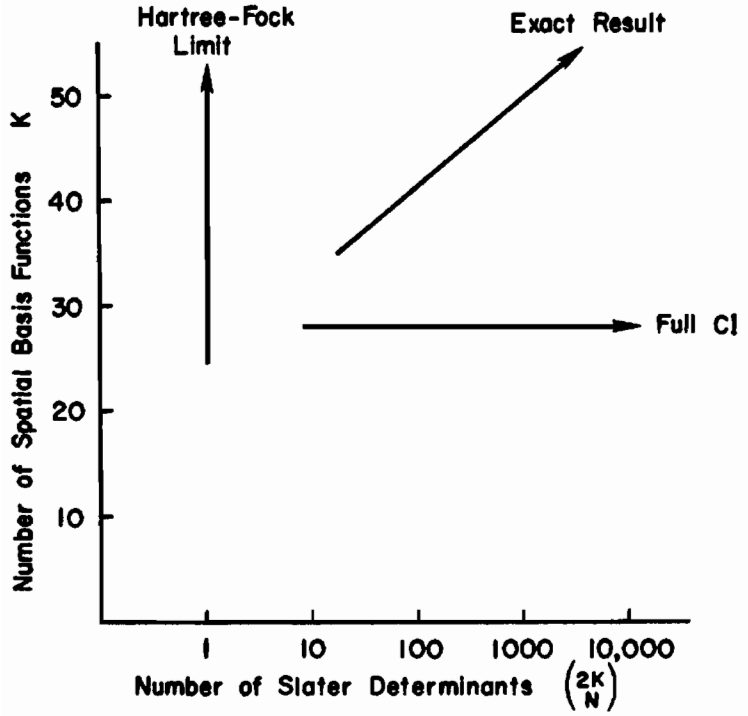


Figure 2.9 Dependence of calculations on size of one-electron and N-electron basis sets.

and χ_4 in this model. Since $N = 2$ we can form $\binom{4}{2} = \frac{4!}{2!2!} = 6$ unique determinants. The Hartree-Fock ground state determinant is

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle \qquad \begin{matrix} u & \text{———} & 2 \\ g & \uparrow\downarrow & 1 \end{matrix} \qquad (2.75)$$

The singly excited determinants are

$$|\Psi_1^2\rangle = |2\bar{1}\rangle \qquad \begin{matrix} u & \uparrow & 2 \\ g & \downarrow & 1 \end{matrix} \qquad (2.76a)$$

$$|\Psi_1^{\bar{2}}\rangle = |\bar{2}\bar{1}\rangle \qquad \begin{matrix} u & \downarrow & 2 \\ g & \downarrow & 1 \end{matrix} \qquad (2.76b)$$

$$|\Psi_{\bar{1}}^2\rangle = |12\rangle \qquad \begin{matrix} u & \uparrow & 2 \\ g & \uparrow & 1 \end{matrix} \qquad (2.76c)$$

$$|\Psi_{\bar{1}}^{\bar{2}}\rangle = |1\bar{2}\rangle \qquad \begin{matrix} u & \downarrow & 2 \\ g & \uparrow & 1 \end{matrix} \qquad (2.76d)$$

There is only one doubly excited determinant,

$$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle = |\chi_3\chi_4\rangle = |\Psi_{12}^{34}\rangle \qquad \begin{matrix} u & \uparrow\downarrow & 2 \\ g & \text{———} & 1 \end{matrix} \qquad (2.77)$$

Within the space spanned by the minimal basis set, the exact wave functions will be linear combinations of these six determinants. The Hartree-Fock ground state has two electrons in a gerade orbital and is of g symmetry (plus times plus equals plus). The doubly excited determinant has two electrons in an ungerade orbital and hence is also of g symmetry (minus times minus equals plus). The singly excited determinants, on the other hand, have one electron in a gerade orbital and one electron in an ungerade orbital and, therefore, are of u symmetry (plus times minus equals minus). The exact ground state wave function of minimal basis H_2, $|\Phi_0\rangle$, like the Hartree-Fock approximation to it, $|\Psi_0\rangle$, is of g symmetry. Therefore, only determinants of g symmetry can appear in the expansion of $|\Phi_0\rangle$ and thus we have

$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = c_0|\Psi_0\rangle + c_{12}^{34}|\Psi_{12}^{34}\rangle \qquad (2.78)$$

The exact value of the coefficients in (2.78), which describe the wave function $|\Phi_0\rangle$ and the value of the exact energy $\langle\Phi_0|\mathscr{H}|\Phi_0\rangle$, can be found by diagonalizing the full CI matrix, i.e., the 2×2 Hamiltonian matrix in the basis $|\Psi_0\rangle$ and $|\Psi_{1\bar{1}}^{2\bar{2}}\rangle$,

$$\mathbf{H} = \begin{pmatrix} \langle\Psi_0|\mathscr{H}|\Psi_0\rangle & \langle\Psi_0|\mathscr{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \\ \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathscr{H}|\Psi_0\rangle & \langle\Psi_{1\bar{1}}^{2\bar{2}}|\mathscr{H}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle \end{pmatrix} \qquad (2.79)$$

To proceed any further with this problem, or with most other formulations encountered in quantum chemistry, we need to be able to evaluate matrix elements of the Hamiltonian between determinants. The evaluation of such matrix elements is discussed in the next section.

2.3 OPERATORS AND MATRIX ELEMENTS

This section considers the problem of evaluating matrix elements of operators between Slater determinants formed from orthonormal orbitals. Given an operator $\mathcal{O}$ and two N-electron determinants $|K\rangle$ and $|L\rangle$, our problem is to evaluate $\langle K|\mathcal{O}|L\rangle$. By evaluating such matrix elements, we mean reducing them to integrals involving the individual spin orbitals χ_i occupied in $|K\rangle$ and $|L\rangle$, and ultimately to integrals involving spatial orbitals ψ_i. Before giving general rules for evaluating such matrix elements, we illustrate the procedure with our minimal basis H_2 model.

2.3.1 Minimal Basis H_2 Matrix Elements

Let us evaluate the matrix elements that appear in the full CI matrix of minimal basis H_2 (see Eq. (2.79)). The exact ground state of this model is a linear combination of the Hartree-Fock ground state $|\Psi_0\rangle = |\chi_1\chi_2\rangle = |1\bar{1}\rangle$ and the doubly excited state $|\Psi_{12}^{34}\rangle = |\chi_3\chi_4\rangle \equiv |\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle$. We need to evaluate the diagonal elements $\langle\Psi_0|\mathscr{H}|\Psi_0\rangle$ and $\langle\Psi_{12}^{34}|\mathscr{H}|\Psi_{12}^{34}\rangle$ (the Hartree-Fock ground state energy and the energy of the doubly excited state, respectively), as well as the off-diagonal elements $\langle\Psi_0|\mathscr{H}|\Psi_{12}^{34}\rangle$ and $\langle\Psi_{12}^{34}|\mathscr{H}|\Psi_0\rangle$.

The Hamiltonian for any two-electron system is

$$\mathscr{H} = \left(-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}}\right) + \frac{1}{r_{12}}$$

$$= h(1) + h(2) + \frac{1}{r_{12}} \tag{2.80}$$

where $h(1)$ is a *core-Hamiltonian* for electron-one, describing its kinetic energy and potential energy in the field of the nuclei (the "core"). It will be convenient to separate the total Hamiltonian into its one- and two-electron parts

$$\mathcal{O}_1 = h(1) + h(2) \tag{2.81}$$

$$\mathcal{O}_2 = r_{12}^{-1} \tag{2.82}$$

Let us first consider the matrix element $\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle$ which, from (2.81), is a sum of two terms. The first term is

$$\langle\Psi_0|h(1)|\Psi_0\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, [2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))]^* \times h(\mathbf{r}_1)[2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))]$$

$$= \frac{1}{2}\int d\mathbf{x}_1\, d\mathbf{x}_2\, \{\chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) - \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) - \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\} \tag{2.83}$$

In the above four terms the integration over $\mathbf{x}_2$ produces either 1 (first two terms) or 0 (last two terms) from the orthonormality of the spin orbitals. Thus

$$\langle\Psi_0|h(1)|\Psi_0\rangle = \frac{1}{2}\int d\mathbf{x}_1\, \chi_1^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1) + \frac{1}{2}\int d\mathbf{x}_1\, \chi_2^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1) \tag{2.84}$$

By exactly the same procedure, one finds that $\langle\Psi_0|h(2)|\Psi_0\rangle = \langle\Psi_0|h(1)|\Psi_0\rangle$ and thus

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \int d\mathbf{x}_1\, \chi_1^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_1(\mathbf{x}_1) + \int d\mathbf{x}_1\, \chi_2^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_2(\mathbf{x}_1) \tag{2.85}$$

The integrals in this expression are *one-electron integrals*, i.e., the integration is over the coordinates of a single electron. The dummy variables of integration are, by convention, chosen to be the coordinates of electron-one. Introducing the following notation for one-electron integrals involving spin orbitals,

$$\langle i|h|j\rangle = \langle\chi_i|h|\chi_j\rangle = \int d\mathbf{x}_1\, \chi_i^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_j(\mathbf{x}_1) \tag{2.86}$$

we have

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle \tag{2.87}$$

Exercise 2.8 Show that

$$\langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_{12}^{34}\rangle = \langle 3|h|3\rangle + \langle 4|h|4\rangle$$

and

$$\langle\Psi_0|\mathcal{O}_1|\Psi_{12}^{34}\rangle = \langle\Psi_{12}^{34}|\mathcal{O}_1|\Psi_0\rangle = 0$$

Now, let us evaluate matrix elements of $\mathcal{O}_2$.

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, [2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))]^* \times r_{12}^{-1}[2^{-1/2}(\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2))]$$

$$= \frac{1}{2}\int d\mathbf{x}_1\, d\mathbf{x}_2\, \{\chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) + \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) - \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) - \chi_2^*(\mathbf{x}_1)\chi_1^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2)\} \tag{2.88}$$

Since $r_{12} = r_{21}$, we can interchange the dummy variables of integration in the second term of the above expression and show that it is equal to the first term. Similarly, the third and fourth terms are equal. Thus

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_1^*(\mathbf{x}_1)\chi_2^*(\mathbf{x}_2)r_{12}^{-1}\chi_2(\mathbf{x}_1)\chi_1(\mathbf{x}_2) \tag{2.89}$$

The integrals in this expression are examples of *two-electron integrals*, i.e., the integration is over the eight space and spin coordinates of electron 1 and 2. It is conventional *always* to choose the dummy variables of integration in a two-electron integral to be the coordinates of electrons 1 and 2. Introducing the following notation for two-electron integrals involving spin orbitals,

$$\langle ij|kl\rangle = \langle\chi_i\chi_j|\chi_k\chi_l\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)r_{12}^{-1}\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) \tag{2.90}$$

we have

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \langle 12|12\rangle - \langle 12|21\rangle \tag{2.91}$$

and the Hartree-Fock ground state energy is

$$\langle\Psi_0|\mathcal{H}|\Psi_0\rangle = \langle\Psi_0|\mathcal{O}_1 + \mathcal{O}_2|\Psi_0\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle \tag{2.92}$$

Exercise 2.9 Using the above approach, show that the full CI matrix for minimal basis H_2 is

$$\mathcal{H} = \begin{pmatrix} \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle & \langle 12|34\rangle - \langle 12|43\rangle \\ \langle 34|12\rangle - \langle 34|21\rangle & \langle 3|h|3\rangle + \langle 4|h|4\rangle + \langle 34|34\rangle - \langle 34|43\rangle \end{pmatrix}$$

and that it is Hermitian.

2.3.2 Notations for One- and Two-Electron Integrals

Before generalizing the above results and presenting general expressions for matrix elements involving N-electron determinants, it is appropriate to summarize the different notations we use in this book for one- and two-electron integrals. The notation for two-electron integrals over spin orbitals that we have introduced in Eq. (2.90), i.e.,

$$\langle ij|kl\rangle = \langle \chi_i\chi_j|\chi_k\chi_l\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)r_{12}^{-1}\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) \quad (2.93)$$

is often referred to as the physicists' notation. Note that the complex conjugated spin orbitals appear side by side on the left and the space-spin coordinate of electron-one appears first. It is clear from this definition that

$$\langle ij|kl\rangle = \langle ji|lk\rangle \quad (2.94)$$

and that

$$\langle ij|kl\rangle = \langle kl|ij\rangle^* \quad (2.95)$$

Because two-electron integrals often appear in the following combination, we introduce a special symbol for an *antisymmetrized* two-electron integral

$$\begin{aligned}\langle ij||kl\rangle &= \langle ij|kl\rangle - \langle ij|lk\rangle \\ &= \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2)r_{12}^{-1}(1 - \mathscr{P}_{12})\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)\end{aligned} \quad (2.96)$$

where $\mathscr{P}_{12}$ is an operator which interchanges the coordinates of electron one and two. Note that

$$\langle ij||kk\rangle = 0 \quad (2.97)$$

It is an unfortunate fact of life that there is another notation for two-electron integrals over spin orbitals in common use, particularly in the literature of Hartree-Fock theory. This notation, often referred to as the chemists' notation, is

$$[ij|kl] = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)r_{12}^{-1}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) \quad (2.98)$$

Note that in this notation spin orbitals, which are functions of the coordinate of electron-one, appear side by side on the left and the complex conjugated spin orbital appears first. By interchanging the dummy variables of integration, one has

$$[ij|kl] = [kl|ij] \quad (2.99a)$$

In addition, if the spin orbitals are real, as is almost always the case in molecular Hartree-Fock calculations, one has

$$[ij|kl] = [ji|kl] = [ij|lk] = [ji|lk] \quad (2.99b)$$

Table 2.2 Notations for one- and two-electron integrals over spin (χ) and spatial (ψ) orbitals

SPIN ORBITALS

$$[i|h|j] = \langle i|h|j\rangle = \int d\mathbf{x}_1\, \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1)$$

$$\langle ij|kl\rangle = \langle \chi_i\chi_j|\chi_k\chi_l\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2) = [ik|jl]$$

$$[ij|kl] = [\chi_i\chi_j|\chi_k\chi_l] = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1) r_{12}^{-1} \chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) = \langle ik|jl\rangle$$

$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle = \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_i^*(\mathbf{x}_1)\chi_j^*(\mathbf{x}_2) r_{12}^{-1}(1 - \mathscr{P}_{12})\chi_k(\mathbf{x}_1)\chi_l(\mathbf{x}_2)$$

SPATIAL ORBITALS

$$(i|h|j) = h_{ij} = (\psi_i|h|\psi_j) = \int d\mathbf{r}_1\, \psi_i^*(\mathbf{r}_1) h(\mathbf{r}_1) \psi_j(\mathbf{r}_1)$$

$$(ij|kl) = (\psi_i\psi_j|\psi_k\psi_l) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi_i^*(\mathbf{r}_1)\psi_j(\mathbf{r}_1) r_{12}^{-1} \psi_k^*(\mathbf{r}_2)\psi_l(\mathbf{r}_2)$$

$J_{ij} = (ii|jj)$ Coulomb integrals

$K_{ij} = (ij|ji)$ Exchange integrals

For one-electron integrals over spin orbitals, the chemists' and physicists' notations are essentially the same.

$$[i|h|j] = \langle i|h|j\rangle = \int d\mathbf{x}_1\, \chi_i^*(\mathbf{x}_1) h(\mathbf{r}_1) \chi_j(\mathbf{x}_1) \tag{2.100}$$

Table 2.2 summarizes all the notations for one- and two-electron integrals used in this book. When we consider the reduction of integrals over spin orbitals to integrals over spatial orbitals later in this chapter, we will introduce a new notation for spatial integrals, which we have included in the table for the sake of completeness and ease of future reference.

2.3.3 General Rules for Matrix Elements

We have seen that it is fairly easy to evaluate matrix elements between two-electron Slater determinants. The N-electron case is more complicated, and here we simply present a set of rules that can be used to evaluate matrix elements and leave their derivation to the next subsection, which can be skipped, if desired.

There are two types of operators in quantum chemistry. The first type is a sum of one-electron operators

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i) \tag{2.101}$$

where $h(i)$ is any operator involving only the ith electron. These operators represent dynamic variables that depend only on the position or momentum

of the electron in question, independent of the position or momentum of other electrons. Examples are operators for the kinetic energy, attraction of an electron to a nucleus, dipole moment, and most of the other operators that one encounters. The second type of operator is a sum of two-electron operators

$$\mathcal{O}_2 = \sum_{i=1}^{N} \sum_{j>i}^{N} v(i,j) \equiv \sum_{i<j} v(i,j) \tag{2.102}$$

where $v(i,j)$ is an operator that depends on the position (or momentum) of both the ith and jth electron. The sum in (2.102) is over all unique pairs of electrons. The coulomb interaction between two electrons

$$v(i,j) = r_{ij}^{-1} \tag{2.103}$$

is a two-electron operator.

The rules for evaluating the matrix element $\langle K|\mathcal{O}|L\rangle$ between the determinants $|K\rangle$ and $|L\rangle$ depend on whether the operator $\mathcal{O}$ is a sum of one-electron operators ($\mathcal{O}_1$) or a sum of two-electron operators ($\mathcal{O}_2$). In addition, the value of $\langle K|\mathcal{O}|L\rangle$ depends on the degree to which the two determinants $|K\rangle$ and $|L\rangle$ differ. We can distinguish three cases. The first, Case 1, is when the two determinants are identical, i.e., the matrix element is a diagonal matrix element $\langle K|\mathcal{O}|K\rangle$. For this case, we choose the determinant to be

$$|K\rangle = |\cdots \chi_m \chi_n \cdots\rangle \tag{2.104}$$

The second, Case 2, is when the two determinants differ by one spin orbital, χ_m in $|K\rangle$ being replaced by χ_p in $|L\rangle$.

$$|L\rangle = |\cdots \chi_p \chi_n \cdots\rangle \tag{2.105}$$

The third, Case 3, is when the two determinants differ by two spin orbitals, χ_m and χ_n in $|K\rangle$ being replaced by χ_p and χ_q, respectively, in $|L\rangle$,

$$|L\rangle = |\cdots \chi_p \chi_q \cdots\rangle \tag{2.106}$$

When the two determinants differ by three or more spin orbitals the matrix element is always zero.

Tables 2.3 and 2.4 summarize the rules for the three cases. Note that the larger the difference in the two determinants, the simpler is the matrix element, i.e., the fewer number of terms it involves. The one-electron matrix elements are zero if the two determinants differ by *two* or more spin orbitals, in the same way that the two-electron matrix elements are zero if the two determinants differ by *three* or more spin orbitals. In the tables, m and n denote spin orbitals occupied in $|K\rangle$, so that sums over these indices include all N spin orbitals in that determinant.

To use the rules, the two determinants must first be in *maximum coincidence*. Consider, for example, a matrix element between $|\Psi_1\rangle$ and $|\Psi_2\rangle$

Table 2.3 Matrix elements between determinants for one-electron operators in terms of spin orbitals

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

Case 1: $|K\rangle = |\cdots mn\cdots\rangle$

$$\langle K|\mathcal{O}_1|K\rangle = \sum_{m}^{N} [m|h|m] = \sum_{m}^{N} \langle m|h|m\rangle$$

Case 2: $|K\rangle = |\cdots mn\cdots\rangle$
$|L\rangle = |\cdots pn\cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = [m|h|p] = \langle m|h|p\rangle$$

Case 3: $|K\rangle = |\cdots mn\cdots\rangle$
$|L\rangle = |\cdots pq\cdots\rangle$

$$\langle K|\mathcal{O}_1|L\rangle = 0$$

Table 2.4 Matrix elements between determinants for two-electron operators in terms of spin orbitals

$$\mathcal{O}_2 = \sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij}^{-1}$$

Case 1: $|K\rangle = |\cdots mn\cdots\rangle$

$$\langle K|\mathcal{O}_2|K\rangle = \frac{1}{2}\sum_{m}^{N}\sum_{n}^{N} [mm|nn] - [mn|nm] = \frac{1}{2}\sum_{m}^{N}\sum_{n}^{N} \langle mn||mn\rangle$$

Case 2: $|K\rangle = |\cdots mn\cdots\rangle$
$|L\rangle = |\cdots pn\cdots\rangle$

$$\langle K|\mathcal{O}_2|L\rangle = \sum_{n}^{N} [mp|nn] - [mn|np] = \sum_{n}^{N} \langle mn||pn\rangle$$

Case 3: $|K\rangle = |\cdots mn\cdots\rangle$
$|L\rangle = |\cdots pq\cdots\rangle$

$$\langle K|\mathcal{O}_2|L\rangle = [mp|nq] - [mq|np] = \langle mn||pq\rangle$$

where

$$|\Psi_1\rangle = |abcd\rangle$$
$$|\Psi_2\rangle = |crds\rangle$$

At first glance, it might appear that the two determinants differ in all four columns; however, by interchanging columns of $|\Psi_2\rangle$ and keeping track of

the sign, we have

$$|\Psi_2\rangle = |crds\rangle = -|crsd\rangle = |srcd\rangle$$

After being placed in maximum coincidence, they differ in two columns, and we can use the Case 3 rules. Using the following correspondence

$$\begin{aligned} |K\rangle &\equiv |\Psi_1\rangle & |L\rangle &\equiv |\Psi_2\rangle \\ m &\equiv a & p &\equiv s \\ n &\equiv b & q &\equiv r \end{aligned}$$

we thus have $\langle\Psi_1|\mathcal{O}_1|\Psi_2\rangle = 0$ and $\langle\Psi_1|\mathcal{O}_2|\Psi_2\rangle = \langle ab||sr\rangle$.

Using Tables 2.3 and 2.4, we can immediately write down the expression for the energy of a single determinant $|K\rangle$, i.e.,

$$\langle K|\mathscr{H}|K\rangle = \langle K|\mathcal{O}_1 + \mathcal{O}_2|K\rangle = \sum_m^N \langle m|h|m\rangle + \frac{1}{2}\sum_m^N \sum_n^N \langle mn||mn\rangle \quad (2.107)$$

where

$$h(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}} \quad (2.108)$$

The sum in (2.107) is over the spin orbitals occupied in $|K\rangle$. Since (see Eq. (2.97))

$$\langle mm||mm\rangle = \langle nn||nn\rangle = 0 \quad (2.109a)$$

and

$$\langle mn||mn\rangle = \langle nm||nm\rangle \quad (2.109b)$$

the expression (2.107) can be rewritten as

$$\begin{aligned} \langle K|\mathscr{H}|K\rangle &= \sum_m^N \langle m|h|m\rangle + \sum_m^N \sum_{n>m}^N \langle mn||mn\rangle \\ &= \sum_m [m|h|m] + \sum_m^N \sum_{n>m}^N [mm|nn] - [mn|nm] \end{aligned} \quad (2.110)$$

The summation of antisymmetrized two-electron integrals is thus over *all unique pairs* of spin orbitals χ_m and χ_n occupied in $|K\rangle$. This observation suggests a simple mnemonic device for writing down the energy of any single determinant in terms of one- and two-electron integrals over spin orbitals. *Each occupied spin orbital χ_i contributes a term $\langle i|h|i\rangle$ to the energy, and every unique pair of occupied spin orbitals χ_i, χ_j contributes a term $\langle ij||ij\rangle$ to the energy.* Thus we can think of the total energy of an N-electron system, *which is described by a Slater determinant*, as the sum of "one-electron-energies" ($\langle i|h|i\rangle$ for an electron in spin orbital χ_i) plus the sum of unique

pair-wise "interaction-energies" ($\langle ij||ij\rangle$ for a pair of electrons in spin orbitals χ_i and χ_j). In using this language, remember that it is only a mnemonic device. The physical interaction between two electrons is described by the coulomb repulsion term (r_{ij}^{-1}) in the Hamiltonian and not by an antisymmetrized two-electron integral.

Exercise 2.10 Derive Eq. (2.110) from Eq. (2.107).

Exercise 2.11 If $|K\rangle = |\chi_1\chi_2\chi_3\rangle$ show that

$$\langle K|\mathscr{H}|K\rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 3|h|3\rangle + \langle 12||12\rangle + \langle 13||13\rangle + \langle 23||23\rangle$$

In this book we will often need matrix elements involving the Hartree-Fock ground state. For convenience, we have rewritten the rules in Tables 2.3 and 2.4 by identifying the labels m and n with a and b (occupied Hartree-Fock spin orbitals) and the labels p and q with r and s (unoccupied Hartree-Fock spin orbitals). Tables 2.5 and 2.6 contain matrix elements between the Hartree-Fock ground state and either itself (Case 1), a singly excited deter-

Table 2.5 Matrix elements with the Hartree-Fock ground state for one-electron operators

$$\mathcal{O}_1 = \sum_{i=1}^{N} h(i)$$

Case 1:	$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_a^N [a|h|a] = \sum_a^N \langle a|h|a\rangle$
Case 2:	$\langle\Psi_0|\mathcal{O}_1|\Psi_a^r\rangle = [a|h|r] = \langle a|h|r\rangle$
Case 3:	$\langle\Psi_0|\mathcal{O}_1|\Psi_{ab}^{rs}\rangle = 0$

Table 2.6 Matrix elements with the Hartree-Fock ground state for two-electron operators

$$\mathcal{O}_2 = \sum_{i=1}^{N}\sum_{j>i}^{N} r_{ij}^{-1}$$

Case 1:	$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_a^N\sum_b^N [aa|bb] - [ab|ba] = \frac{1}{2}\sum_a^N\sum_b^N \langle ab||ab\rangle$
Case 2:	$\langle\Psi_0|\mathcal{O}_2|\Psi_a^r\rangle = \sum_b^N [ar|bb] - [ab|br] = \sum_b^N \langle ab||rb\rangle$
Case 3:	$\langle\Psi_0|\mathcal{O}_2|\Psi_{ab}^{rs}\rangle = [ar|bs] - [as|br] = \langle ab||rs\rangle$

minant (Case 2), or a doubly excited determinant (Case 3). Using these tables, we see that the energy of the Hartree-Fock ground state is

$$E_0 = \langle \Psi_0 | \mathscr{H} | \Psi_0 \rangle = \sum_a^N [a|h|a] + \frac{1}{2} \sum_a^N \sum_b^N [aa|bb] - [ab|ba] \quad (2.111)$$

using the chemists' notation, or equivalently

$$E_0 = \sum_a^N \langle a|h|a\rangle + \frac{1}{2} \sum_a^N \sum_b^N \langle ab||ab\rangle \quad (2.112)$$

using the physicists' notation. As shown above, expression (2.112) can be rewritten as

$$E_0 = \sum_a^N \langle a|h|a\rangle + \sum_a^N \sum_{b>a}^N \langle ab||ab\rangle \quad (2.113)$$

For minimal basis set H_2, $|\Psi_0\rangle = |\chi_1\chi_2\rangle$ so that from (2.113), we have

$$\begin{aligned} E_0 &= \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12||12\rangle \\ &= \langle 1|h|1\rangle + \langle 2|h|2\rangle + \langle 12|12\rangle - \langle 12|21\rangle \end{aligned} \quad (2.114)$$

in agreement with our previous result in Eq. (2.92).

Exercise 2.12 Evaluate the matrix elements that occur in the minimal basis H_2 full CI matrix (Eq. (2.79)) using the rules. Compare with the result obtained in Exercise 2.9.

Exercise 2.13 Show that $\langle \Psi_a^r | \mathscr{O}_1 | \Psi_b^s \rangle$

$$\begin{aligned} &= 0 && \text{if } a \neq b, r \neq s \\ &= \langle r|h|s\rangle && \text{if } a = b, r \neq s \\ &= -\langle b|h|a\rangle && \text{if } a \neq b, r = s \\ &= \sum_c^N \langle c|h|c\rangle - \langle a|h|a\rangle + \langle r|h|r\rangle && \text{if } a = b, r = s \end{aligned}$$

Exercise 2.14 The Hartree-Fock ground state energy for an N-electron system is ${}^N E_0 = \langle {}^N\Psi_0 | \mathscr{H} | {}^N\Psi_0 \rangle$. Consider a state of the ionized system (in which an electron has been removed from spin orbital χ_a) with energy ${}^{N-1}E_a = \langle {}^{N-1}\Psi_a | \mathscr{H} | {}^{N-1}\Psi_a \rangle$, where $|{}^{N-1}\Psi_a\rangle$ is a single determinant with all spin orbitals but χ_a occupied,

$$|{}^{N-1}\Psi_a\rangle = |\chi_1\chi_2 \cdots \chi_{a-1}\chi_{a+1} \cdots \chi_N\rangle$$

Show, using the rules in the tables, that the energy required for this ionization process is

$${}^N E_0 - {}^{N-1}E_a = \langle a|h|a\rangle + \sum_b^N \langle ab||ab\rangle$$

To show the power and simplicity of the mnemonic device introduced in this subsection, let us derive the above result without doing any algebra. Consider the representation of $|^N\Psi_0\rangle$ in Fig. 2.4. If we remove an electron from χ_a, we lose the "one-electron energy" contribution $\langle a|h|a\rangle$ to ${}^NE_0$. Moreover, we lose the pair-wise contributions arising from the "interaction" of the electron in χ_a with the remaining electrons $\left(\text{i.e., } \sum_{b\neq a}^{N} \langle ab||ab\rangle\right)$ Because $\langle aa||aa\rangle = 0$, the above result follows immediately.

2.3.4 Derivation of the Rules for Matrix Elements

In this section we derive the rules in Tables 2.3 and 2.4 for matrix elements of one- and two-electron operators between N-electron determinants formed from orthonormal spin orbitals. The definition of an N-electron Slater determinants containing the spin orbitals $\chi_i(\mathbf{x}_1), \chi_j(\mathbf{x}_2), \ldots, \chi_k(\mathbf{x}_N)$ is (see Eq. (1.38))

$$|\chi_i\chi_j\cdots\chi_k\rangle = (N!)^{-1/2}\sum_{n=1}^{N!}(-1)^{p_n}\mathscr{P}_n\{\chi_i(1)\chi_j(2)\cdots\chi_k(N)\} \tag{2.115}$$

where we have let $\chi(\mathbf{x}_l) \equiv \chi(l)$. $\mathscr{P}_n$ is an operator that generates the nth permutation of the electron labels $1, 2, \ldots, N$ and p_n is the number of transpositions (simple interchanges) required to obtain this permutation.

Exercise 2.15 Generalize the result of Exercise 2.4 to N-electron Slater determinants. Show that the Slater determinant $|\chi_i\chi_j\cdots\chi_k\rangle$ formed from spin orbitals, which are eigenfunctions of the one-electron operator h as in Eq. (2.29), is an eigenfunction of the independent-electron Hamiltonian (2.28), $\mathscr{H} = \sum_{i=1}^{N} h(i)$, with an eigenvalue $\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$. *Hint:* Since $\mathscr{H}$ is invariant to permutations of the electron labels, it commutes with the permutation operator $\mathscr{P}_n$.

We wish to evaluate matrix elements of the form $\langle K|\mathcal{O}|L\rangle$ where

$$|K\rangle = |\chi_m(1)\chi_n(2)\cdots\rangle \tag{2.116}$$

is a determinant, which occupies the spin orbitals $\chi_m, \chi_n, \ldots$. The determinant $|L\rangle$ differs from $|K\rangle$ in some known way. Prior to considering one- and two-electron operators and Cases 1, 2, and 3 let us set $\mathcal{O}$ equal to the unit operator and evaluate the overlap $\langle K|L\rangle$ between $|K\rangle$ and an arbitrary determinant $|L\rangle$ formed from the same set of spin orbitals,

$$|L\rangle = |\chi'_m(1)\chi'_n(2)\cdots\rangle \tag{2.117}$$

It is assumed that the two determinants have been placed in maximum coincidence. Using expression (2.115) for a determinant, we then have

$$\langle K|L\rangle = (N!)^{-1}\sum_{i}^{N!}\sum_{j}^{N!}(-1)^{p_i}(-1)^{p_j}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N \times \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}\mathscr{P}_j\{\chi_m'(1)\chi_n'(2)\cdots\} \tag{2.118}$$

The spin orbitals are assumed to form an orthonormal set. If the above overlap is to be nonzero, the primed spin orbitals must be identical with the unprimed spin orbitals. Otherwise a zero would always result from the orthogonality of some spin orbital χ_n' in $|L\rangle$ to the spin orbitals $\chi_m, \chi_n, \ldots$ in $|K\rangle$. Thus a determinant $|K\rangle$ is orthogonal to any other determinant that does not contain identical spin orbitals. If two determinants contain identical spin orbitals and are in perfect coincidence, i.e., if they are the same determinant, then

$$\langle K|K\rangle = (N!)^{-1}\sum_{i}^{N!}\sum_{j}^{N!}(-1)^{p_i}(-1)^{p_j}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N \times \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}\mathscr{P}_j\{\chi_m(1)\chi_n(2)\cdots\} \tag{2.119}$$

Now, in the above sum, integration will give zero unless each electron occupies the same spin orbital in both the ith permutation and the jth permutation. Thus the two permutations must be identical ($i = j$) and, since $(-1)^{2p_i} = 1$, we have

$$\langle K|K\rangle = (N!)^{-1}\sum_{i}^{N!}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N\, \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}\mathscr{P}_i\{\chi_m(1)\chi_n(2)\cdots\} \tag{2.120}$$

Each term in this sum is unity and, therefore,

$$\langle K|K\rangle = (N!)^{-1}\sum_{i}^{N!}1 = 1 \tag{2.121}$$

showing that $|K\rangle$ is normalized. Thus we have

$$\begin{aligned} \langle K|K\rangle &= 1 \qquad \text{Case 1} \\ \langle K|L\rangle &= 0 \qquad \text{Case 2} \end{aligned} \tag{2.122}$$

Next let us consider matrix elements of a sum of one-electron operators,

$$\langle K|\mathscr{O}_1|L\rangle = \langle K|h(1) + h(2) + \cdots + h(N)|L\rangle \tag{2.123}$$

Because the electrons in a determinant are indistinguishable, matrix elements of $h(1)$ will be identical to those of $h(2)$, $h(3)$, etc. Thus each term of the sum

in (2.123) is identical, and we can write

$$\langle K|\mathcal{O}_1|L\rangle = N\langle K|h(1)|L\rangle \tag{2.124}$$

where, by convention, we choose to use the operator for electron 1. We begin with Case 1,

$$\begin{aligned}\langle K|\mathcal{O}_1|K\rangle &= N\langle K|h(1)|K\rangle \\ &= N(N!)^{-1}\sum_{i}^{N!}\sum_{j}^{N!}(-1)^{p_i}(-1)^{p_j}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N \\ &\quad\times \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}h(1)\mathscr{P}_j\{\chi_m(1)\chi_n(2)\cdots\}\end{aligned} \tag{2.125}$$

Now in the integration over electrons 2, 3, . . . , N, we will obtain zero unless these electrons occupy the same spin orbitals in the ith permutation as in the jth permutation, since the spin orbitals are orthonormal. If electrons 2, 3, . . . , N occupy identical spin orbitals in both permutations, it must be that electron 1 also occupies the same spin orbital in both permutations. Thus only if the two permutations are identical ($i = j$) will we obtain a result different from zero.

$$\begin{aligned}\langle K|\mathcal{O}_1|K\rangle &= [(N-1)!]^{-1}\sum_{i}^{N!}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N \\ &\quad\times \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}h(1)\mathscr{P}_i\{\chi_m(1)\chi_n(2)\cdots\}\end{aligned} \tag{2.126}$$

In the sum over the $N!$ permutations, electron 1 will occupy each of the spin orbitals, $\{\chi_m|m = 1, 2, \ldots, N\}$, $(N-1)!$ times, i.e., if electron 1 is in a specific spin orbital χ_m, there will be $(N-1)!$ ways of arranging electrons 2, 3, . . . , N amongst the other $N-1$ spin orbitals. Integration over electrons 2, 3, . . . , N will always give a factor of 1 since the spin orbitals are normalized and thus,

$$\begin{aligned}\langle K|\mathcal{O}_1|K\rangle &= (N-1)![(N-1)!]^{-1}\sum_{m}^{N}\int d\mathbf{x}_1\, \chi_m^*(1)h(1)\chi_m(1) \\ &= \sum_{m}^{N}\langle m|h|m\rangle \qquad \text{Case 1}\end{aligned} \tag{2.127}$$

We now turn to Case 2, in which the two determinants differ by a single spin orbital, χ_p appearing in $|L\rangle$ where χ_m appears in $|K\rangle$,

$$|K\rangle = |\chi_m(1)\chi_n(2)\cdots\rangle \tag{2.128}$$

$$|L\rangle = |\chi_p(1)\chi_n(2)\cdots\rangle \tag{2.129}$$

By the same arguments we used for Case 1, to obtain (2.126) from (2.125), identical permutations must appear on either side of the operator to obtain

a result different from zero

$$\langle K|\mathcal{O}_1|L\rangle = [(N-1)!]^{-1}\sum_i^{N!}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N$$
$$\times\, \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}h(1)\mathscr{P}_i\{\chi_p(1)\chi_n(2)\cdots\} \qquad (2.130)$$

Because the spin orbital χ_m in the first permutation is orthogonal to any spin orbital in the second permutation, it must be occupied by electron 1, to "associate" it with $h(1)$ and yield a nonzero result. There are $(N-1)!$ ways of permuting the remaining electrons $2, 3, \ldots, N$ amongst the other $N-1$ spin orbitals $\chi_n, \ldots$. Integrating over these electrons always yields a factor of 1 from their normalization and, hence,

$$\langle K|\mathcal{O}_1|L\rangle = (N-1)![(N-1)!]^{-1}\int d\mathbf{x}_1\, \chi_m^*(1)h(1)\chi_p(1)$$
$$= \langle m|h|p\rangle \qquad \text{Case 2} \qquad (2.131)$$

Case 3 has the two determinants differing by two spin orbitals, χ_p and χ_q appearing in $|L\rangle$, where χ_m and χ_n appear in $|K\rangle$

$$|K\rangle = |\chi_m(1)\chi_n(2)\cdots\rangle \qquad (2.132)$$
$$|L\rangle = |\chi_p(1)\chi_q(2)\cdots\rangle \qquad (2.133)$$

Analogous to (2.125) we write

$$\langle K|\mathcal{O}_1|L\rangle = N(N!)^{-1}\sum_i^{N!}\sum_j^{N!}(-1)^{p_i}(-1)^{p_j}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N$$
$$\times\, \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}h(1)\mathscr{P}_j\{\chi_p(1)\chi_q(2)\cdots\} \qquad (2.134)$$

Because χ_m and χ_n are orthogonal to any spin orbital in the second permutation, and because they both cannot be occupied by electron 1 to "associate" with $h(1)$, no combination of permutations is possible that does not result in zero by spin orbital orthogonality. Hence,

$$\langle K|\mathcal{O}_1|L\rangle = 0 \qquad \text{Case 3} \qquad (2.135)$$

We now turn to two-electron operators. The general matrix element is

$$\langle K|\mathcal{O}_2|L\rangle = \langle K|r_{12}^{-1} + r_{13}^{-1} + r_{14}^{-1} + \cdots + r_{23}^{-1} + r_{24}^{-1} + \cdots + r_{N-1,N}^{-1}|L\rangle \qquad (2.136)$$

where the sum is over all pairs of electrons. Because determinants do not distinguish between identical electrons, each of the terms in this equation will give the same result, and we may replace $\mathcal{O}_2$ by a single operator r_{12}^{-1}, provided we multiply by the number of pairs of electrons,

$$\langle K|\mathcal{O}_2|L\rangle = \frac{N(N-1)}{2}\langle K|r_{12}^{-1}|L\rangle \qquad (2.137)$$

We begin again with Case 1,

$$\langle K|\mathcal{O}_2|K\rangle = \frac{N(N-1)}{2}(N!)^{-1}\sum_i^{N!}\sum_j^{N!}(-1)^{p_i}(-1)^{p_j}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N$$
$$\times \mathcal{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}r_{12}^{-1}\mathcal{P}_j\{\chi_m(1)\chi_n(2)\cdots\} \tag{2.138}$$

Because the operator in (2.138) involves only electrons 1 and 2, it must be that electrons $3, 4, \ldots, N$ occupy the same spin orbitals in both the ith permutation and the jth permutation or we would obtain zero by orthogonality on integrating over the coordinates of these electrons. If electrons $3, 4, \ldots, N$ occupy the same spin orbitals in the two permutations and electrons 1 and 2 occupy two spin orbitals, say χ_k and χ_l in the permutation $\mathcal{P}_i$, then there are two possibilities for electrons 1 and 2 in the permutation $\mathcal{P}_j$: they could occupy the same spin orbitals as in the permutation $\mathcal{P}_i$ (i.e., $\mathcal{P}_j = \mathcal{P}_i$) or they could occupy the spin orbitals χ_l and χ_k (i.e., $\mathcal{P}_j$ differs from $\mathcal{P}_i$ by an interchange of the coordinates of electrons 1 and 2). Thus if

$$\mathcal{P}_i\{\chi_m(1)\chi_n(2)\cdots\} = [\chi_k(1)\chi_l(2)\cdots] \tag{2.139}$$

then

$$\mathcal{P}_j\{\chi_m(1)\chi_n(2)\cdots\} = [\chi_k(1)\chi_l(2)\cdots] \quad \text{or} \quad [\chi_k(2)\chi_l(1)\cdots] \tag{2.140}$$

If $\mathcal{P}_{12}$ is an operator that interchanges the coordinates of electrons 1 and 2, we can thus write our matrix element as

$$\langle K|\mathcal{O}_2|K\rangle = [2(N-2)!]^{-1}\sum_i^{N!}\int d\mathbf{x}_1\, d\mathbf{x}_2\cdots d\mathbf{x}_N\, \mathcal{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\}$$
$$\times r_{12}^{-1}[\mathcal{P}_i\{\chi_m(1)\chi_n(2)\cdots\} - \mathcal{P}_{12}\mathcal{P}_i\{\chi_m(1)\chi_n(2)\cdots\}] \tag{2.141}$$

where there is a minus sign in front of $\mathcal{P}_{12}$ because the permutation $\mathcal{P}_{12}\mathcal{P}_i$ differs from the permutation $\mathcal{P}_i$ by the interchange of the coordinates of electrons 1 and 2, and hence will be an odd permutation if $\mathcal{P}_i$ is an even permutation, and vice versa. In the sum of $N!$ permutations $\mathcal{P}_i$, electrons 1 and 2 of (2.141) will occupy any two different spin orbitals χ_m and χ_n of the set of N spin orbitals contained in $|K\rangle$. For each choice of these two spin orbitals there are $(N-2)!$ ways of permuting the other $N-2$ electrons amongst the $N-2$ remaining spin orbitals, and hence

$$\langle K|\mathcal{O}_2|K\rangle = \frac{(N-2)!}{2(N-2)!}\sum_m^N\sum_{n\neq m}^N\int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2)r_{12}^{-1}(1-\mathcal{P}_{12})\{\chi_m(1)\chi_n(2)\}$$
$$= \frac{1}{2}\sum_m^N\sum_{n\neq m}^N\int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2)r_{12}^{-1}[\chi_m(1)\chi_n(2)-\chi_m(2)\chi_n(1)]$$
$$= \frac{1}{2}\sum_m^N\sum_{n\neq m}^N \langle mn|mn\rangle - \langle mn|nm\rangle \tag{2.142}$$

Since $\langle mn||mn\rangle = \langle mn|mn\rangle - \langle mn|nm\rangle$ vanishes when $m = n$, we can eliminate the restriction on the summation above and write

$$\langle K|\mathcal{O}_2|K\rangle = \frac{1}{2}\sum_m^N \sum_n^N \langle mn||mn\rangle \qquad \text{Case 1} \tag{2.143}$$

For Case 2 we replace χ_m in $|K\rangle$ by χ_p in $|L\rangle$ and obtain

$$\langle K|\mathcal{O}_2|L\rangle = \frac{N(N-1)}{2}(N!)^{-1}\sum_i^{N!}\sum_j^{N!}(-1)^{p_i}(-1)^{p_j}\int d\mathbf{x}_1\, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$
$$\times \mathcal{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\} r_{12}^{-1} \mathcal{P}_j\{\chi_p(1)\chi_n(2)\cdots\} \tag{2.144}$$

By the same argument that leads to Eq. (2.141) for Case 1, we can write for Case 2,

$$\langle K|\mathcal{O}_2|L\rangle = [2(N-2)!]^{-1}\sum_i^{N!}\int d\mathbf{x}_1\, d\mathbf{x}_2 \cdots d\mathbf{x}_N$$
$$\times \mathcal{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\} r_{12}^{-1}(1-\mathcal{P}_{12})\mathcal{P}_i\{\chi_p(1)\chi_n(2)\cdots\} \tag{2.145}$$

Now, since the spin orbital χ_m in the first permutation is orthogonal to any spin orbital in the second permutation, it must be occupied by either electron 1 or electron 2, to associate it with r_{12}^{-1}, and yield a nonzero result. If χ_m is occupied by electron 1, electron 2 can be in any of the remaining $N-1$ spin orbitals common to both $|K\rangle$ and $|L\rangle$. If χ_m is occupied by electron 2, then electron 1 can be in any of the remaining $N-1$ spin orbitals common to both $|K\rangle$ and $|L\rangle$. There are $(N-2)!$ ways of permuting electrons $3, 4, \ldots, N$ and integrating over these electrons gives

$$\langle K|\mathcal{O}_2|L\rangle = \frac{(N-2)!}{2(N-2)!}\sum_{n\neq m}^{N}\int d\mathbf{x}_1\, d\mathbf{x}_2\,[\chi_m^*(1)\chi_n^*(2)r_{12}^{-1}(1-\mathcal{P}_{12})\{\chi_p(1)\chi_n(2)\}$$
$$+ \chi_n^*(1)\chi_m^*(2)r_{12}^{-1}(1-\mathcal{P}_{12})\{\chi_n(1)\chi_p(2)\}] \tag{2.146}$$

where the two terms arise from placing electron 1 in χ_m or electron 2 in χ_m. Since $r_{12}^{-1} = r_{21}^{-1}$ and $\mathcal{P}_{12} = \mathcal{P}_{21}$, we can interchange the definition of the two dummy variables of integration in the second term and show that it is equal to the first,

$$\int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_n^*(1)\chi_m^*(2)r_{12}^{-1}(1-\mathcal{P}_{12})\{\chi_n(1)\chi_p(2)\}$$
$$= \int d\mathbf{x}_2\, d\mathbf{x}_1\, \chi_n^*(2)\chi_m^*(1)r_{21}^{-1}(1-\mathcal{P}_{21})\{\chi_n(2)\chi_p(1)\}$$
$$= \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2)r_{12}^{-1}(1-\mathcal{P}_{12})\{\chi_p(1)\chi_n(2)\} \tag{2.147}$$

We thus obtain

$$\begin{aligned}\langle K|\mathcal{O}_2|L\rangle &= \sum_{n\neq m}^{N} \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2) r_{12}^{-1}(1-\mathscr{P}_{12})\{\chi_p(1)\chi_n(2)\} \\ &= \sum_{n\neq m}^{N} \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2) r_{12}^{-1}[\chi_p(1)\chi_n(2) - \chi_n(1)\chi_p(2)] \\ &= \sum_{n\neq m}^{N} \langle mn|pn\rangle - \langle mn|np\rangle = \sum_{n}^{N} \langle mn||pn\rangle \qquad \text{Case 2}\end{aligned} \tag{2.148}$$

where we have removed the restriction on the summation since $\langle mm||pm\rangle = 0$.

For Case 3, we replace χ_m and χ_n in $|K\rangle$ by χ_p and χ_q in $|L\rangle$ and use the same argument as in the previous two cases to begin with

$$\begin{aligned}\langle K|\mathcal{O}_2|L\rangle = [2(N-2)!]^{-1} \sum_{i}^{N!} \int d\mathbf{x}_1\, d\mathbf{x}_2 \cdots d\mathbf{x}_N \\ \times \mathscr{P}_i\{\chi_m^*(1)\chi_n^*(2)\cdots\} r_{12}^{-1}(1-\mathscr{P}_{12})\mathscr{P}_i\{\chi_p(1)\chi_q(2)\cdots\}\end{aligned} \tag{2.149}$$

Because χ_m and χ_n are orthogonal to any spin orbitals in the second permutation, they must be occupied by electrons 1 and 2 (or 2 and 1). There are $(N-2)!$ permutations of the remaining electrons $3, 4, \ldots, N$, and integrating over these electrons gives

$$\begin{aligned}\langle K|\mathcal{O}_2|L\rangle = \frac{1}{2}\int d\mathbf{x}_1\, d\mathbf{x}_2\, [\chi_m^*(1)\chi_n^*(2) r_{12}^{-1}(1-\mathscr{P}_{12})\{\chi_p(1)\chi_q(2)\} \\ + \chi_n^*(1)\chi_m^*(2) r_{12}^{-1}(1-\mathscr{P}_{12})\{\chi_q(1)\chi_p(2)\}]\end{aligned} \tag{2.150}$$

As in the last case, we can show that the two terms are identical by interchanging the dummy variables of integration, so that

$$\begin{aligned}\langle K|\mathcal{O}_2|L\rangle &= \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2) r_{12}^{-1}(1-\mathscr{P}_{12})\{\chi_p(1)\chi_q(2)\} \\ &= \int d\mathbf{x}_1\, d\mathbf{x}_2\, \chi_m^*(1)\chi_n^*(2) r_{12}^{-1}[\chi_p(1)\chi_q(2) - \chi_q(1)\chi_p(2)] \\ &= \langle mn|pq\rangle - \langle mn|qp\rangle = \langle mn||pq\rangle \qquad \text{Case 3}\end{aligned} \tag{2.151}$$

In the same way that matrix elements of a sum of one-electron operators are zero if the determinants differ by two or more spin orbitals, matrix elements of a sum of two-electron operators are zero if the determinants differ by three or more spin orbitals,

$$\langle K|\mathcal{O}_2|L\rangle = 0 \tag{2.152}$$

This completes the derivation of the rules for matrix elements between Slater determinants.

Exercise 2.16 A different procedure for deriving the above matrix elements uses the theorem that $\langle K|\mathscr{H}|L\rangle = (N!)^{1/2}\langle K^{HP}|\mathscr{H}|L\rangle$ where $|K^{HP}\rangle$ is the Hartree product corresponding to the determinant $|K\rangle$, i.e.,

$$|K\rangle = |\chi_m(\mathbf{x}_1)\chi_n(\mathbf{x}_2)\cdots\rangle$$

and

$$|K^{HP}\rangle = \chi_m(\mathbf{x}_1)\chi_n(\mathbf{x}_2)\cdots$$

Prove this theorem. Use it to derive the matrix elements of a sum of one-electron operators.

2.3.5 Transition from Spin Orbitals to Spatial Orbitals

All of our development so far has involved spin orbitals χ_i rather than spatial orbitals ψ_i. The use of spin orbitals simplifies the algebraic manipulations and notation associated with the general formulation of various theories encountered in quantum chemistry. For most computational purposes, however, the spin functions α and β must be integrated out, to reduce spin orbital formulations to ones which involve only spatial functions and spatial integrals that are amenable to numerical computation. We will show how this is done and introduce a notation for spatial integrals.

To illustrate the procedure in the simplest possible context, consider the Hartree-Fock energy of our minimal basis H_2 model (see Eq. (2.92))

$$E_0 = \langle\chi_1|h|\chi_1\rangle + \langle\chi_2|h|\chi_2\rangle + \langle\chi_1\chi_2|\chi_1\chi_2\rangle - \langle\chi_1\chi_2|\chi_2\chi_1\rangle \quad (2.153)$$

using the physicists' notation, or

$$E_0 = [\chi_1|h|\chi_1] + [\chi_2|h|\chi_2] + [\chi_1\chi_1|\chi_2\chi_2] - [\chi_1\chi_2|\chi_2\chi_1] \quad (2.154)$$

using the chemists' notation. Recall (see Eq. (2.60)) that

$$\chi_1(\mathbf{x}) \equiv \psi_1(\mathbf{x}) = \psi_1(\mathbf{r})\alpha(\omega) \quad (2.155)$$

$$\chi_2(\mathbf{x}) \equiv \bar{\psi}_1(\mathbf{x}) = \psi_1(\mathbf{r})\beta(\omega) \quad (2.156)$$

Substituting these expressions for the spin orbitals in Eq. (2.154), we have

$$E_0 = [\psi_1|h|\psi_1] + [\bar{\psi}_1|h|\bar{\psi}_1] + [\psi_1\psi_1|\bar{\psi}_1\bar{\psi}_1] - [\psi_1\bar{\psi}_1|\bar{\psi}_1\psi_1] \quad (2.157)$$

Consider the one-electron integral

$$[\bar{\psi}_1|h|\bar{\psi}_1] = \int d\mathbf{r}_1\, d\omega_1\, \psi_1^*(\mathbf{r}_1)\beta^*(\omega_1)h(\mathbf{r}_1)\psi_1(\mathbf{r}_1)\beta(\omega_1) \quad (2.158)$$

where we have assumed (as is the case for nonrelativistic Hamiltonians) that the one-electron operator does not depend on spin. Integrating over the

spin variable ω_1 and using $\langle\beta|\beta\rangle = 1$, we have

$$[\bar{\psi}_1|h|\bar{\psi}_1] = \int d\mathbf{r}_1\, \psi_1^*(\mathbf{r}_1)h(\mathbf{r}_1)\psi_1(\mathbf{r}_1) \equiv (\psi_1|h|\psi_1) \tag{2.159}$$

where we have introduced a new notation for a one-electron spatial integral (see Table 2.2). Since $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$ and $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$, the general reduction is

$$[\psi_i|h|\psi_j] = [\bar{\psi}_i|h|\bar{\psi}_j] = (\psi_i|h|\psi_j) \tag{2.160}$$

$$[\psi_i|h|\bar{\psi}_j] = [\bar{\psi}_i|h|\psi_j] = 0 \tag{2.161}$$

so that the one-electron contribution to E_0 is $2(\psi_1|h|\psi_1)$.

Consider, next, the first of the two-electron integrals in expression (2.157) for the ground state energy,

$$[\psi_1\psi_1|\bar{\psi}_1\bar{\psi}_1] = \int d\mathbf{r}_1\, d\omega_1\, d\mathbf{r}_2\, d\omega_2\, \psi_1^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_1(\mathbf{r}_1)\alpha(\omega_1)r_{12}^{-1}$$
$$\times\, \psi_1^*(\mathbf{r}_2)\beta^*(\omega_2)\psi_1(\mathbf{r}_2)\beta(\omega_2) \tag{2.162}$$

Integrating over the spin variables ω_1 and ω_2 and using $\langle\alpha|\alpha\rangle = \langle\beta|\beta\rangle = 1$, we have

$$[\psi_1\psi_1|\bar{\psi}_1\bar{\psi}_1] = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi_1^*(\mathbf{r}_1)\psi_1(\mathbf{r}_1)r_{12}^{-1}\psi_1^*(\mathbf{r}_2)\psi_1(\mathbf{r}_2)$$
$$\equiv (\psi_1\psi_1|\psi_1\psi_1) \tag{2.163}$$

where we have introduced a new notation for spatial two-electron integrals (see Table 2.2). This notation for spatial integrals is just the chemists' notation with *round*, instead of square, brackets. We shall not introduce a comparable notation for spatial integrals written using the physicists' notation. Thus whether $\langle ij|kl\rangle$ refers to an integral over spin or over spatial orbitals can be determined only from the context. The last integral in (2.157),

$$[\psi_1\bar{\psi}_1|\bar{\psi}_1\psi_1] = \int d\mathbf{r}_1\, d\omega_1\, d\mathbf{r}_2\, d\omega_2\, \psi_1^*(\mathbf{r}_1)\alpha^*(\omega_1)\psi_1(\mathbf{r}_1)\beta(\omega_1)r_{12}^{-1}$$
$$\times\, \psi_1^*(\mathbf{r}_2)\beta(\omega_2)\psi_1(\mathbf{r}_2)\alpha(\omega_2) = 0 \tag{2.164}$$

since $\langle\alpha|\beta\rangle = \langle\beta|\alpha\rangle = 0$. In general, when only a single bar appears on either side of the two electron integral (e.g., $[\psi_i\bar{\psi}_j|\psi_k\psi_l]$), the integral vanishes by spin orthogonality. The general reduction is

$$[\psi_i\psi_j|\psi_k\psi_l] = [\psi_i\psi_j|\bar{\psi}_k\bar{\psi}_l] = [\bar{\psi}_i\bar{\psi}_j|\psi_k\psi_l] = [\bar{\psi}_i\bar{\psi}_j|\bar{\psi}_k\bar{\psi}_l] = (\psi_i\psi_j|\psi_k\psi_l) \tag{2.165}$$

with all other combinations of bars giving zero. Therefore, the Hartree-Fock energy of minimal basis H_2 is

$$E_0 = 2(\psi_1|h|\psi_1) + (\psi_1\psi_1|\psi_1\psi_1)$$
$$= 2(1|h|1) + (11|11) \tag{2.166}$$

Exercise 2.17 By integrating out spin, show that the full CI matrix for minimal basis H_2 (see Exercise 2.9) is

$$\mathbf{H} = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix}$$

Let us generalize the above results to obtain an expression involving spatial integrals for the Hartree-Fock energy of an N-electron system containing an *even* number of electrons. The analogue of the minimal basis H_2 Hartree-Fock wave function,

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle \tag{2.167}$$

in an N-electron system is the *closed-shell restricted* Hartree-Fock wave function

$$\begin{aligned} |\Psi_0\rangle &= |\chi_1\chi_2\chi_3\chi_4\cdots\chi_{N-1}\chi_N\rangle \\ &= |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\cdots\psi_{N/2}\bar{\psi}_{N/2}\rangle \end{aligned} \tag{2.168}$$

This wave function is represented in Fig. 2.10. Note that the spatial orbitals are restricted to be the same for α and β spins, and each spatial orbital is occupied by two electrons with different spin. The energy of this wave function, expressed in terms of the set of spin orbitals $\{\chi_a | a = 1, 2, \ldots, N\}$, is given by Eq. (2.111),

$$E_0 = \sum_a^N [a|h|a] + \frac{1}{2}\sum_a^N \sum_b^N [aa|bb] - [ab|ba] \tag{2.169}$$

Since the wave function (2.168) contains $N/2$ spin orbitals with α spin function and $N/2$ spin orbitals with β spin function, we can write a sum over all N spin oribtals χ_a as

$$\sum_a^N \chi_a = \sum_a^{N/2} \psi_a + \sum_a^{N/2} \bar{\psi}_a \tag{2.170}$$

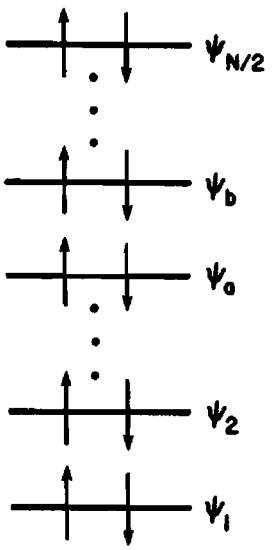


Figure 2.10 A closed-shell restricted Hartree-Fock ground state determinant, $|\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\cdots\psi_a\bar{\psi}_a\psi_b\bar{\psi}_b\cdots\psi_{N/2}\bar{\psi}_{N/2}\rangle$.

where we have used the bar notation. Symbolically this becomes

$$\sum_{a}^{N} = \sum_{a}^{N/2} + \sum_{\bar{a}}^{N/2} \tag{2.171}$$

which means that the sum over all spin orbitals is equal to the sum of those with spin up and those with spin down. For double sums, we have

$$\begin{aligned}\sum_{a}^{N}\sum_{b}^{N} \chi_a\chi_b &= \sum_{a}^{N}\chi_a \sum_{b}^{N}\chi_b \\ &= \sum_{a}^{N/2}(\psi_a + \bar{\psi}_a)\sum_{b}^{N/2}(\psi_b + \bar{\psi}_b) \\ &= \sum_{a}^{N/2}\sum_{b}^{N/2}\psi_a\psi_b + \psi_a\bar{\psi}_b + \bar{\psi}_a\psi_b + \bar{\psi}_a\bar{\psi}_b\end{aligned} \tag{2.172}$$

or symbolically,

$$\sum_{a}^{N}\sum_{b}^{N} = \sum_{a}^{N/2}\sum_{b}^{N/2} + \sum_{a}^{N/2}\sum_{\bar{b}}^{N/2} + \sum_{\bar{a}}^{N/2}\sum_{b}^{N/2} + \sum_{\bar{a}}^{N/2}\sum_{\bar{b}}^{N/2} \tag{2.173}$$

Let us use these to reduce (2.169) to an equation involving spatial orbitals. We treat the one-electron integrals first,

$$\sum_{a}^{N}[a|h|a] = \sum_{a}^{N/2}[a|h|a] + \sum_{a}^{N/2}[\bar{a}|h|\bar{a}] = 2\sum_{a}^{N/2}(\psi_a|h|\psi_a) \tag{2.174}$$

The two-electron integral term is

$$\begin{aligned}&\frac{1}{2}\sum_{a}^{N}\sum_{b}^{N}[aa|bb] - [ab|ba] \\ &\quad= \frac{1}{2}\left\{\sum_{a}^{N/2}\sum_{b}^{N/2}[aa|bb] - [ab|ba] + \sum_{a}^{N/2}\sum_{b}^{N/2}[aa|\bar{b}\bar{b}] - [a\bar{b}|\bar{b}a]\right. \\ &\qquad\left. + \sum_{a}^{N/2}\sum_{b}^{N/2}[\bar{a}a|bb] - [\bar{a}b|b\bar{a}] + \sum_{a}^{N/2}\sum_{b}^{N/2}[\bar{a}a|\bar{b}\bar{b}] - [\bar{a}\bar{b}|\bar{b}\bar{a}]\right\} \\ &\quad= \sum_{a}^{N/2}\sum_{b}^{N/2} 2(\psi_a\psi_a|\psi_b\psi_b) - (\psi_a\psi_b|\psi_b\psi_a)\end{aligned} \tag{2.175}$$

Thus the Hartree-Fock energy of a closed-shell ground state is

$$E_0 = 2\sum_{a}^{N/2}(\psi_a|h|\psi_a) + \sum_{a}^{N/2}\sum_{b}^{N/2} 2(\psi_a\psi_a|\psi_b\psi_b) - (\psi_a\psi_b|\psi_b\psi_a) \tag{2.176}$$

The upper limits of summation, which indicate that we are summing over spatial orbitals, are redundant since we are using the round brackets. Thus

Eq. (2.176) can be rewritten as

$$E_0 = 2\sum_a (a|h|a) + \sum_{ab} 2(aa|bb) - (ab|ba) \tag{2.177}$$

When using the physicists' notation, it is necessary to show the upper limits of summation, since we have not introduced a notation analogous to round brackets. The convention we use is as follows. If no upper limit appears, the sum is over spin orbitals. If the upper limit is $N/2$, the sum is over spatial orbitals. Thus using the physicists' notation Eq. (2.177) is

$$E_0 = 2\sum_a^{N/2} \langle a|h|a\rangle + \sum_{ab}^{N/2} 2\langle ab|ab\rangle - \langle ab|ba\rangle \tag{2.178}$$

Exercise 2.18 In Chapter 6, where we consider perturbation theory, we show that the leading correction to the Hartree-Fock ground state energy is

$$E_0^{(2)} = \frac{1}{4}\sum_{abrs} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}$$

Show that for a closed-shell system (where $\varepsilon_i = \varepsilon_{\bar{i}}$) this becomes

$$E_0^{(2)} = \sum_{a,b=1}^{N/2} \sum_{r,s=(N/2+1)}^{K} \frac{\langle ab|rs\rangle(2\langle rs|ab\rangle - \langle rs|ba\rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s},$$

2.3.6 Coulomb and Exchange Integrals

Let us consider the physical interpretation of the result given in Eq. (2.177) for the Hartree-Fock energy of a closed-shell ground state, i.e.,

$$E_0 = 2\sum_a (a|h|a) + \sum_{ab} 2(aa|bb) - (ab|ba) \tag{2.179}$$

Consider the one-electron terms first,

$$(a|h|a) \equiv h_{aa} = \int d\mathbf{r}_1\, \psi_a^*(\mathbf{r}_1)\left(-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}}\right)\psi_a(\mathbf{r}_1) \tag{2.180}$$

Thus h_{aa} is the average kinetic and nuclear attraction energy of an electron described by the wave function $\psi_a(\mathbf{r}_1)$. Next consider the two-electron integral

$$(aa|bb) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, |\psi_a(\mathbf{r}_1)|^2 r_{12}^{-1} |\psi_b(\mathbf{r}_2)|^2 \tag{2.181}$$

which is the classical coulomb repulsion between the charge clouds $|\psi_a(\mathbf{r}_1)|^2$ and $|\psi_b(\mathbf{r}_2)|^2$. This integral is called a *coulomb* integral and is denoted by J_{ab}. In general,

$$J_{ij} = (ii|jj) = \langle ij|ij\rangle \tag{2.182}$$

Finally, consider the two-electron integral

$$(ab|ba) = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \psi_a^*(\mathbf{r}_1)\psi_b(\mathbf{r}_1)r_{12}^{-1}\psi_b^*(\mathbf{r}_2)\psi_a(\mathbf{r}_2) \tag{2.183}$$

This integral does not have a simple classical interpretation. It is called an *exchange* integral and is denoted by K_{ab}. In general,

$$K_{ij} = (ij|ji) = \langle ij|ji\rangle \tag{2.184}$$

Both exchange and coulomb integrals have positive values. We will now show that the appearance of exchange integrals in the expression for the energy of a determinant is the result of *exchange correlation* (i.e., the motion of electrons with parallel spins is correlated within the single determinantal approximation to the wave function). We have seen in Subsection 2.2.3 that antisymmetrizing a Hartree product to yield a Slater determinant introduces correlation. Before proceeding, let us rewrite the Hartree-Fock energy of a closed-shell system given in (2.179) in terms of coulomb and exchange integrals

$$E_0 = 2\sum_a h_{aa} + \sum_{ab} 2J_{ab} - K_{ab} \tag{2.185}$$

Exercise 2.19 Prove the following properties of coulomb and exchange integrals

$$J_{ii} = K_{ii}$$

$$J_{ij}^* = J_{ij} \qquad K_{ij}^* = K_{ij}$$

$$J_{ij} = J_{ji} \qquad K_{ij} = K_{ji}$$

Exercise 2.20 Show that for *real* spatial orbitals

$$K_{ij} = (ij|ij) = (ji|ji)$$
$$= \langle ii|jj\rangle = \langle jj|ii\rangle$$

Exercise 2.21 Show that the full CI matrix for minimal basis H_2 (see Exercise 2.17) is

$$\mathbf{H} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix}$$

The spatial molecular orbitals of this model are real because they were constructed as linear combinations of real atomic orbitals (see Eqs. (2.54), (2.55), (2.57), and (2.58)).

A feeling for the occurance of exchange integrals can be gained by reconsidering the example discussed at the end of Subsection 2.2.3 from the energetic point of view. We have seen that in a system containing two elec-

trons with parallel spin, described by the wave function $|\bar{\psi}_1\bar{\psi}_2\rangle$, the probability of finding two electrons at the same point in space is zero, whereas in a system containing two electrons with opposite spin, described by the wave function $|\psi_1\bar{\psi}_2\rangle$, it is not. Therefore, it is reasonable to expect that the energy of $|\bar{\psi}_1\bar{\psi}_2\rangle$ is lower than the energy of $|\psi_1\bar{\psi}_2\rangle$ when the coulomb repulsion between electrons is taken into account. Using Eq. (2.110), the energy of $|\psi_1\bar{\psi}_2\rangle$, denoted by $E(\uparrow\downarrow)$, is

$$\begin{aligned} E(\uparrow\downarrow) &= [\psi_1|h|\psi_1] + [\bar{\psi}_2|h|\bar{\psi}_2] + [\psi_1\psi_1|\bar{\psi}_2\bar{\psi}_2] - [\psi_1\bar{\psi}_2|\bar{\psi}_2\psi_1] \\ &= (1|h|1) + (2|h|2) + (11|22) \\ &= h_{11} + h_{22} + J_{12} \end{aligned} \tag{2.186}$$

and the energy of $|\bar{\psi}_1\bar{\psi}_2\rangle$, denoted by $E(\downarrow\downarrow)$, is

$$\begin{aligned} E(\downarrow\downarrow) &= [\bar{\psi}_1|h|\bar{\psi}_1] + [\bar{\psi}_2|h|\bar{\psi}_2] + [\bar{\psi}_1\bar{\psi}_1|\bar{\psi}_2\bar{\psi}_2] - [\bar{\psi}_1\bar{\psi}_2|\bar{\psi}_2\bar{\psi}_1] \\ &= (1|h|1) + (2|h|2) + (11|22) - (12|21) \\ &= h_{11} + h_{22} + J_{12} - K_{12} \end{aligned} \tag{2.187}$$

where we have used Eqs. (2.160), (2.161), and (2.165) to integrate out the spin. Because K_{12} is positive, $E(\downarrow\downarrow)$ is indeed lower than $E(\uparrow\downarrow)$. Thus the appearance of exchange integrals in the energy of a Slater determinant is a manifestation of the fact that, even within the single determinantal approximation to the wave function, the motion of electrons with parallel spins is correlated.

Exercise 2.22 Show that the energies of the Hartree products

$$\Psi^{HP}_{\uparrow\downarrow} = \psi_1(\mathbf{r}_1)\alpha(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2)$$

and

$$\Psi^{HP}_{\downarrow\uparrow} = \psi_1(\mathbf{r}_1)\beta(\omega_1)\psi_2(\mathbf{r}_2)\beta(\omega_2)$$

are the same and equal to $E(\uparrow\downarrow)$ as to be expected since the motion of electrons with parallel spin is not correlated within the Hartree product approximation to the wave function.

2.3.7 Pseudo-Classical Interpretation of Determinantal Energies

In Subsection 2.3.3, we introduced a simple mnemonic device for writing down the energy of a single determinant, constructed from a set of spin orbitals $\{\chi_i\}$, in terms of one-electron integrals over spin orbitals ($\langle i|h|i\rangle$) and antisymmetrized two-electron integrals over spin orbitals ($\langle ij||ij\rangle$). Here we will show how one can express, with equal ease, the energy of any restricted determinant, constructed from spin orbitals $\{\psi_i\alpha\}$ and $\{\psi_i\beta\}$, in terms of h_{ii}, coulomb (J_{ij}), and exchange (K_{ij}) integrals.

We begin with the one-electron contributions to the energy. Recall that an electron in spin orbital χ_i contributed the term $\langle i|h|i\rangle$ to the energy. If $\chi_i = \psi_i\alpha$, then $\langle i|h|i\rangle = \langle\psi_i\alpha|h|\psi_i\alpha\rangle = (\psi_i|h|\psi_i) = h_{ii}$. Similarly, if $\chi_i = \psi_i\beta$, then $\langle i|h|i\rangle = h_{ii}$, *Therefore, an electron (irrespective of its spin) in spatial orbital ψ_i contributes the term h_{ii} to the energy.*

Next we consider the two-electron contributions to the energy. Recall that each unique pair of electrons in spin orbitals χ_i and χ_j contributes the term $\langle ij||ij\rangle$ to the energy. A pair of electrons can have either parallel or opposite spins. If they have opposite spins, say $\chi_i = \psi_i\alpha$ and $\chi_j = \psi_j\beta$, then

$$\langle ij||ij\rangle = [\psi_i\psi_i|\bar{\psi}_j\bar{\psi}_j] - [\psi_i\bar{\psi}_j|\bar{\psi}_j\psi_i] = J_{ij} \tag{2.188}$$

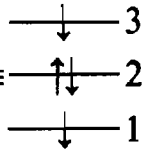
On the other hand, if they have parallel spins, say $\chi_i = \psi_i\beta$ and $\chi_j = \psi_j\beta$, then

$$\langle ij||ij\rangle = [\bar{\psi}_i\bar{\psi}_i|\bar{\psi}_j\bar{\psi}_j] - [\bar{\psi}_i\bar{\psi}_j|\bar{\psi}_j\bar{\psi}_i] = J_{ij} - K_{ij} \tag{2.189}$$

Therefore, each unique pair of electrons (irrespective of their spin) in spatial orbitals ψ_i and ψ_j contributes the term J_{ij} to the energy, and each unique pair of electrons with parallel spins in spatial orbitals ψ_i and ψ_j contributes the term $-K_{ij}$ to the energy. The total energy of the determinant is the sum of all these contributions.

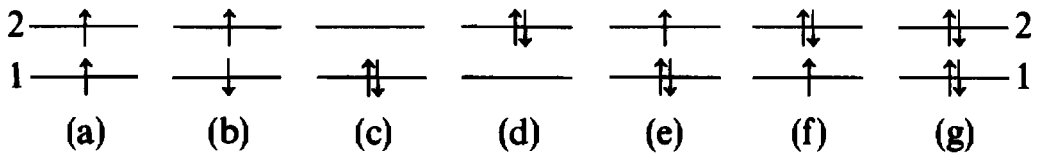
Thus we can think of the total energy of an N-electron system, which is described by a restricted determinant, as a sum of "one-electron-energies" (h_{ii} for an electron in spatial orbital ψ_i) plus all unique coulomb interaction energies (J_{ij} for a pair of electrons in spatial orbitals ψ_i and ψ_j) plus all unique exchange interaction energies between electrons with parallel spins ($-K_{ij}$ for a pair of electrons with parallel spin in spatial orbitals ψ_i and ψ_j). In using this language, it must be remembered that exchange interactions between electrons with parallel spin are not real physical interactions but a convenient way of representing the energy of a system described by a single determinant. The physical interaction between two electrons, as described by the coulomb repulsion term (r_{ij}^{-1}) in the Hamiltonian, does not depend on the spin of the electrons.

As an illustration of the above approach, consider the energy of the determinant

$|\bar{\psi}_1\psi_2\bar{\psi}_2\bar{\psi}_3\rangle \equiv$ 

The one-electron contributions to the energy are h_{11}, $2h_{22}$, and h_{33}. The coulomb contributions are J_{22}, J_{13}, $2J_{12}$, and $2J_{23}$. The exchange contributions are $-K_{23}$, $-K_{12}$, and $-K_{13}$. Thus the total energy is $h_{11} + 2h_{22} + h_{33} + J_{22} + J_{13} + 2J_{12} + 2J_{23} - K_{23} - K_{12} - K_{13}$.

Exercise 2.23 Verify the energies of the following determinants by inspection.



a. $h_{11} + h_{22} + J_{12} - K_{12}$.
b. $h_{11} + h_{22} + J_{12}$.
c. $2h_{11} + J_{11}$.
d. $2h_{22} + J_{22}$.
e. $2h_{11} + h_{22} + J_{11} + 2J_{12} - K_{12}$.
f. $2h_{22} + h_{11} + J_{22} + 2J_{12} - K_{12}$.
g. $2h_{11} + 2h_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$.

2.4 SECOND QUANTIZATION

The antisymmetry principle is an axiom of quantum mechanics quite apart from the Schrödinger equation. We have insured that this principle is satisfied by using Slater determinants and linear combinations of such determinants for wave functions. Can we satisfy the antisymmetry principle without using Slater determinants? Second quantization is a formalism in which the antisymmetry property of the wave function has been transferred onto the algebraic properties of certain operators. Second quantization introduces no new physics. It is just another, although very elegant, way of treating many-electron systems, which shifts much of the emphasis away from N-electron wave functions to the one- and two-electron integrals $\langle i|h|j\rangle$ and $\langle ij\,|\,kl\rangle$ that were discussed in the preceding section. The formalism of second quantization is widely used in the literature dealing with many-electron problems. We introduce it here not only as an interesting way of rederiving some of our previous results but also as a background for approaching such literature. Since we will not make general use of second quantization in the remaining chapters, this section can be considered optional.

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

We shall gradually construct the formalism of second quantization by showing how the properties of determinants can be transferred onto the algebraic properties of operators. We begin by associating a *creation* operator $a_i^\dagger$ with each spin orbital χ_i. We define $a_i^\dagger$ by its action on an arbitrary Slater

determinant $|\chi_k \cdots \chi_l\rangle$, as

$$a_i^\dagger|\chi_k \cdots \chi_l\rangle = |\chi_i\chi_k \cdots \chi_l\rangle \tag{2.190}$$

Thus $a_i^\dagger$ creates an electron in spin orbital χ_i. The order in which two creation operators are applied to a determinant is crucial. Consider

$$a_i^\dagger a_j^\dagger|\chi_k \cdots \chi_l\rangle = a_i^\dagger|\chi_j\chi_k \cdots \chi_l\rangle = |\chi_i\chi_j\chi_k \cdots \chi_l\rangle \tag{2.191}$$

On the other hand,

$$\begin{aligned} a_j^\dagger a_i^\dagger|\chi_k \cdots \chi_l\rangle = a_j^\dagger|\chi_i\chi_k \cdots \chi_l\rangle &= |\chi_j\chi_i\chi_k \cdots \chi_l\rangle \\ &= -|\chi_i\chi_j\chi_k \cdots \chi_l\rangle \end{aligned} \tag{2.192}$$

where we have used the antisymmetry property of Slater determinants (see Eq. (2.40)). Adding Eqs. (2.191) and (2.192), we have

$$(a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger)|\chi_k \cdots \chi_l\rangle = 0 \tag{2.193}$$

Because $|\chi_k \cdots \chi_l\rangle$ is an arbitrary determinant, we have discovered the operator relation

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0 = \{a_i^\dagger, a_j^\dagger\} \tag{2.194}$$

where we have used the notation for the *anticommutator* of two operators introduced in Eq. (1.19a). Since,

$$a_i^\dagger a_j^\dagger = -a_j^\dagger a_i^\dagger \tag{2.195}$$

we can interchange the order of two creation operators provided we change the sign. If $i = j$, we have

$$a_i^\dagger a_i^\dagger = -a_i^\dagger a_i^\dagger = 0 \tag{2.196}$$

which states that we cannot create two electrons in the same spin orbital χ_i (Pauli exclusion principle). Thus

$$a_1^\dagger a_1^\dagger|\chi_2\chi_3\rangle = a_1^\dagger|\chi_1\chi_2\chi_3\rangle = |\chi_1\chi_1\chi_2\chi_3\rangle = 0 \tag{2.197}$$

In general,

$$a_i^\dagger|\chi_k \cdots \chi_l\rangle = 0 \qquad \text{if } i \in \{k, \ldots, l\} \tag{2.198}$$

which states we cannot create an electron in spin orbital χ_i if there is one already there.

Exercise 2.24 Show, using the properties of determinants, that

$$(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger)|K\rangle = 0$$

for every $|K\rangle$ in the set $\{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$.

We now introduce the *annihilation* operator a_i, which is the adjoint of the creation operator $a_i^\dagger$ (i.e., $(a_i^\dagger)^\dagger = a_i$). In analogy with Eq. (2.190), a_i is

defined by

$$a_i|\chi_i\chi_k\cdots\chi_l\rangle = |\chi_k\cdots\chi_l\rangle \tag{2.199}$$

Thus a_i annihilates or destroys an electron in spin orbital χ_i. Note that the annihilation operator can only act on a determinant if the spin orbital, which will disappear, is immediately to the left. If a spin orbital is not in the proper position, it must be placed there by interchanging the columns of the determinant, e.g.,

$$a_i|\chi_k\chi_l\chi_i\rangle = -a_i|\chi_i\chi_l\chi_k\rangle = -|\chi_l\chi_k\rangle = |\chi_k\chi_l\rangle \tag{2.200}$$

Why is the annihilation operator defined as the adjoint of the creation operator? Consider the determinant

$$|K\rangle = |\chi_i\chi_j\rangle \tag{2.201}$$

Clearly,

$$|K\rangle = a_i^\dagger|\chi_j\rangle \tag{2.202}$$

The adjoint of this equation (see Eqs. (1.52) and (1.57)) is

$$\langle K| = \langle\chi_j|(a_i^\dagger)^\dagger = \langle\chi_j|a_i \tag{2.203}$$

Multiplying (2.203) on the right by $|K\rangle$, we have

$$\langle K|K\rangle = \langle\chi_j|a_i|K\rangle \tag{2.204}$$

Since $\langle K|K\rangle = 1 = \langle\chi_j|\chi_j\rangle$, our formalism is consistent when

$$a_i|K\rangle \equiv a_i|\chi_i\chi_j\rangle = |\chi_j\rangle \tag{2.205}$$

in agreement with the definition of (2.199) of the annihilation operator. From Eq. (2.203) we see that a_i acts like a creation operator if it operates on a determinant to the left. Similarly, $a_i^\dagger$ acts like an annihilation operator if it operates to the left. For example, the adjoint of Eq. (2.205) is

$$\langle K|a_i^\dagger = \langle\chi_j| \tag{2.206}$$

To obtain the anticommutation relation satisfied by annihilation operators we take the adjoint of (2.194). Since (c.f. Exercise 1.3)

$$(\mathscr{A}\mathscr{B})^\dagger = \mathscr{B}^\dagger\mathscr{A}^\dagger \tag{2.207}$$

we have

$$a_ja_i + a_ia_j = 0 = \{a_j, a_i\} \tag{2.208}$$

Since

$$a_ia_j = -a_ja_i \tag{2.209}$$

we can interchange the order of two annihilation operators provided we change the sign. If $i = j$, we have

$$a_ia_i = -a_ia_i = 0 \tag{2.210}$$

which states that we cannot destroy an electron twice. A consequence of this is that we cannot remove an electron from a spin orbital χ_i, if it is not already there,

$$a_i|\chi_k \cdots \chi_l\rangle = 0 \qquad \text{if } i \notin \{k, \ldots, l\} \tag{2.211}$$

It remains for us to discover how we can interchange creation and annihilation operators. Consider the operator $a_i a_i^\dagger + a_i^\dagger a_i$ acting on an arbitrary determinant, $|\chi_k \cdots \chi_l\rangle$. If spin orbital χ_i is *not* occupied in this determinant, we have

$$\begin{aligned}(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_k \cdots \chi_l\rangle &= a_i a_i^\dagger |\chi_k \cdots \chi_l\rangle \\ &= a_i|\chi_i \chi_k \cdots \chi_l\rangle \\ &= |\chi_k \cdots \chi_l\rangle\end{aligned} \tag{2.212}$$

on the other hand, if χ_i is occupied, we have

$$\begin{aligned}(a_i a_i^\dagger + a_i^\dagger a_i)|\chi_k \cdots \chi_i \cdots \chi_l\rangle &= a_i^\dagger a_i|\chi_k \cdots \chi_i \cdots \chi_l\rangle \\ &= -a_i^\dagger a_i|\chi_i \cdots \chi_k \cdots \chi_l\rangle \\ &= -a_i^\dagger|\cdots \chi_k \cdots \chi_l\rangle \\ &= -|\chi_i \cdots \chi_k \cdots \chi_l\rangle \\ &= |\chi_k \cdots \chi_i \cdots \chi_l\rangle\end{aligned} \tag{2.213}$$

Since we recover the same determinant in both cases, we have discovered the operator relation

$$a_i a_i^\dagger + a_i^\dagger a_i = 1 = \{a_i, a_i^\dagger\} \tag{2.214}$$

Finally, consider $(a_j^\dagger a_i + a_i a_j^\dagger)|\chi_k \cdots \chi_l\rangle$ when $i \neq j$. This expression can be nonzero only if the spin orbital χ_i appears and the spin orbital χ_j does not appear in $|\chi_k \cdots \chi_l\rangle$. Otherwise, we obtain zero either because $a_j^\dagger$ tries to create an electron that is already there or a_i tries to destroy one that is not there. However, even when $i \in \{k, \ldots, l\}$ and $j \notin \{k, \ldots, l\}$ we obtain zero as a result of the antisymmetry property of determinants,

$$\begin{aligned}(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_k \cdots \chi_i \cdots \chi_l\rangle &= -(a_i a_j^\dagger + a_j^\dagger a_i)|\chi_i \cdots \chi_k \cdots \chi_l\rangle \\ &= -a_i|\chi_j \chi_i \cdots \chi_k \cdots \chi_l\rangle - a_j^\dagger|\cdots \chi_k \cdots \chi_l\rangle \\ &= a_i|\chi_i \chi_j \cdots \chi_k \cdots \chi_l\rangle - |\chi_j \cdots \chi_k \cdots \chi_l\rangle \\ &= |\chi_j \cdots \chi_k \cdots \chi_l\rangle - |\chi_j \cdots \chi_k \cdots \chi_l\rangle \\ &= 0\end{aligned} \tag{2.215}$$

Thus we have

$$a_i a_j^\dagger + a_j^\dagger a_i = 0 = \{a_i, a_j^\dagger\} \qquad i \neq j \tag{2.216}$$

Combining this with (2.214), the anticommutation relation between a creation and an annihilation operator is

$$a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij} = \{a_i, a_j^\dagger\} \tag{2.217}$$

Thus we can interchange a creation and an annihilation operator, which refer to different spin orbitals, provided we change the sign, i.e.,

$$a_i a_j^\dagger = -a_j^\dagger a_i \qquad i \neq j \tag{2.218a}$$

However, if the operators refer to the same spin orbital, we have

$$a_i a_i^\dagger = 1 - a_i^\dagger a_i \tag{2.218b}$$

Exercise 2.25 Show, using the properties of determinants, that

$$(a_1 a_2^\dagger + a_2^\dagger a_1)|K\rangle = 0$$

$$(a_1 a_1^\dagger + a_1^\dagger a_1)|K\rangle = |K\rangle$$

for every $|K\rangle$ in the set $\{|\chi_1\chi_2\rangle, |\chi_1\chi_3\rangle, |\chi_1\chi_4\rangle, |\chi_2\chi_3\rangle, |\chi_2\chi_4\rangle, |\chi_3\chi_4\rangle\}$.

All the properties of Slater determinants are contained in the anti-commutation relations between two creation operators (Eq. (2.194)), between two annihilation operators (Eq. (2.208)), and between a creation and an annihilation operator (Eq. (2.217)). In order to define a Slater determinant in the formalism of second quantization, we introduce a vacuum state denoted by $|\ \rangle$. The vacuum state represents a state of the system that contains no electrons. It is normalized,

$$\langle\ |\ \rangle = 1 \tag{2.219}$$

and has the property that

$$a_i|\ \rangle = 0 = \langle\ | a_i^\dagger \tag{2.220}$$

that is, since the vacuum state contains no electrons, we cannot remove an electron from it. We can construct any state of the system by applying a succession of creation operators to the vacuum state. For example,

$$|\chi_i\rangle = a_i^\dagger|\ \rangle \tag{2.221}$$

or, in general,

$$a_i^\dagger a_k^\dagger \cdots a_l^\dagger|\ \rangle = |\chi_i\chi_k \cdots \chi_l\rangle \tag{2.222}$$

This relation is the second-quantized representation of a Slater determinant. Any result that can be obtained using the properties of determinants can also be proved using only the algebraic properties of creation and annihilation operators.

In Exercise 2.5 we evaluated the overlap between the two determinants

$$|K\rangle = |\chi_i\chi_j\rangle = a_i^\dagger a_j^\dagger|\ \rangle \tag{2.223}$$

$$|L\rangle = |\chi_k\chi_l\rangle = a_k^\dagger a_l^\dagger|\ \rangle \tag{2.224}$$

by expanding out the determinants, integrating over the space and spin coordinates of the two electrons, and using the orthonormality relation of

spin orbitals. Here we evaluate the overlap by using the formalism of second quantization. Since the adjoint of Eq. (2.223) is

$$\langle K| = \langle\ |(a_i^\dagger a_j^\dagger)^\dagger = \langle\ |a_j a_i \tag{2.225}$$

we have

$$\langle K|L\rangle = \langle\ |a_j a_i a_k^\dagger a_l^\dagger|\ \rangle \tag{2.226}$$

The general strategy for evaluating such matrix elements is to move, using the anticommutation relations, the annihilation operators to the right until they operate directly on the vacuum state. We begin with a_i. Since

$$a_i a_k^\dagger = \delta_{ik} - a_k^\dagger a_i \tag{2.227}$$

we have

$$\begin{aligned}\langle K|L\rangle &= \langle\ |a_j(\delta_{ik} - a_k^\dagger a_i)a_l^\dagger|\ \rangle \\ &= \delta_{ik}\langle\ |a_j a_l^\dagger|\ \rangle - \langle\ |a_j a_k^\dagger a_i a_l^\dagger|\ \rangle\end{aligned} \tag{2.228}$$

To continue, we move a_j to the right in the first term and keep moving a_i to the right in the second,

$$\langle K|L\rangle = \delta_{ik}\delta_{jl}\langle\ |\ \rangle - \delta_{ik}\langle\ |a_l^\dagger a_j|\ \rangle - \delta_{il}\langle\ |a_j a_k^\dagger|\ \rangle + \langle\ |a_j a_k^\dagger a_l^\dagger a_i|\ \rangle \tag{2.229}$$

The second and last terms now have an annihilation operator acting on the vacuum and hence are zero. Finally, moving a_j to the right in the third term, we have

$$\begin{aligned}\langle K|L\rangle &= \delta_{ik}\delta_{jl}\langle\ |\ \rangle - \delta_{il}\delta_{jk}\langle\ |\ \rangle + \delta_{il}\langle\ |a_k^\dagger a_j|\ \rangle \\ &= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}\end{aligned} \tag{2.230}$$

since the vacuum is normalized. This result is the same as found in Exercise 2.5.

Exercise 2.26 Show using second quantization that $\langle \chi_i|\chi_j\rangle = \delta_{ij}$

Exercise 2.27 Given a state

$$|K\rangle = |\chi_1\chi_2\cdots\chi_N\rangle = a_1^\dagger a_2^\dagger\cdots a_N^\dagger|\ \rangle$$

show that $\langle K|a_i^\dagger a_j|K\rangle = 1$ if $i = j$ and $i \in \{1, 2, \ldots, N\}$, but is zero otherwise.

Exercise 2.28 Let $|\Psi_0\rangle = |\chi_1\cdots\chi_a\chi_b\cdots\chi_N\rangle$ be the Hartree-Fock ground state wave function. Show that

a. $a_r|\Psi_0\rangle = 0 = \langle\Psi_0|a_r^\dagger$.
b. $a_a^\dagger|\Psi_0\rangle = 0 = \langle\Psi_0|a_a$.
c. $|\Psi_a^r\rangle = a_r^\dagger a_a|\Psi_0\rangle$.

d. $\langle \Psi_a^r| = \langle \Psi_0 | a_a^\dagger a_r$.
e. $|\Psi_{ab}^{rs}\rangle = a_s^\dagger a_b a_r^\dagger a_a |\Psi_0\rangle = a_r^\dagger a_s^\dagger a_b a_a |\Psi_0\rangle$.
f. $\langle \Psi_{ab}^{rs}| = \langle \Psi_0 | a_a^\dagger a_r a_b^\dagger a_s = \langle \Psi_0 | a_a^\dagger a_b^\dagger a_s a_r$.

2.4.2 Second-Quantized Operators and Their Matrix Elements

We have seen that we can represent determinants by using creation and annihilation operators, which obey a set of anticommutation relations and a vacuum state. Thus we have found a representation of a many-electron wave function that satisfies the requirement of the antisymmetry principle, but which can be manipulated without any knowledge of the properties of determinants. To be able to develop the entire theory of many-electron systems without using determinants, we must express the many-particle operators, $\mathcal{O}_1$ and $\mathcal{O}_2$, in terms of creation and annihilation operators. We can then evaluate matrix elements of these operators using only the algebraic properties of creation and annihilation operators. Clearly, the expression for an operator $\mathcal{O}$ in second quantization must be such that the value of the matrix element $\langle K|\mathcal{O}|L\rangle$ is the same irrespective of whether we obtained it using the properties of determinants or using the algebra of creation and annihilation operators. The appropriate expressions for $\mathcal{O}_1$ (our sum of one-electron operators) and $\mathcal{O}_2$ (the operator describing the total coulomb repulsion between electrons) in second quantization are

$$\mathcal{O}_1 = \sum_{ij} \langle i|h|j\rangle a_i^\dagger a_j \tag{2.231}$$

$$\mathcal{O}_2 = \frac{1}{2} \sum_{ijkl} \langle ij|kl\rangle a_i^\dagger a_j^\dagger a_l a_k \tag{2.232}$$

where the sums run over the set spin orbitals $\{\chi_i\}$. Note that the one- and two-electron integrals appear explicitly and that the form of these operators is independent of the number of electrons. One of the advantages of second quantization is that it treats systems with different numbers of particles on an equal footing. This is particularly convenient when one is dealing with infinite systems such as solids.

Exercise 2.29 Let $|\Psi_0\rangle = |\chi_1\chi_2\rangle = a_1^\dagger a_2^\dagger|\ \rangle$ be the Hartree-Fock wave function for minimal basis H_2. Show using second quantization that

$$\langle \Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ij} \langle i|h|j\rangle \langle\ |a_2 a_1 a_i^\dagger a_j a_1^\dagger a_2^\dagger|\ \rangle$$
$$= \langle 1|h|1\rangle + \langle 2|h|2\rangle$$

As an illustration of the equivalence of second quantization with our previous development, based on Slater determinants, we calculate the energy of the Hartree-Fock ground state, $|\Psi_0\rangle = |\chi_1 \cdots \chi_a \chi_b \cdots \chi_N\rangle$, using second

quantization. For the sum of one-electron operators, we have

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ij}\langle i|h|j\rangle\langle\Psi_0|a_i^\dagger a_j|\Psi_0\rangle \tag{2.233}$$

Since both a_j and $a_i^\dagger$ are trying to destroy an electron (a_j to the right and $a_i^\dagger$ to the left), the indices i and j must belong to the set $\{a, b, \ldots\}$ and thus

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|h|b\rangle\langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle \tag{2.234}$$

Using

$$a_a^\dagger a_b = \delta_{ab} - a_b a_a^\dagger$$

to move $a_a^\dagger$ to the right, we have

$$\langle\Psi_0|a_a^\dagger a_b|\Psi_0\rangle = \delta_{ab}\langle\Psi_0|\Psi_0\rangle - \langle\Psi_0|a_b a_a^\dagger|\Psi_0\rangle \tag{2.235}$$

The second term on the right is zero since $a_a^\dagger$ is trying to create an electron in χ_a, which is already occupied in $|\Psi_0\rangle$. Since $\langle\Psi_0|\Psi_0\rangle = 1$, we finally have

$$\langle\Psi_0|\mathcal{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|h|b\rangle\delta_{ab} = \sum_a\langle a|h|a\rangle \tag{2.236}$$

in agreement with our previous result in Table 2.5.

For the sum of two-electron operators, we have

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{ijkl}\langle ij|kl\rangle\langle\Psi_0|a_i^\dagger a_j^\dagger a_l a_k|\Psi_0\rangle \tag{2.237}$$

By the same argument we used for one-electron operators, the indices i, j, k, l must belong to the set $\{a, b, \ldots\}$,

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\langle\Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle \tag{2.238}$$

Our strategy, as before, is to move $a_a^\dagger$ and $a_b^\dagger$ to the right until they operate on $|\Psi_0\rangle$,

$$\begin{aligned}\langle\Psi_0|a_a^\dagger a_b^\dagger a_d a_c|\Psi_0\rangle &= \delta_{bd}\langle\Psi_0|a_a^\dagger a_c|\Psi_0\rangle - \langle\Psi_0|a_a^\dagger a_d a_b^\dagger a_c|\Psi_0\rangle \\ &= \delta_{bd}\delta_{ac}\langle\Psi_0|\Psi_0\rangle - \delta_{bd}\langle\Psi_0|a_c a_a^\dagger|\Psi_0\rangle \\ &\quad - \delta_{bc}\langle\Psi_0|a_a^\dagger a_d|\Psi_0\rangle + \langle\Psi_0|a_a^\dagger a_d a_c a_b^\dagger|\Psi_0\rangle \\ &= \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\langle\Psi_0|\Psi_0\rangle + \delta_{bc}\langle\Psi_0|a_d a_a^\dagger|\Psi_0\rangle \\ &= \delta_{bd}\delta_{ac} - \delta_{bc}\delta_{ad}\end{aligned}$$

We thus get two terms; in the first term we set $c = a$ and $d = b$, and in the second term we set $c = b$ and $d = a$,

$$\langle\Psi_0|\mathcal{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{ab}\langle ab|ab\rangle - \langle ab|ba\rangle \tag{2.239}$$

in agreement with our previous result in Table 2.6.

Exercise 2.30 Show that

$$\langle \Psi_a^r | \mathcal{O}_1 | \Psi_0 \rangle = \sum_{ij} \langle i|h|j \rangle \langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j | \Psi_0 \rangle$$
$$= \langle r|h|a \rangle$$

by moving $a_a^\dagger$ and a_r to the right.

Exercise 2.31 Show that

$$\langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle = \sum_b^N \langle rb||ab \rangle$$

Hint: first show that

$$\langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle = \delta_{rj}\delta_{al} \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle - \delta_{rj}\delta_{ak} \langle \Psi_0 | a_i^\dagger a_l | \Psi_0 \rangle$$
$$+ \delta_{ri}\delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle - \delta_{ri}\delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle$$

then refer to Exercise 2.27.

2.5 SPIN-ADAPTED CONFIGURATIONS

We have described the spin of a single electron by the two spin functions $\alpha(\omega) \equiv \alpha$ and $\beta(\omega) \equiv \beta$. In this section we will discuss spin in more detail and consider the spin states of many-electron systems. We will describe *restricted* Slater determinants that are formed from spin orbitals whose spatial parts are restricted to be the same for α and β spins (i.e., $\{\chi_i\} = \{\psi_i\alpha, \psi_i\beta\}$). Restricted determinants, except in special cases, are not eigenfunctions of the total electron spin operator. However, by taking appropriate linear combinations of such determinants we can form *spin-adapted configurations*, which are proper eigenfunctions. Finally, we will describe *unrestricted* determinants, which are formed from spin orbitals that have different spatial parts for different spins (i.e., $\{\chi_i\} = \{\psi_i^\alpha\alpha, \psi_i^\beta\beta\}$).

2.5.1 Spin Operators

The spin angular momentum of a particle is a vector operator $\vec{s}$,

$$\vec{s} = s_x\vec{i} + s_y\vec{j} + s_z\vec{k} \tag{2.240}$$

where $\vec{i}, \vec{j}$, and $\vec{k}$ are unit vectors along the x, y, and z directions. The squared magnitude of $\vec{s}$ is a scalar operator

$$s^2 = \vec{s} \cdot \vec{s} = s_x^2 + s_y^2 + s_z^2 \tag{2.241}$$

The components of the spin angular momentum satisfy the commutation relations

$$[s_x, s_y] = is_z, \qquad [s_y, s_z] = is_x, \qquad [s_z, s_x] = is_y \tag{2.242}$$

The complete set of states describing the spin of a single particle can be taken to be the simultaneous eigenfunctions of s^2 and a single component of $\vec{s}$, usually chosen to be s_z,

$$s^2|s, m_s\rangle = s(s+1)|s, m_s\rangle \tag{2.243a}$$

$$s_z|s, m_s\rangle = m_s|s, m_s\rangle \tag{2.243b}$$

where s is a quantum number describing the total spin and m_s is a quantum number describing the z component of the spin. The possible values of s are $0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$ and m_s has $2s+1$ possible values $-s, -s+1, -s+2, \ldots, s-1, s$. An electron is a particle with $s = \frac{1}{2}$ and $m_s = \pm\frac{1}{2}$. Thus the complete set of states describing the spin of the electron are

$$|\tfrac{1}{2}, \tfrac{1}{2}\rangle \equiv |\alpha\rangle \tag{2.244a}$$

$$|\tfrac{1}{2}, -\tfrac{1}{2}\rangle \equiv |\beta\rangle \tag{2.244b}$$

These spin states are eigenfunctions of s^2 and s_z,

$$s^2|\alpha\rangle = \tfrac{3}{4}|\alpha\rangle, \qquad s^2|\beta\rangle = \tfrac{3}{4}|\beta\rangle \tag{2.245a}$$

$$s_z|\alpha\rangle = \tfrac{1}{2}|\alpha\rangle, \qquad s_z|\beta\rangle = -\tfrac{1}{2}|\beta\rangle \tag{2.245b}$$

but are not eigenfunctions of s_x and s_y,

$$s_x|\alpha\rangle = \tfrac{1}{2}|\beta\rangle, \qquad s_x|\beta\rangle = \tfrac{1}{2}|\alpha\rangle \tag{2.245c}$$

$$s_y|\alpha\rangle = \frac{i}{2}|\beta\rangle, \qquad s_y|\beta\rangle = -\frac{i}{2}|\alpha\rangle \tag{2.245d}$$

Instead of using s_x and s_y, it is often more convenient to work with the "step-up" and "step-down" ladder operators, s_+ and s_-, defined as

$$s_+ = s_x + is_y \tag{2.246a}$$

$$s_- = s_x - is_y \tag{2.246b}$$

These operators increase or decrease the value of m_s by one,

$$s_+|\alpha\rangle = 0, \qquad s_+|\beta\rangle = |\alpha\rangle \tag{2.247a}$$

$$s_-|\alpha\rangle = |\beta\rangle, \qquad s_-|\beta\rangle = 0 \tag{2.247b}$$

Using the commutation relations (2.242), the expression (2.241) for s^2 can be rewritten as

$$s^2 = s_+s_- - s_z + s_z^2 \tag{2.248a}$$

$$s^2 = s_-s_+ + s_z + s_z^2 \tag{2.248b}$$

Exercise 2.32 a) Derive (2.247) from (2.245); b) Derive (2.248).

Exercise 2.33 Find the 2×2 matrix representations of s^2, s_z, s_+, and s_- in the basis $|\alpha\rangle$, $|\beta\rangle$. Verify the identities analogous to (2.248a,b) for these matrix representations.

Exercise 2.34 Using the commutation relations (2.242), show that $[s^2, s_z] = 0$.

In a many-electron system, the total spin angular momentum operator is simply the vector sum of the spin vectors of each of the electrons

$$\vec{\mathcal{S}} = \sum_{i=1}^{N} \vec{s}(i) \tag{2.249}$$

From this relation it is evident that the components of the total spin and the ladder operators are analogous sums of one-electron operators

$$\mathcal{S}_I = \sum_{i=1}^{N} s_I(i) \qquad I = x, y, z \tag{2.250a}$$

$$\mathcal{S}_\pm = \sum_{i=1}^{N} s_\pm(i) \tag{2.250b}$$

The total squared-magnitude of the spin,

$$\begin{aligned} \mathcal{S}^2 = \vec{\mathcal{S}} \cdot \vec{\mathcal{S}} &= \sum_{i=1}^{N} \sum_{j=1}^{N} \vec{s}(i) \cdot \vec{s}(j) \\ &= \mathcal{S}_+ \mathcal{S}_- - \mathcal{S}_z + \mathcal{S}_z^2 \\ &= \mathcal{S}_- \mathcal{S}_+ + \mathcal{S}_z + \mathcal{S}_z^2 \end{aligned} \tag{2.251}$$

is the sum of one-electron operators (the diagonal terms $i = j$) plus the sum of two-electron operators (the cross-terms $i \neq j$).

In the usual nonrelativistic treatment, such as considered in this book, the Hamiltonian does not contain any spin coordinates and hence both $\mathcal{S}^2$ and $\mathcal{S}_z$ commute with the Hamiltonian,

$$[\mathcal{H}, \mathcal{S}^2] = 0 = [\mathcal{H}, \mathcal{S}_z] \tag{2.252}$$

Consequently, the exact eigenfunctions of the Hamiltonian are also eigenfunctions of the two spin operators,

$$\mathcal{S}^2|\Phi\rangle = S(S+1)|\Phi\rangle \tag{2.253a}$$

$$\mathcal{S}_z|\Phi\rangle = M_S|\Phi\rangle \tag{2.253b}$$

where S and M_S are the spin quantum numbers describing the total spin and its z component of an N-electron state $|\Phi\rangle$. States with $S = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$

have multiplicity $(2S + 1) = 1, 2, 3, 4, \ldots$ and are called singlets, doublets, triplets, quartets, etc. Approximate solutions of the Schrödinger equation are not necessarily pure spin states. However, it is often convenient to constrain approximate wave functions to be pure singlets, doublets, triplets, etc.

Any single determinant is an eigenfunction of $\mathscr{S}_z$ (see Exercise 2.37). In particular

$$\mathscr{S}_z|\chi_i\chi_j\cdots\chi_k\rangle = \tfrac{1}{2}(N^\alpha - N^\beta)|\chi_i\chi_j\cdots\chi_k\rangle = M_S|\chi_i\chi_j\cdots\chi_k\rangle \quad (2.254)$$

where N^α is the number of spin orbitals with α spin and N^β is the number of spin orbitals with β spin. However, single determinants are not necessarily eigenfunctions of $\mathscr{S}^2$. As we will discuss in the next subsection, by combining a small number of single determinants it is possible to form spin-adapted configurations that are correct eigenfunctions of $\mathscr{S}^2$.

Exercise 2.35 Consider an operator $\mathscr{A}$ that commutes with the Hamiltonian. Suppose $|\Phi\rangle$ is an eigenfunction of $\mathscr{H}$ with eigenvalue E. Show that $\mathscr{A}|\Phi\rangle$ is also an eigenfunction of $\mathscr{H}$ with eigenvalue E. Thus if $|\Phi\rangle$ is (energetically) nondegenerate, then $\mathscr{A}|\Phi\rangle$ is at most a constant multiple of $|\Phi\rangle$ (i.e., $\mathscr{A}|\Phi\rangle = a|\Phi\rangle$) and hence $|\Phi\rangle$ is an eigenfunction of $\mathscr{A}$. In case of degeneracies, we can always construct appropriate linear combinations of the degenerate eigenfunctions of $\mathscr{H}$ that are also eigenfunctions of $\mathscr{A}$.

Exercise 2.36 Given two nondegenerate eigenfunctions of a hermitian operator $\mathscr{A}$ that commutes with $\mathscr{H}$, i.e., $\mathscr{A}|\Psi_1\rangle = a_1|\Psi_1\rangle$, $\mathscr{A}|\Psi_2\rangle = a_2|\Psi_2\rangle$, $a_1 \neq a_2$, show that $\langle\Psi_1|\mathscr{H}|\Psi_2\rangle = 0$. Thus the matrix element of the Hamiltonian between, say, singlet and triplet spin-adapted configurations is zero.

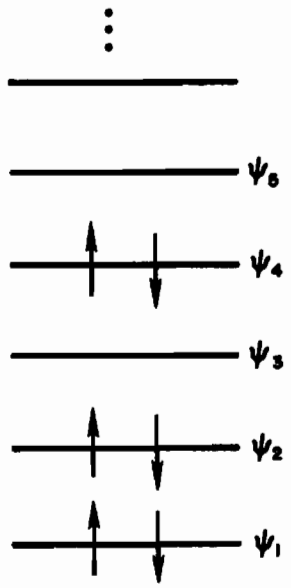
Exercise 2.37 Prove Eq. (2.254). *Hint*: Use expansion (2.115) for a Slater determinant and note that $\mathscr{S}_z$, since it is invariant to any permutation of the electron labels, commutes with $\mathscr{P}_n$.

2.5.2 Restricted Determinants and Spin-Adapted Configurations

As we have seen in Subsection 2.2.1, given a set of K orthonormal spatial orbitals $\{\psi_i | i = 1, 2, \ldots, K\}$ we can form a set of $2K$ spin orbitals $\{\chi_i | i = 1, 2, \ldots, 2K\}$ by multiplying each spatial orbital by either the α or β spin function

$$\begin{aligned} \chi_{2i-1}(\mathbf{x}) &= \psi_i(\mathbf{r})\alpha(\omega) \\ \chi_{2i}(\mathbf{x}) &= \psi_i(\mathbf{r})\beta(\omega) \end{aligned} \qquad i = 1, 2, \ldots, K \quad (2.255)$$

Such spin orbitals are called *restricted* spin orbitals, and determinants formed from them are restricted determinants. In such a determinant a given spatial



$|^1\Psi\rangle = |\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2\psi_4\bar{\psi}_4\rangle$ **Figure 2.11** A singlet closed-shell determinant.

orbital ψ_i can be occupied either by a single electron (spin up or down) or by two electrons (one with spin up and the other with spin down). It is convenient to classify the types of restricted determinants according to the number of spatial orbitals that are singly occupied. A determinant in which each spatial orbital is doubly occupied is called a *closed-shell* determinant (see Fig. 2.11). An *open shell* refers to a spatial orbital that contains a single electron. One refers to determinants by the number of open shells they contain.

All the electron spins are paired in a closed-shell determinant, and it is not surprising that a closed-shell determinant is a pure singlet. That is, it is an eigenfunction of $\mathscr{S}^2$ with eigenvalue zero,

$$\mathscr{S}^2|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle = 0(0+1)|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j\cdots\rangle = 0 \tag{2.256}$$

as shown in Exercise 2.38. The simplest example of a closed-shell determinant is the Hartree-Fock ground state wave function of minimal basis H_2,

$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle = [\psi_1(1)\psi_1(2)]2^{-1/2}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \tag{2.257}$$

where we have expanded out the determinant. The spin part of this wave function is just the singlet spin function of a two-electron system. The doubly excited state $|\Psi_{11}^{2\bar{2}}\rangle = |2\bar{2}\rangle$ is, of course, also a singlet.

Exercise 2.38 Prove Eq. (2.256). *Hints*: 1) $\mathscr{S}^2 = \mathscr{S}_-\mathscr{S}_+ + \mathscr{S}_z + \mathscr{S}_z^2$, 2) as a result of Eq. (2.254) it is sufficient to show $\mathscr{S}_+|\psi_i\bar{\psi}_i\cdots\rangle = 0$, 3) use expansion (2.115) for the determinant, and note the $\mathscr{S}_+$ commutes with the permutation operator, 4) $s_+\psi\alpha = 0$, 5) finally, $s_+\psi\beta = \psi\alpha$, but the determinant vanishes because it has two indentical columns.

We now consider open-shell restricted determinants. Open-shell determinants are *not* eigenfunctions of $\mathcal{S}^2$, except when all the open-shell electrons have parallel spin, as in Fig. 2.12. As an illustration, let us consider the four singly excited determinants that arise in the minimal basis H_2 model (see Eq. (2.76)). The open-shell determinants

$$|\Psi_1^{\bar{2}}\rangle = |\bar{2}\,\bar{1}\rangle = -2^{-1/2}[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)]\beta(1)\beta(2) \quad (2.258a)$$

$$|\Psi_{\bar{1}}^{2}\rangle = |1\,2\rangle = 2^{-1/2}[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)]\alpha(1)\alpha(2) \quad (2.258b)$$

are eigenfunctions of $\mathcal{S}^2$ with eigenvalue $1(1+1) = 2$ and thus are both triplets. On the other hand, the determinants

$$|\Psi_1^2\rangle = |2\,\bar{1}\rangle \quad (2.259a)$$

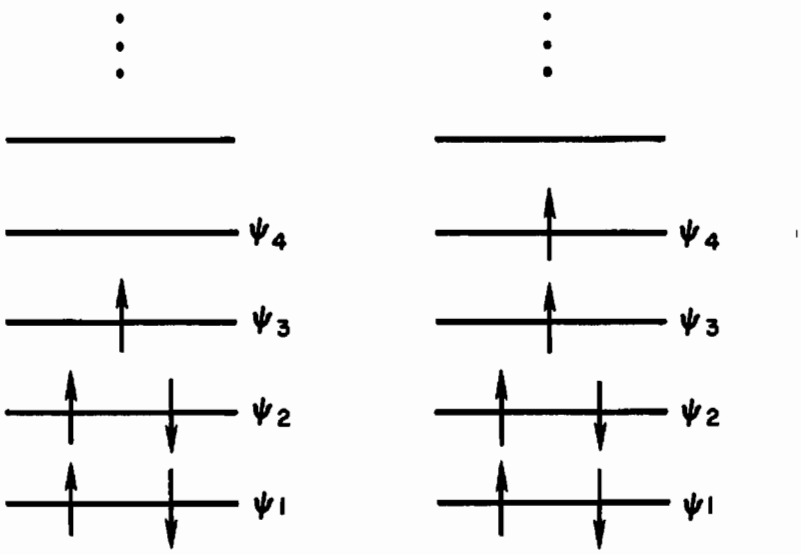
$$|\Psi_{\bar{1}}^{\bar{2}}\rangle = |1\,\bar{2}\rangle \quad (2.259b)$$

are not pure spin states. However, by taking appropriate linear combinations of these determinants we can form spin-adapted configurations, which are eigenfunctions of $\mathcal{S}^2$. In particular, the singlet spin-adapted configuration is

$$\begin{aligned} |^1\Psi_1^2\rangle &= 2^{-1/2}(|\Psi_{\bar{1}}^{\bar{2}}\rangle + |\Psi_1^2\rangle) \\ &= 2^{-1/2}(|1\,\bar{2}\rangle + |2\,\bar{1}\rangle) \\ &= 2^{-1/2}[\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)]2^{-1/2}(\alpha(1)\beta(2) - \beta(1)\alpha(2)) \end{aligned} \quad (2.260)$$

and the triplet spin-adapted configuration is

$$\begin{aligned} |^3\Psi_1^2\rangle &= 2^{-1/2}(|\Psi_{\bar{1}}^{\bar{2}}\rangle - |\Psi_1^2\rangle) \\ &= 2^{-1/2}(|1\,\bar{2}\rangle - |2\,\bar{1}\rangle) \\ &= 2^{-1/2}[\psi_1(1)\psi_2(2) - \psi_1(2)\psi_2(1)]2^{-1/2}(\alpha(1)\beta(2) + \beta(1)\alpha(2)) \end{aligned} \quad (2.261)$$



$$|^2\Psi\rangle = |\psi_1\,\bar{\psi}_1\,\psi_2\,\bar{\psi}_2\,\psi_3\rangle \qquad |^3\Psi\rangle = |\psi_1\,\bar{\psi}_1\,\psi_2\,\bar{\psi}_2\,\psi_3\,\psi_4\rangle$$

Figure 2.12 Doublet and triplet restricted single determinants.

As expected, the spin part of $|^1\Psi_1^2\rangle$ is identical to the spin part of the closed-shell wave function (2.257) since both wave functions are singlets.

Exercise 2.39 Using $\mathscr{S}^2 = \mathscr{S}_-\mathscr{S}_+ + \mathscr{S}_z + \mathscr{S}_z^2$, show that $|^1\Psi_1^2\rangle$ is a singlet while $|^3\Psi_1^2\rangle$, $|\Psi_1^{\bar{2}}\rangle$ and $|\Psi_{\bar{1}}^2\rangle$ are triplets.

Exercise 2.40 Show that

$$\langle {}^1\Psi_1^2|\mathscr{H}|{}^1\Psi_1^2\rangle = h_{11} + h_{22} + J_{12} + K_{12}$$

$$\langle {}^3\Psi_1^2|\mathscr{H}|{}^3\Psi_1^2\rangle = h_{11} + h_{22} + J_{12} - K_{12}$$

Note that the energy of the triplet is lower than the energy of the singlet. Why is this to be expected from the space parts of the two wave functions?

Let us generalize the above results for minimal basis H_2. In Chapters 4 and 5 we use singlet spin-adapted configurations that arise as a result of single and double excitations from a closed-shell Hartree-Fock ground state,

$$|\Psi_0\rangle = |1\bar{1}\cdots a\bar{a}\, b\bar{b}\cdots\rangle \tag{2.262}$$

The procedure for finding the appropriate linear combinations of singly and doubly excited determinants to form spin-adapted configurations is beyond the scope of this book; we shall merely quote the results. A variety of methods are available for constructing spin eigenfunctions. An authoritative and clear description of many of these methods has been given by Paunz.[2]

The singlet spin-adapted configuration corresponding to the single excitation in which an electron has been promoted from spatial orbital ψ_a to spatial orbital ψ_r is

$$|{}^1\Psi_a^r\rangle = 2^{-1/2}(|\Psi_{\bar{a}}^r\rangle + |\Psi_a^r\rangle) \tag{2.263}$$

Note that if $a = 1$ and $r = 2$, this expression reduces to the minimal basis result (2.260).

For double excitations, a number of different types of singlet spin-adapted configurations can occur. They are presented in Table 2.7. The spin-adapted configuration corresponding to the situation that both electrons come from the same spatial orbital and go into the same spatial orbital is $|{}^1\Psi_{aa}^{rr}\rangle$. This is the generalization of the doubly excited state ($|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle$) of minimal basis H_2. If two electrons come from the same spatial orbital but go to different spatial orbitals, the appropriate spin-adapted configuration is $|{}^1\Psi_{aa}^{rs}\rangle$. If two electrons come from the different spatial orbitals but go to the same spatial orbital, the appropriate spin-adapted configuration is $|{}^1\Psi_{ab}^{rr}\rangle$. Finally, for the situation that both electrons come from different spatial orbitals and go to different spatial orbitals there are two linearly independent spin-adapted configurations, $|{}^A\Psi_{ab}^{rs}\rangle$ and $|{}^B\Psi_{ab}^{rs}\rangle$.

Table 2.7 Doubly-excited singlet spin-adapted configurations

s —— r —⇅— b —⇅— a ——	$\lvert {}^1\Psi^{rr}_{aa}\rangle = \lvert \Psi^{r\bar{r}}_{a\bar{a}}\rangle$
s —— r —•— b —⇅— a ——	$\lvert {}^1\Psi^{rs}_{aa}\rangle = 2^{-1/2}(\lvert \Psi^{r\bar{s}}_{a\bar{a}}\rangle + \lvert \Psi^{s\bar{r}}_{a\bar{a}}\rangle)$
s —— r —⇅— b —•— a —•—	$\lvert {}^1\Psi^{rr}_{ab}\rangle = 2^{-1/2}(\lvert \Psi^{\bar{r}r}_{\bar{a}b}\rangle + \lvert \Psi^{r\bar{r}}_{a\bar{b}}\rangle)$
s —•— r —•— b —•— a —•—	$\lvert {}^A\Psi^{rs}_{ab}\rangle = (12)^{-1/2}(2\lvert \Psi^{rs}_{ab}\rangle + 2\lvert \Psi^{\bar{r}\bar{s}}_{\bar{a}\bar{b}}\rangle - \lvert \Psi^{\bar{s}r}_{\bar{a}b}\rangle + \lvert \Psi^{\bar{r}s}_{\bar{a}b}\rangle + \lvert \Psi^{r\bar{s}}_{a\bar{b}}\rangle - \lvert \Psi^{s\bar{r}}_{a\bar{b}}\rangle)$ $\lvert {}^B\Psi^{rs}_{ab}\rangle = \frac{1}{2}(\lvert \Psi^{\bar{s}r}_{\bar{a}b}\rangle + \lvert \Psi^{\bar{r}s}_{\bar{a}b}\rangle + \lvert \Psi^{r\bar{s}}_{a\bar{b}}\rangle + \lvert \Psi^{s\bar{r}}_{a\bar{b}}\rangle)$

2.5.3 Unrestricted Determinants

With restricted spin orbitals and restricted determinants, the spatial orbitals are constrained to be identical for α and β spins. For example, the restricted Hartree-Fock (RHF) ground state of the Li atom is

$$\lvert {}^2\Psi_{\text{RHF}}\rangle = \lvert \psi_{1s}\bar{\psi}_{1s}\psi_{2s}\rangle \tag{2.264}$$

as shown in Fig. 2.13. The spatial description of the $1s\alpha$ electron is forced to be identical to that of the $1s\beta$ electron. This is a real constraint since the $1s\alpha$ electron has an exchange interaction with the $2s\alpha$ electron, whereas the $1s\beta$ electron does not. The $2s\alpha$ electron spin "polarizes" the $1s$ shell. The $1s\alpha$ and $1s\beta$ electrons will experience different effective potentials and would "prefer" not to be described by the same spatial function. Intuitively, we expect that if this constraint is relaxed by using different orbitals for different spins,

$$\lvert \Psi_{\text{UHF}}\rangle = \lvert \psi^{\alpha}_{1s}\bar{\psi}^{\beta}_{1s}\psi^{\alpha}_{2s}\rangle \tag{2.265}$$

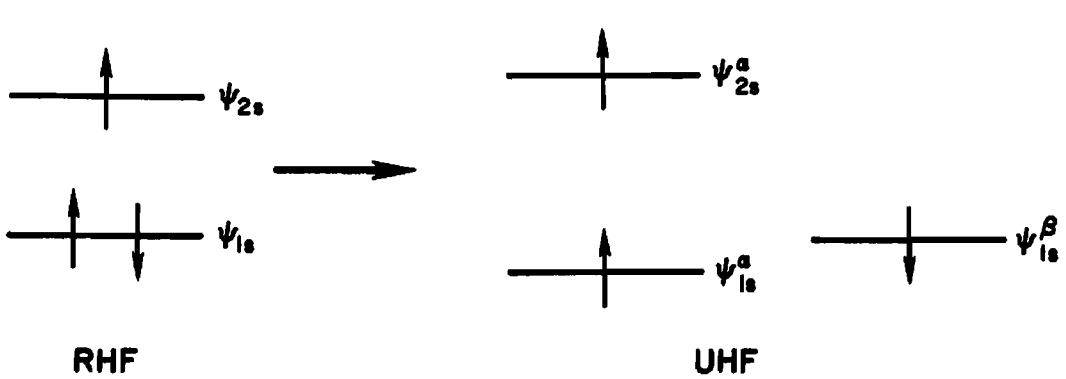


Figure 2.13 Relaxation of a restricted single determinant to an unrestricted single determinant for the Li atom.

we will obtain a lower energy. This is indeed the case. The wave function (2.265) is an example of an *unrestricted* determinant. It is, in fact, the unrestricted Hartree-Fock (UHF) ground state wave function of the Li atom.

Unrestricted determinants are formed from unrestricted spin orbitals. Unrestricted spin orbitals have different spatial orbitals for different spins. Given a set of K orthonormal spatial orbitals $\{\psi_i^\alpha\}$,

$$\langle \psi_i^\alpha | \psi_j^\alpha \rangle = \delta_{ij} \tag{2.266}$$

and a different set of K orthonormal spatial orbitals $\{\psi_i^\beta\}$

$$\langle \psi_i^\beta | \psi_j^\beta \rangle = \delta_{ij} \tag{2.267}$$

such that the two sets are not orthogonal,

$$\langle \psi_i^\alpha | \psi_j^\beta \rangle = S_{ij}^{\alpha\beta} \tag{2.268}$$

where $\mathbf{S}^{\alpha\beta}$ is an overlap matrix, we can form $2K$ *unrestricted* spin orbitals as

$$\begin{aligned} \chi_{2i-1}(\mathbf{x}) &= \psi_i^\alpha(\mathbf{r})\alpha(\omega) \\ \chi_{2i}(\mathbf{x}) &= \psi_i^\beta(\mathbf{r})\beta(\omega) \end{aligned} \qquad i = 1, 2, \ldots, K \tag{2.269}$$

As shown in Exercise 2.1, the $2K$ unrestricted spin orbitals form an orthonormal set, in spite of the fact that the α and β spatial orbitals are not orthogonal.

Unrestricted determinants are not eigenfunctions of $\mathscr{S}^2$. Moreover, they cannot be spin-adapted by combining a small number of unrestricted determinants as is the case for restricted determinants. Thus the UHF ground state (2.265) of the Li atom is not a pure doublet as is the RHF ground state (2.264). Nevertheless, unrestricted wave functions are commonly used as a first approximation to doublet and triplet states.

Figure 2.14 shows a representation of an unrestricted wave function, which is approximately a singlet. Note that $N^\alpha = N^\beta$. The α and β orbitals

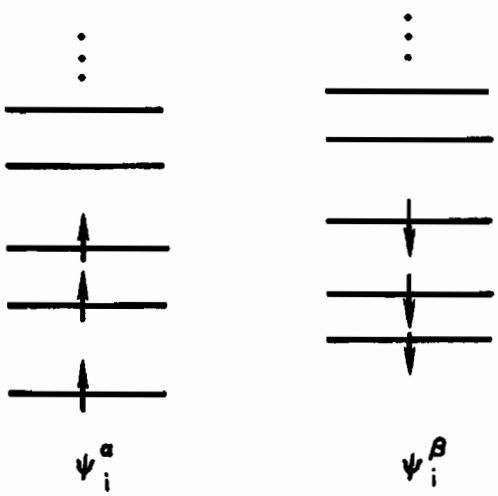


Figure 2.14 An unrestricted determinant that is *approximately* a singlet.

are drawn as nondegenerate for emphasis. Unrestricted singlets frequently collapse to the corresponding restricted singlets, i.e., to a closed-shell state. In our minimal basis H_2 problem, for example, the closed-shell ground state is $|\psi_1\bar{\psi}_1\rangle$ and at normal bond lengths the energy is raised rather than lowered by using different spatial orbitals for the two electrons. However, when the bond length is very large, one electron is effectively around one hydrogen atom, and the other electron, around the other hydrogen atom, should have a very different spatial description. Thus at large bond lengths, the energy is lowered by using an unrestricted rather than a restricted description, as we shall see in the next chapter.

If $N_\alpha = N_\beta + 1$, then an unrestricted determinant is approximately a doublet (see Fig. 2.15). An unrestricted doublet is often used as the first description of free radicals with one unpaired electron such as CH_3. An approximate triplet determinant has two more α electrons than β electrons as shown in Fig. 2.16.

If $|1\rangle$, $|2\rangle$, $|3\rangle$, etc. are exact singlet, doublet, triplet states etc., then the unrestricted states in Figs. 2.14, 2.15, and 2.16, can be expanded as

$$|^1\Psi\rangle = c_1^1|1\rangle + c_3^1|3\rangle + c_5^1|5\rangle + \cdots \tag{2.270a}$$

$$|^2\Psi\rangle = c_2^2|2\rangle + c_4^2|4\rangle + c_6^2|6\rangle + \cdots \tag{2.270b}$$

$$|^3\Psi\rangle = c_3^3|3\rangle + c_5^3|5\rangle + c_7^3|7\rangle + \cdots \tag{2.270c}$$

Thus an unrestricted wave function is contaminated by higher, not lower, multiplicity components. If the leading term in the above expansion is dominant, then one can describe, to a good approximation, unrestricted

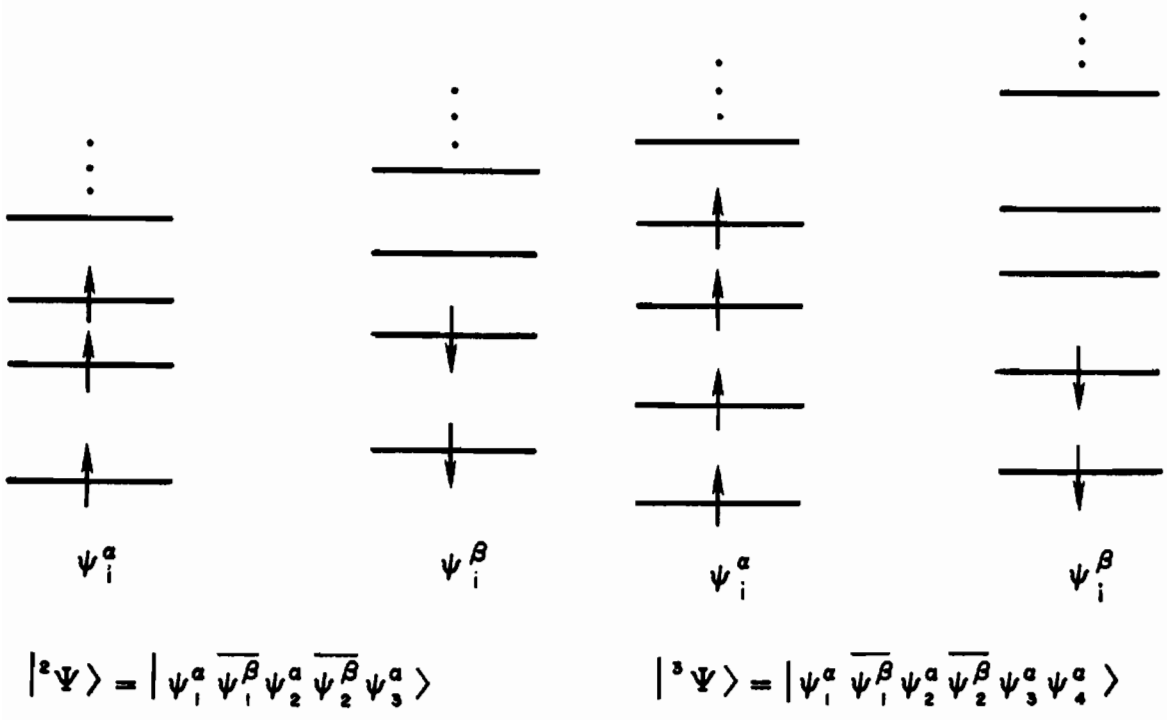


Figure 2.15 An unrestricted determinant that is *approximately* a doublet.

Figure 2.16 An unrestricted determinant that is *approximately* a triplet.

determinants as doublet, triplet, etc. The expectation value of $\mathscr{S}^2$ for an unrestricted determinant is always too large because the contaminants have larger values of S. In particular, it can be shown that

$$\langle \mathscr{S}^2 \rangle_{\text{UHF}} = \langle \mathscr{S}^2 \rangle_{\text{Exact}} + N^\beta - \sum_i^N \sum_j^N |S_{ij}^{\alpha\beta}|^2 \tag{2.271}$$

where we have assumed, as always, that $N^\alpha \geq N^\beta$ and where

$$\langle \mathscr{S}^2 \rangle_{\text{Exact}} = \left(\frac{N^\alpha - N^\beta}{2}\right)\left(\frac{N^\alpha - N^\beta}{2} + 1\right) \tag{2.272}$$

In spite of spin contamination, an unrestricted determinant is often used as a first approximation to the wave function for doublets and triplets because unrestricted wave functions have lower energies than the corresponding restricted wave functions.

Exercise 2.41 Consider the determinant $|K\rangle = |\psi_1^\alpha \bar{\psi}_1^\beta\rangle$ formed from *nonorthogonal* spatial orbitals, $\langle \psi_1^\alpha | \psi_1^\beta \rangle = S_{11}^{\alpha\beta}$. a. Show that $|K\rangle$ is an eigenfunction of $\mathscr{S}^2$ only if $\psi_1^\alpha = \psi_1^\beta$. b. Show that $\langle K|\mathscr{S}^2|K\rangle = 1 - |S_{11}^{\alpha\beta}|^2$ in agreement with Eq. (2.271).

NOTES

1. B. T. Sutcliffe, Fundamentals of computational quantum chemistry, in *Computational Techniques in Quantum Chemistry*, G. H. F. Diercksen, B. T. Sutcliffe, and A. Veillard (Eds.), Reidel, Boston, 1975, p. 1.
2. R. Paunz, *Spin Eigenfunctions*, Plenum, New York, 1979.

FURTHER READING

Avery, J., *Creation and Annihilation Operators*, McGraw-Hill, New York, 1976. Chapter 2 formulates a number of quantum mechanical approximations, including the Hartree-Fock approximation, in the language of second quantization.

Flurry, R. L. Jr., *Symmetry Groups*, Prentice-Hall, Englewood Cliffs, New Jersey, 1980. An excellent introduction to chemical applications of group theory. Our text assumes familarity with only the most elementary group theoretical ideas and notations.

Mattuck, R. D., 2nd ed., *A Guide to Feynman Diagrams in the Many-Body Problem*, McGraw-Hill, New York, 1976. Chapter 7 introduces second quantization using a more sophisticated point of view than adopted here.

McWeeny, R. and Sutcliffe, B. T., *Methods of Molecular Quantum Mechanics*, 2nd ed., Academic Press, New York, 1976. Discusses the rules for evaluating matrix elements between Slater determinants formed from *nonorthogonal* spin orbitals. This book also contains a concise introduction to methods for obtaining spin eigenfunctions.

Slater, J. C., *Quantum Theory of Matter*, 2nd ed., McGraw-Hill, New York, 1968. Chapter 11 discusses determinantal wave functions and derives expressions for matrix elements between determinants in a somewhat different way than we have done.