Exercise 2.30 Show that

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

$$= \langle r|h|a \rangle$$

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

Exercise 2.31 Show that

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

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

$$[s_x, s_y] = is_z, \qquad [s_y, s_z] = is_x, \qquad [s_z, s_x] = is_y, \qquad (2.242)$$

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,

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

$$s_z|s, m_s\rangle = m_s|s, m_s\rangle \qquad (2.243b)$$

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

$$\left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle \equiv |\alpha\rangle \qquad (2.244a)$$

$$\left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle \equiv |\beta\rangle \qquad (2.244b)$$

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

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

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

but are not eigenfunctions of s_x and s_y,

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

$$s_y|\alpha\rangle = \tfrac{i}{2}|\beta\rangle, \qquad s_y|\beta\rangle = -\tfrac{i}{2}|\alpha\rangle \qquad (2.245d)$$

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

$$s_+ = s_x + is_y \qquad (2.246a)$$

$$s_- = s_x - is_y \qquad (2.246b)$$

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

$$s_+|\alpha\rangle = 0, \qquad s_+|\beta\rangle = |\alpha\rangle \qquad (2.247a)$$

$$s_-|\alpha\rangle = |\beta\rangle, \qquad s_-|\beta\rangle = 0 \qquad (2.247b)$$

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

$$s^2 = s_+s_- - s_z + s_z^2 \qquad (2.248a)$$

$$s^2 = s_-s_+ + s_z + s_z^2 \qquad (2.248b)$$

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

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

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

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

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

The total squared-magnitude of the spin,

$$\mathscr{S}^2 = \vec{\mathscr{S}} \cdot \vec{\mathscr{S}} = \sum_{i=1}^{N}\sum_{j=1}^{N} \vec{s}(i) \cdot \vec{s}(j)$$
$$= \mathscr{S}_+\mathscr{S}_- - \mathscr{S}_z + \mathscr{S}_z^2$$
$$= \mathscr{S}_-\mathscr{S}_+ + \mathscr{S}_z + \mathscr{S}_z^2 \qquad (2.251)$$

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 $\mathscr{S}^2$ and $\mathscr{S}_z$ commute with the Hamiltonian,

$$[\mathscr{H}, \mathscr{S}^2] = 0 = [\mathscr{H}, \mathscr{S}_z] \qquad (2.252)$$

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

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

$$\mathscr{S}_z|\Phi\rangle = M_S|\Phi\rangle \qquad (2.253b)$$

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

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

Such spin orbitals are called *restricted* spin orbitals, and determinants formed from them are restricted determinants. In such a determinant a given spatial
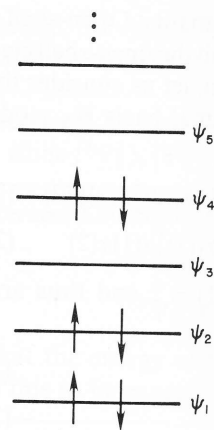
$|^1\Psi\rangle = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \psi_4 \bar{\psi}_4 \ldots$

orbital ψ_i can be occupied by two electrons (one with venient to classify the typ number of spatial orbitals each spatial orbital is doul (see Fig. 2.11). An *open she* electron. One refers to de contain.

All the electron spins a not surprising that a closed an eigenfunction of $\mathscr{S}^2$ wit

$$\mathscr{S}^2|\psi_i\bar{\psi}_i\psi_j\bar{\psi}_j$$

as shown in Exercise 2.38. minant is the Hartree-Fock

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

where we have expanded o function is just the singlet sp excited state $|\Psi_{11}^{2\bar{2}}\rangle = |2\bar{2}\rangle$ is

Exercise 2.38 Prove Eq 2) as a result of Eq. (2.254) i expansion (2.115) for the det permutation operator, 4) s_+ minant vanishes because it h