1 SECOND QUANTIZATION

In the standard formulation of quantum mechanics, observables are represented by operators and states by functions. In the language of second quantization, the wave functions are also expressed in terms of operators – the creation and annihilation operators working on the vacuum state. The antisymmetry of the electronic wave function follows from the algebra of these operators and requires no special attention. From the creation and annihilation operators, we construct also the standard operators of first-quantization quantum mechanics such as the Hamiltonian operator. This unified description of states and operators in terms of a single set of elementary creation and annihilation operators reduces much of the formal manipulation of quantum mechanics to algebra, allowing important relationships to be developed in an elegant manner. In this chapter, we develop the formalism of second quantization, laying the foundation for our subsequent treatment of molecular electronic structure.

1.1 The Fock space

Let $\{\phi_P(\mathbf{x})\}$ be a basis of M orthonormal *spin orbitals*, where the coordinates $\mathbf{x}$ represent collectively the spatial coordinates $\mathbf{r}$ and the spin coordinate σ of the electron. A *Slater determinant* is an antisymmetrized product of one or more spin orbitals. For example, a normalized Slater determinant for N electrons may be written as

$$|\phi_{P_1}\phi_{P_2}\cdots\phi_{P_N}| = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{P_1}(\mathbf{x}_1) & \phi_{P_2}(\mathbf{x}_1) & \cdots & \phi_{P_N}(\mathbf{x}_1) \\ \phi_{P_1}(\mathbf{x}_2) & \phi_{P_2}(\mathbf{x}_2) & \cdots & \phi_{P_N}(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{P_1}(\mathbf{x}_N) & \phi_{P_2}(\mathbf{x}_N) & \cdots & \phi_{P_N}(\mathbf{x}_N) \end{vmatrix} \tag{1.1.1}$$

We now introduce an abstract linear vector space – the *Fock space* – where each determinant is represented by an *occupation-number (ON) vector* $|\mathbf{k}\rangle$,

$$|\mathbf{k}\rangle = |k_1, k_2, \ldots, k_M\rangle, k_P = \begin{cases} 1 & \phi_P \text{ occupied} \\ 0 & \phi_P \text{ unoccupied} \end{cases} \tag{1.1.2}$$

Thus, the *occupation number* k_P is 1 if ϕ_P is present in the determinant and 0 if it is absent. For an orthonormal set of spin orbitals, we define the *inner product* between two ON vectors $|\mathbf{k}\rangle$ and $|\mathbf{m}\rangle$ as

$$\langle\mathbf{k}|\mathbf{m}\rangle = \delta_{\mathbf{k},\mathbf{m}} = \prod_{P=1}^{M} \delta_{k_P m_P} \tag{1.1.3}$$

This definition is consistent with the overlap between two Slater determinants containing the same number of electrons. However, the extension of (1.1.3) to have a well-defined but zero overlap

between states with different electron numbers is a special feature of the Fock-space formulation of quantum mechanics that allows for a unified description of systems with variable numbers of electrons.

In a given spin-orbital basis, there is a one-to-one mapping between the Slater determinants with spin orbitals in canonical order and the ON vectors in the Fock space. Much of the terminology for Slater determinants is therefore used for ON vectors as well. Still, the ON vectors are not Slater determinants – unlike the Slater determinants, the ON vectors have no spatial structure but are just basis vectors in an abstract vector space. This Fock space can be manipulated as an ordinary inner-product vector space. For example, for two general vectors or states in the Fock space

$$|\mathbf{c}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k}\rangle \tag{1.1.4}$$

$$|\mathbf{d}\rangle = \sum_{\mathbf{k}} d_{\mathbf{k}} |\mathbf{k}\rangle \tag{1.1.5}$$

the inner product is given by

$$\langle \mathbf{c}|\mathbf{d}\rangle = \sum_{\mathbf{km}} c_{\mathbf{k}}^{*} \langle \mathbf{k}|\mathbf{m}\rangle d_{\mathbf{m}} = \sum_{\mathbf{k}} c_{\mathbf{k}}^{*} d_{\mathbf{k}} \tag{1.1.6}$$

The resolution of the identity likewise may be written in the usual manner as

$$1 = \sum_{\mathbf{k}} |\mathbf{k}\rangle\langle\mathbf{k}| \tag{1.1.7}$$

where the summation is over the full set of ON vectors for all numbers of electrons.

The ON vectors in (1.1.2) constitute an orthonormal basis in the 2^M-dimensional Fock space $F(M)$. This Fock space may be decomposed as a direct sum of subspaces $F(M, N)$

$$F(M) = F(M, 0) \oplus F(M, 1) \oplus \cdots \oplus F(M, M) \tag{1.1.8}$$

where $F(M, N)$ contains all ON vectors obtained by distributing N electrons among the M spin orbitals – that is, all ON vectors for which the sum of the occupation numbers is N:

$$N = \sum_{P=1}^{M} k_P \tag{1.1.9}$$

The subspace $F(M, 0)$, which consists of ON vectors with no electrons, contains a single vector – the true *vacuum state*

$$|\text{vac}\rangle = |0_1, 0_2, \ldots, 0_M\rangle \tag{1.1.10}$$

which, according to (1.1.3), is normalized to unity:

$$\langle \text{vac}|\text{vac}\rangle = 1 \tag{1.1.11}$$

Approximations to an exact N-electron wave function are expressed in terms of vectors in the Fock subspace $F(M, N)$ of dimension equal to the binomial coefficient $\binom{M}{N}$.

1.2 Creation and annihilation operators

In second quantization, all operators and states can be constructed from a set of elementary creation and annihilation operators. In this section we introduce these operators and explore their basic algebraic properties.

1.2.1 CREATION OPERATORS

The M elementary *creation operators* are defined by the relations

$$\hat{a}_P^\dagger|k_1, k_2, \ldots, 0_P, \ldots, k_M\rangle = \Gamma_P^{\mathbf{k}}|k_1, k_2, \ldots, 1_P, \ldots, k_M\rangle \tag{1.2.1}$$

$$\hat{a}_P^\dagger|k_1, k_2, \ldots, 1_P, \ldots, k_M\rangle = 0 \tag{1.2.2}$$

where

$$\Gamma_P^{\mathbf{k}} = \prod_{Q=1}^{P-1}(-1)^{k_Q} \tag{1.2.3}$$

The phase factor $\Gamma_P^{\mathbf{k}}$ is equal to $+1$ if there are an even number of electrons in the spin orbitals $Q < P$ (i.e. to the left of P in the ON vector) and equal to -1 if there are an odd number of electrons in these spin orbitals. As we shall see, this factor is necessary to obtain a representation of wave functions and operators consistent with first quantization. The requirement (1.2.2) that $\hat{a}_P^\dagger$ produces zero when it operates on a vector with $k_P = 1$ is in agreement with the fact that a Slater determinant vanishes if a spin orbital appears twice.

The spin orbitals that are unoccupied in an ON vector (1.1.2) may be identified from the specification of the occupied spin orbitals. The explicit reference to the unoccupied spin orbitals may be avoided altogether by expressing the ON vector as a string of creation operators in the canonical order (i.e. in the same order as in the ON vector) working on the vacuum state:

$$|\mathbf{k}\rangle = \left[\prod_{P=1}^{M}(\hat{a}_P^\dagger)^{k_P}\right]|\text{vac}\rangle \tag{1.2.4}$$

We shall later see that the phase factor (1.2.3) is automatically kept track of by the anticommutation relations of the creation operators in (1.2.4), making any reference to this factor unnecessary.

The properties of the creation operators can be deduced from the relations (1.2.1) and (1.2.2), which we here combine in a single defining equation:

$$a_P^\dagger|\mathbf{k}\rangle = \delta_{k_P 0}\Gamma_P^{\mathbf{k}}|k_1, \ldots, 1_P, \ldots, k_M\rangle \tag{1.2.5}$$

Operating twice with $a_P^\dagger$ on an ON vector, we obtain from (1.2.5)

$$a_P^\dagger a_P^\dagger|\mathbf{k}\rangle = a_P^\dagger \delta_{k_P 0}\Gamma_P^{\mathbf{k}}|k_1, \ldots, 1_P, \ldots, k_M\rangle = 0 \tag{1.2.6}$$

Since the product $a_P^\dagger a_P^\dagger$ gives zero when applied to any vector, it must be identical to the zero operator:

$$\hat{a}_P^\dagger \hat{a}_P^\dagger = 0 \tag{1.2.7}$$

For $P \neq Q$, the operators $\hat{a}_P^\dagger$ and $\hat{a}_Q^\dagger$ may act on an ON vector in two ways. For $Q > P$, we obtain

$$\begin{aligned}\hat{a}_P^\dagger \hat{a}_Q^\dagger|\ldots, k_P, \ldots, k_Q, \ldots\rangle &= \hat{a}_P^\dagger \delta_{k_Q 0}\Gamma_Q^{\mathbf{k}}|\ldots, k_P, \ldots, 1_Q, \ldots\rangle \\ &= \delta_{k_P 0}\delta_{k_Q 0}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}|\ldots, 1_P, \ldots, 1_Q, \ldots\rangle\end{aligned} \tag{1.2.8}$$

where the phase factor for P is unaffected by the application of $\hat{a}_Q^\dagger$ since P appears before Q in the ON vector. Reversing the order of the creation operators, we obtain

$$\begin{aligned} a_Q^\dagger a_P^\dagger |\ldots k_P, \ldots, k_Q, \ldots\rangle &= a_Q^\dagger \delta_{k_P 0} \Gamma_P^{\mathbf{k}} |\ldots 1_P, \ldots, k_Q, \ldots\rangle \\ &= \delta_{k_P 0}\delta_{k_Q 0}\Gamma_P^{\mathbf{k}}(-\Gamma_Q^{\mathbf{k}})|\ldots, 1_P, \ldots, 1_Q, \ldots\rangle \end{aligned} \tag{1.2.9}$$

The factor $-\Gamma_Q^{\mathbf{k}}$ arises since $a_P^\dagger|\mathbf{k}\rangle$ – if it does not vanish – contains one more electron before spin orbital Q than does $|\mathbf{k}\rangle$. Adding together (1.2.8) and (1.2.9), we obtain

$$(a_P^\dagger a_Q^\dagger + a_Q^\dagger a_P^\dagger)|\mathbf{k}\rangle = 0 \tag{1.2.10}$$

for $Q > P$. Substitution of dummy indices shows that this equation is valid also for $Q < P$. Finally, from (1.2.7) we see that it is true also for $P = Q$. Since $|\mathbf{k}\rangle$ is an arbitrary ON vector, we conclude that the anticommutation relation

$$a_P^\dagger a_Q^\dagger + a_Q^\dagger a_P^\dagger = [a_P^\dagger, a_Q^\dagger]_+ = 0 \tag{1.2.11}$$

holds for any pair of creation operators.

1.2.2 ANNIHILATION OPERATORS

Having introduced the creation operators $a_P^\dagger$ of second quantization, we now proceed to the study of their Hermitian adjoints a_P. We shall see that the creation operators and their adjoints are distinct operators and consequently that these operators are not self-adjoint (Hermitian).

The properties of the adjoint or conjugate operators a_P can be inferred from those of the creation operators. Thus, from (1.2.11) the adjoint operators are seen to satisfy the anticommutation relation

$$a_P a_Q + a_Q a_P = [a_P, a_Q]_+ = 0 \tag{1.2.12}$$

To determine the action of a_P on an ON vector $|\mathbf{k}\rangle$, we invoke the resolution of the identity (1.1.7):

$$a_P|\mathbf{k}\rangle = \sum_{\mathbf{m}} |\mathbf{m}\rangle\langle\mathbf{m}|a_P|\mathbf{k}\rangle \tag{1.2.13}$$

The matrix element in this expression may be written as

$$\langle\mathbf{m}|a_P|\mathbf{k}\rangle = \langle\mathbf{k}|a_P^\dagger|\mathbf{m}\rangle^* = \begin{cases} \delta_{m_P 0}\Gamma_P^{\mathbf{m}} & \text{if } k_Q = m_Q + \delta_{QP} \\ 0 & \text{otherwise} \end{cases} \tag{1.2.14}$$

where we have used (1.2.5). From the definition of $\Gamma_P^{\mathbf{k}}$ in (1.2.3) and from $k_Q = m_Q + \delta_{QP}$, we see that $\Gamma_P^{\mathbf{m}} = \Gamma_P^{\mathbf{k}}$. Equation (1.2.14) may therefore be written as

$$\langle\mathbf{m}|a_P|\mathbf{k}\rangle = \begin{cases} \delta_{k_P 1}\Gamma_P^{\mathbf{k}} & \text{if } m_Q = k_Q - \delta_{QP} \\ 0 & \text{otherwise} \end{cases} \tag{1.2.15}$$

Hence, only one term in (1.2.13) survives and we conclude

$$a_P|\mathbf{k}\rangle = \delta_{k_P 1}\Gamma_P^{\mathbf{k}}|k_1, \ldots, 0_P, \ldots, k_M\rangle \tag{1.2.16}$$

The operator a_P reduces k_P from 1 to 0 if spin orbital P is occupied and it gives 0 if the spin orbital is unoccupied. It is therefore called an electron *annihilation operator*. An interesting special

case of (1.2.16) is

$$a_P|\text{vac}\rangle = 0 \tag{1.2.17}$$

which states that there are no electrons to be destroyed in the vacuum state.

1.2.3 ANTICOMMUTATION RELATIONS

We have seen that the creation operators anticommute among themselves (1.2.11) and that the same is true for the annihilation operators (1.2.12). We shall now establish the commutation relations between creation and annihilation operators. Combining (1.2.5) and (1.2.16), we obtain

$$a_P^\dagger a_P|\mathbf{k}\rangle = \delta_{k_P 1}|\mathbf{k}\rangle \tag{1.2.18}$$

$$a_P a_P^\dagger|\mathbf{k}\rangle = \delta_{k_P 0}|\mathbf{k}\rangle \tag{1.2.19}$$

The phase factors cancel since they appear twice. Adding these equations together, we arrive at the following expression:

$$(a_P^\dagger a_P + a_P a_P^\dagger)|\mathbf{k}\rangle = (\delta_{k_P 1} + \delta_{k_P 0})|\mathbf{k}\rangle = |\mathbf{k}\rangle \tag{1.2.20}$$

for any ON vector $|\mathbf{k}\rangle$. The operator $a_P^\dagger a_P + a_P a_P^\dagger$ is therefore equal to the identity operator

$$a_P^\dagger a_P + a_P a_P^\dagger = 1 \tag{1.2.21}$$

For $P > Q$, we obtain

$$a_P^\dagger a_Q|\mathbf{k}\rangle = -\delta_{k_P 0}\delta_{k_Q 1}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}|k_1, \ldots, 0_Q, \ldots, 1_P, \ldots, k_M\rangle, \quad P > Q \tag{1.2.22}$$

$$a_Q a_P^\dagger|\mathbf{k}\rangle = \delta_{k_P 0}\delta_{k_Q 1}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}|k_1, \ldots, 0_Q, \ldots, 1_P, \ldots, k_M\rangle, \quad P > Q \tag{1.2.23}$$

where the minus sign arises since, in $a_Q|\mathbf{k}\rangle$, the number of occupied spin orbitals to the left of spin orbital P has been reduced by one. Adding these two equations together, we obtain

$$(a_P^\dagger a_Q + a_Q a_P^\dagger)|\mathbf{k}\rangle = 0, \quad P > Q \tag{1.2.24}$$

Since $|\mathbf{k}\rangle$ is an arbitrary ON vector, we have the operator identity

$$a_P^\dagger a_Q + a_Q a_P^\dagger = 0, \quad P > Q \tag{1.2.25}$$

The case $P < Q$ is obtained by taking the conjugate of this equation and renaming the dummy indices. Combination of (1.2.21) and (1.2.25) shows that, for all P and Q,

$$a_P^\dagger a_Q + a_Q a_P^\dagger = [a_P^\dagger, a_Q]_+ = \delta_{PQ} \tag{1.2.26}$$

The *anticommutation relations* (1.2.11), (1.2.12), and (1.2.26) constitute the fundamental properties of the creation and annihilation operators. In view of their importance, they are here collected and listed in full:

$$[a_P^\dagger, a_Q^\dagger]_+ = 0 \tag{1.2.27}$$

$$[a_P, a_Q]_+ = 0 \tag{1.2.28}$$

$$[a_P^\dagger, a_Q]_+ = \delta_{PQ} \tag{1.2.29}$$

From these simple relations, all other algebraic properties of the second-quantization formalism follow.

1.3 Number-conserving operators

The creation and annihilation operators introduced in Section 1.2 change the number of particles in a state and therefore couple ON vectors belonging to different subspaces $F(M, N)$. We now turn to operators that conserve the particle number and thus couple ON vectors in the same subspace.

1.3.1 OCCUPATION-NUMBER OPERATORS

We first introduce the *occupation-number (ON) operators* as

$$\hat{N}_P = \hat{a}_P^\dagger \hat{a}_P \tag{1.3.1}$$

The ON operator $\hat{N}_P$ counts the number of electrons in spin orbital P:

$$\hat{N}_P|\mathbf{k}\rangle = \hat{a}_P^\dagger \hat{a}_P|\mathbf{k}\rangle = \delta_{k_P 1}|\mathbf{k}\rangle = k_P|\mathbf{k}\rangle \tag{1.3.2}$$

Here we have used (1.2.18). The ON operators are Hermitian

$$\hat{N}_P^\dagger = (\hat{a}_P^\dagger \hat{a}_P)^\dagger = \hat{a}_P^\dagger \hat{a}_P = \hat{N}_P \tag{1.3.3}$$

and commute among themselves

$$\hat{N}_P \hat{N}_Q|\mathbf{k}\rangle = k_P k_Q|\mathbf{k}\rangle = k_Q k_P|\mathbf{k}\rangle = \hat{N}_Q \hat{N}_P|\mathbf{k}\rangle \tag{1.3.4}$$

The ON vectors are thus the simultaneous eigenvectors of the commuting set of Hermitian operators $\hat{N}_P$. Moreover, the set of ON operators is complete in the sense that there is a one-to-one mapping between the ON vectors in the Fock space and the eigenvalues of the ON operators. The eigenvalues of the ON operators characterize the ON vectors completely, consistent with the introduction of the ON vectors as an orthonormal basis for the Fock space.

In the spin-orbital basis, the ON operators are projection operators since, in addition to being Hermitian (1.3.3), they are also idempotent:

$$\hat{N}_P^2 = \hat{a}_P^\dagger \hat{a}_P \hat{a}_P^\dagger \hat{a}_P = \hat{a}_P^\dagger (1 - \hat{a}_P^\dagger \hat{a}_P)\hat{a}_P = \hat{a}_P^\dagger \hat{a}_P = \hat{N}_P \tag{1.3.5}$$

Here we have used the anticommutators (1.2.29) and (1.2.28) in that order. Applied to a linear combination of ON vectors (1.1.4), the operator $\hat{N}_P$ leaves unaffected vectors where ϕ_P is occupied and annihilates all others:

$$\hat{N}_P|\mathbf{c}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} \hat{N}_P|\mathbf{k}\rangle = \sum_{\mathbf{k}} k_P c_{\mathbf{k}}|\mathbf{k}\rangle \tag{1.3.6}$$

Note that this property of the ON operators holds only in the spin-orbital basis where the occupations are either zero or one.

Using the basic anticommutation relations of creation and annihilation operators, we obtain for the commutators of the ON operators with the creation operators

$$\begin{aligned}
[\hat{N}_P, \hat{a}_Q^\dagger] &= \hat{a}_P^\dagger \hat{a}_P \hat{a}_Q^\dagger - \hat{a}_Q^\dagger \hat{a}_P^\dagger \hat{a}_P \\
&= \hat{a}_P^\dagger (\delta_{PQ} - \hat{a}_Q^\dagger \hat{a}_P) - \hat{a}_Q^\dagger \hat{a}_P^\dagger \hat{a}_P \\
&= \hat{a}_P^\dagger \delta_{PQ} - \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_P - \hat{a}_Q^\dagger \hat{a}_P^\dagger \hat{a}_P \\
&= \hat{a}_P^\dagger \delta_{PQ} + \hat{a}_Q^\dagger \hat{a}_P^\dagger \hat{a}_P - \hat{a}_Q^\dagger \hat{a}_P^\dagger \hat{a}_P
\end{aligned} \tag{1.3.7}$$

and therefore

$$[\hat{N}_P, a_Q^\dagger] = \delta_{PQ} a_Q^\dagger \tag{1.3.8}$$

Taking the conjugate of this equation, we obtain the corresponding commutator with the annihilation operator

$$[\hat{N}_P, a_Q] = -\delta_{PQ} a_Q \tag{1.3.9}$$

From these commutators, we may also conclude that, for an arbitrary string $\hat{X}$ of creation and annihilation operators such as

$$\hat{X} = a_P^\dagger a_Q a_P a_R^\dagger a_S \tag{1.3.10}$$

the commutators with the ON operators become

$$[\hat{N}_P, \hat{X}] = N_P^X \hat{X} \tag{1.3.11}$$

where N_P^X is the number of times $a_P^\dagger$ occurs in $\hat{X}$ minus the number of times a_P occurs in the same string. To arrive at relation (1.3.11), we have used the commutator expansion (1.8.5) of Section 1.8.

1.3.2 THE NUMBER OPERATOR

Adding together all ON operators in the Fock space, we obtain the Hermitian operator

$$\hat{N} = \sum_{P=1}^{M} a_P^\dagger a_P \tag{1.3.12}$$

which returns the number of electrons in an ON vector

$$\hat{N}|\mathbf{k}\rangle = \sum_{P=1}^{M} k_P |\mathbf{k}\rangle = N|\mathbf{k}\rangle \tag{1.3.13}$$

and therefore is known as the *particle-number operator* or simply the *number operator*. From (1.3.11), we see that the commutator of the number operator with an arbitrary string of operators is given by

$$[\hat{N}, \hat{X}] = N^X \hat{X} \tag{1.3.14}$$

where N^X is the excess of creation operators over annihilation operators in the string. In particular, we find that the number operator commutes with any string $\hat{T}$ that contains an equal number of creation and annihilation operators. Such strings are called *number-conserving*, since they conserve the number of particles in any vector:

$$\hat{N}\hat{T}|\mathbf{k}\rangle = \hat{T}\hat{N}|\mathbf{k}\rangle = \hat{T}N|\mathbf{k}\rangle = N\hat{T}|\mathbf{k}\rangle \tag{1.3.15}$$

In general, the application of the string $\hat{X}$ to a Fock-space vector increases the number of electrons by N^X.

1.3.3 EXCITATION OPERATORS

Apart from the particle-number operators (1.3.12), the simplest number-conserving operators are the elementary *excitation operators* $a_P^\dagger a_Q$, for which we shall occasionally use the notation

$$\hat{X}_Q^P = a_P^\dagger a_Q \tag{1.3.16}$$

Applied to an ON vector, these operators give (see Exercise 1.1)

$$a_P^\dagger a_Q|\mathbf{k}\rangle = \varepsilon_{PQ}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}(1 - k_P + \delta_{PQ})k_Q \left| \begin{matrix} k_P \to 1 \\ k_Q \to \delta_{PQ} \end{matrix} \right\rangle \tag{1.3.17}$$

where

$$\varepsilon_{PQ} = \begin{cases} 1 & P \leq Q \\ -1 & P > Q \end{cases} \tag{1.3.18}$$

and where the ket on the right-hand side of (1.3.17) is an ON vector with the same occupation numbers as $|\mathbf{k}\rangle$ except as indicated for spin orbitals P and Q. Equation (1.3.17) shows that $a_P^\dagger a_Q$ excites an electron from spin orbital Q to spin orbital P, thus turning $|\mathbf{k}\rangle$ into another ON vector in the same subspace $F(M, N)$. In fact, each ON vector in $F(M, N)$ can be obtained from any other ON vector in the same subspace by applying a sequence of excitation operators $a_P^\dagger a_Q$. The application of a single such operator yields a single excitation, two operators give a double excitation, and so on. The 'diagonal' excitation operators $a_P^\dagger a_P$ correspond to the occupation-number operators (1.3.1).

In Box 1.1, we summarize the fundamentals of the second-quantization formalism. In Section 1.4, we proceed to discuss the second-quantization representation of standard first-quantization operators such as the electronic Hamiltonian.

Box 1.1 The fundamentals of second quantization

Occupation-number vectors:	$\|\mathbf{k}\rangle = \|k_1, k_2, \ldots, k_M\rangle, \quad k_P = 0, 1$
Inner products:	$\langle\mathbf{k}\|\mathbf{m}\rangle = \prod_{P=1}^{M} \delta_{k_P m_P}$
Creation operators:	$a_P^\dagger\|\mathbf{k}\rangle = \delta_{k_P 0}\Gamma_P^{\mathbf{k}}\|k_1, \ldots, 1_P, \ldots, k_M\rangle$
	$\Gamma_P^{\mathbf{k}} = \prod_{Q=1}^{P-1}(-1)^{k_Q}$
Annihilation operators:	$a_P\|\mathbf{k}\rangle = \delta_{k_P 1}\Gamma_P^{\mathbf{k}}\|k_1, \ldots, 0_P, \ldots, k_M\rangle$
Anticommutation relations:	$a_P^\dagger a_Q + a_Q a_P^\dagger = \delta_{PQ}$
	$a_P^\dagger a_Q^\dagger + a_Q^\dagger a_P^\dagger = 0$
	$a_P a_Q + a_Q a_P = 0$
Occupation-number operators:	$\hat{N}_P\|\mathbf{k}\rangle = a_P^\dagger a_P\|\mathbf{k}\rangle = k_P\|\mathbf{k}\rangle$
Particle-number operator:	$\hat{N}\|\mathbf{k}\rangle = \sum_{P=1}^{M} \hat{N}_P\|\mathbf{k}\rangle = \sum_{P=1}^{M} k_P\|\mathbf{k}\rangle$
Excitation operators:	$\hat{X}_Q^P = a_P^\dagger a_Q$
Vacuum state:	$\langle\text{vac}\|\text{vac}\rangle = 1$ $a_P\|\text{vac}\rangle = 0$

1.4 The representation of one- and two-electron operators

Expectation values correspond to observables and should therefore be independent of the representation given to the operators and the states. Since expectation values may be expressed as sums of matrix elements of operators, we require the matrix element of a second-quantization operator between two ON vectors to be equal to its counterpart in first quantization. An operator in the Fock space can thus be constructed by requiring its matrix elements between ON vectors to be equal to the corresponding matrix elements between Slater determinants of the first-quantization operator.

Before proceeding to determine the form of the operators in second quantization, we recall that the matrix elements between Slater determinants depend on the spatial form of the spin orbitals. Since the ON vectors are independent of the spatial form of spin orbitals, we conclude that the second-quantization operators – in contrast to their first-quantization counterparts – must depend on the spatial form of the spin orbitals.

First-quantization operators conserve the number of electrons. Following the discussion in Section 1.3, such operators are in the Fock space represented by linear combinations of operators that contain an equal number of creation and annihilation operators. The explicit form of these number-conserving operators depends on whether the first-quantized operator is a one-electron operator or a two-electron operator. One-electron operators are discussed in Section 1.4.1 and two-electron operators in Section 1.4.2. Finally, in Section 1.4.3 we consider the second-quantization representation of the electronic Hamiltonian operator.

1.4.1 ONE-ELECTRON OPERATORS

In first quantization, *one-electron operators* are written as

$$f^{\mathrm{c}} = \sum_{i=1}^{N} f^{\mathrm{c}}(\mathbf{x}_i) \tag{1.4.1}$$

where the summation is over the N electrons of the system. Superscript c indicates that we are working in the coordinate representation of first quantization. Since each term in the operator (1.4.1) involves a single electron, this operator gives a vanishing matrix element whenever the Slater determinants differ in more than one pair of spin orbitals. The second-quantization analogue of (1.4.1) therefore has the structure

$$\hat{f} = \sum_{PQ} f_{PQ} a_P^\dagger a_Q \tag{1.4.2}$$

since the excitation operators $a_P^\dagger a_Q$ shift a single electron in an ON vector. The summation is over all pairs of spin orbitals to secure the highest possible flexibility in the description. The order of the creation and annihilation operators in each term ensures that the one-electron operator $\hat{f}$ produces zero when it works on the vacuum state.

To determine the numerical parameters f_{PQ} in (1.4.2), we evaluate the matrix elements of $\hat{f}$ between two ON vectors and compare with the usual *Slater–Condon rules* for matrix elements between determinants [1]. For one-electron operators there are three distinct cases.

1. The ON vectors are identical:

$$\langle \mathbf{k}|\hat{f}|\mathbf{k}\rangle = \sum_P f_{PP} \langle \mathbf{k}|a_P^\dagger a_P|\mathbf{k}\rangle = \sum_P k_P f_{PP} \tag{1.4.3}$$

2. The ON vectors differ in one pair of occupation numbers:

$$|\mathbf{k}_1\rangle = |k_1, \ldots 0_I, \ldots, 1_J, \ldots, k_M\rangle \tag{1.4.4}$$

$$|\mathbf{k}_2\rangle = |k_1, \ldots, 1_I, \ldots, 0_J, \ldots, k_M\rangle \tag{1.4.5}$$

$$\langle \mathbf{k}_2|\hat{f}|\mathbf{k}_1\rangle = 1^{\mathbf{k}_2}_I 1^{\mathbf{k}_1}_J f_{IJ} \tag{1.4.6}$$

3. The ON vectors differ in more than one pair of occupation numbers:

$$\langle \mathbf{k}_2|\hat{f}|\mathbf{k}_1\rangle = 0 \tag{1.4.7}$$

In these expressions, we have used indices I and J for the spin orbitals with different occupations in the bra and ket vectors.

Let us see how the above results are obtained. For the diagonal element

$$\langle \mathbf{k}|\hat{f}|\mathbf{k}\rangle = \sum_{PQ}{}^{\prime} f_{PQ}\langle \mathbf{k}|a^\dagger_P a_Q|\mathbf{k}\rangle \tag{1.4.8}$$

we note from the orthogonality of ON vectors that nonzero contributions can only arise when

$$a_P|\mathbf{k}\rangle = \pm a_Q|\mathbf{k}\rangle \tag{1.4.9}$$

which occurs for $P = Q$ only. This observation gives (1.4.3). For the ON vectors $|\mathbf{k}_1\rangle$ and $|\mathbf{k}_2\rangle$ in (1.4.6), the transition-matrix element

$$\langle \mathbf{k}_2|\hat{f}|\mathbf{k}_1\rangle = \sum_{PQ}{}^{\prime} f_{PQ}\langle \mathbf{k}_2|a^\dagger_P a_Q|\mathbf{k}_1\rangle \tag{1.4.10}$$

has nonvanishing contributions only if

$$a_P|\mathbf{k}_2\rangle = \pm a_Q|\mathbf{k}_1\rangle \tag{1.4.11}$$

This requirement is only fulfilled for $P = I$ and $Q = J$. Substitution of these values in (1.4.10) gives (1.4.6). Finally, the matrix element (1.4.7) vanishes trivially since the one-electron operator (1.4.2) can change only one pair of occupation numbers.

Comparing with the Slater–Condon rules for one-electron operators, we note that the second-quantization matrix elements (1.4.3), (1.4.6) and (1.4.7) will agree with their first-quantization counterparts if we make the identification

$$f_{PQ} = \int \phi^*_P(\mathbf{x}) f^c(\mathbf{x}) \phi_Q(\mathbf{x})\, d\mathbf{x} \tag{1.4.12}$$

The recipe for constructing a second-quantization representation of a one-electron operator is therefore to use (1.4.2) with the integrals (1.4.12). For real spin orbitals, the integrals exhibit the following permutational symmetry

$$f_{PQ} = f_{QP} \qquad \text{(real spin orbitals)} \tag{1.4.13}$$

In conclusion, we note that the phase factors (1.2.3) were necessary to reproduce the Slater–Condon rules for matrix elements between Slater determinants.

1.4.2 TWO-ELECTRON OPERATORS

In first quantization, *two-electron operators* such as the electronic-repulsion operator are given by the expression

$$g^{\mathrm{e}} = \tfrac{1}{2} \sum_{i \neq j} g^{\mathrm{e}}(\mathbf{x}_i, \mathbf{x}_j) \tag{1.4.14}$$

Other examples of two-electron operators are the two-electron part of the spin–orbit operator and the mass-polarization operator. A two-electron operator gives nonvanishing matrix elements between Slater determinants if the determinants contain at least two electrons and if they differ in the occupations of at most two pairs of electrons. The second-quantization representation of a two-electron operator therefore has the structure

$$\hat{g} = \tfrac{1}{2} \sum_{PQRS} g_{PQRS} \hat{a}_P^\dagger \hat{a}_R^\dagger a_S a_Q \tag{1.4.15}$$

The annihilation operators appear to the right of the creation operators in order to ensure that $\hat{g}$ gives zero when it works on an ON vector with less than two electrons. The factor of one-half in (1.4.15) is conventional. Anticommuting the creation and annihilation operators and renaming the dummy indices, we obtain

$$\sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q = \sum_{PQRS} g_{PQRS} \hat{a}_R^\dagger \hat{a}_P^\dagger a_Q a_S = \sum_{PQRS} g_{RSPQ} a_P^\dagger a_R^\dagger a_S a_Q \tag{1.4.16}$$

The parameters g_{PQRS} may therefore be chosen in a symmetric fashion

$$g_{PQRS} = g_{RSPQ} \tag{1.4.17}$$

The numerical values of the parameters g_{PQRS} may be determined by evaluating the matrix element of $\hat{g}$ between two ON vectors and setting the result equal to the matrix element between the corresponding Slater determinants. There are four cases.

1. The ON vectors are identical:

$$\langle \mathbf{k} | \hat{g} | \mathbf{k} \rangle = \tfrac{1}{2} \sum_{PQRS} g_{PQRS} \langle \mathbf{k} | a_P^\dagger a_R^\dagger a_S a_Q | \mathbf{k} \rangle = \tfrac{1}{2} \sum_{PR} k_P k_R (g_{PPRR} - g_{PRRP}) \tag{1.4.18}$$

2. The ON vectors differ in one pair of occupation numbers:

$$|\mathbf{k}_1\rangle = |k_1, \ldots, 0_I, \ldots, 1_J, \ldots, k_M\rangle \tag{1.4.19}$$

$$|\mathbf{k}_2\rangle = |k_1, \ldots, 1_I, \ldots, 0_J, \ldots, k_M\rangle \tag{1.4.20}$$

$$\langle \mathbf{k}_2 | \hat{g} | \mathbf{k}_1 \rangle = \Gamma_I^{\mathbf{k}_2} \Gamma_J^{\mathbf{k}_1} \sum_R k_R (g_{IJRR} - g_{IRRJ}) \tag{1.4.21}$$

3. The ON vectors differ in two pairs of occupation numbers:

$$|\mathbf{k}_1\rangle = |k_1, \ldots 0_I, \ldots, 0_J, \ldots, 1_K \ldots 1_L, \ldots, k_M\rangle \tag{1.4.22}$$

$$|\mathbf{k}_2\rangle = |k_1, \ldots, 1_I, \ldots, 1_J, \ldots, 0_K, \ldots, 0_L, \ldots, k_M\rangle \tag{1.4.23}$$

where $I < J$ and $K < L$

$$\langle \mathbf{k}_2 | \hat{g} | \mathbf{k}_1 \rangle = \Gamma_I^{\mathbf{k}_2} \Gamma_J^{\mathbf{k}_2} \Gamma_K^{\mathbf{k}_1} \Gamma_L^{\mathbf{k}_1} (g_{IKJL} - g_{ILJK}) \tag{1.4.24}$$

4. The ON vectors differ in more than two pairs of occupation numbers:

$$\langle \mathbf{k}_2|\hat{g}|\mathbf{k}_1\rangle = 0 \tag{1.4.25}$$

We have in these expressions used the indices I, J, K and L for the spin orbitals with different occupations in the bra and ket vectors.

Let us consider the derivation of these matrix elements in some detail. The diagonal element

$$\langle \mathbf{k}|\hat{g}|\mathbf{k}\rangle = \tfrac{1}{2}\sum_{PQRS}\langle \mathbf{k}|a_P^\dagger a_R^\dagger a_S a_Q|\mathbf{k}\rangle g_{PQRS} \tag{1.4.26}$$

has nonvanishing contributions if

$$a_R a_P|\mathbf{k}\rangle = \pm a_S a_Q|\mathbf{k}\rangle \tag{1.4.27}$$

This condition holds in two different cases

$$\begin{aligned} P &= Q \text{ and } R = S \\ P &= S \text{ and } Q = R \end{aligned} \tag{1.4.28}$$

If both sets of relations are fulfilled, then the expectation value of the creation and annihilation operators vanishes. We may therefore write the diagonal matrix element in the form

$$\begin{aligned} \langle \mathbf{k}|\hat{g}|\mathbf{k}\rangle &= \tfrac{1}{2}\sum_{PR}\langle \mathbf{k}|\hat{a}_P^\dagger a_R^\dagger a_R a_P|\mathbf{k}\rangle g_{PPRR} + \tfrac{1}{2}\sum_{PR}\langle \mathbf{k}|\hat{a}_P^\dagger a_R^\dagger a_P a_R|\mathbf{k}\rangle g_{PRRP} \\ &= \tfrac{1}{2}\sum_{PR}\langle \mathbf{k}|\hat{a}_P^\dagger a_R^\dagger a_R a_P|\mathbf{k}\rangle (g_{PPRR} - g_{PRRP}) \end{aligned} \tag{1.4.29}$$

From the definition of the ON operators (1.3.1) and the commutator (1.3.9), we obtain

$$\hat{a}_P^\dagger a_R^\dagger a_R a_P = \hat{a}_P^\dagger \hat{N}_R a_P = -\delta_{PR}\hat{N}_P + \hat{N}_P\hat{N}_R \tag{1.4.30}$$

The diagonal element (1.4.29) therefore becomes

$$\begin{aligned} \langle \mathbf{k}|\hat{g}|\mathbf{k}\rangle &= \tfrac{1}{2}\sum_{PR}\langle \mathbf{k}| - \delta_{PR}\hat{N}_P + \hat{N}_P\hat{N}_R|\mathbf{k}\rangle (g_{PPRR} - g_{PRRP}) \\ &= \tfrac{1}{2}\sum_{PR} k_P k_R (g_{PPRR} - g_{PRRP}) \end{aligned} \tag{1.4.31}$$

Next, we consider the case where the ON vectors (1.4.19) and (1.4.20) differ in the occupation numbers of one pair of spin orbitals. The matrix element

$$\langle \mathbf{k}_2|\hat{g}|\mathbf{k}_1\rangle = \tfrac{1}{2}\sum_{PQRS}\langle \mathbf{k}_2|a_P^\dagger a_R^\dagger a_S a_Q|\mathbf{k}_1\rangle g_{PQRS} \tag{1.4.32}$$

has nonvanishing contributions if

$$a_R a_P|\mathbf{k}_2\rangle = \pm a_S a_Q|\mathbf{k}_1\rangle \tag{1.4.33}$$

This condition holds in four different cases:

$$\begin{aligned} P &= I,\ Q = J \text{ and } R = S \\ P &= I,\ S = J \text{ and } R = Q \\ R &= I,\ Q = J \text{ and } P = S \\ R &= I,\ S = J \text{ and } P = Q \end{aligned} \tag{1.4.34}$$

Since the matrix element vanishes if several of the above sets of relations hold, we obtain

$$\langle \mathbf{k}_2|\hat{g}|\mathbf{k}_1\rangle = \tfrac{1}{2}\sum_R \langle \mathbf{k}_2|\overset{*}{a}{}_I^\dagger \overset{*}{a}{}_R^\dagger a_R a_J|\mathbf{k}_1\rangle g_{IJRR} + \tfrac{1}{2}\sum_R \langle \mathbf{k}_2|a_I^\dagger \overset{*}{a}{}_R^\dagger a_J a_R|\mathbf{k}_1\rangle g_{IRRJ}$$
$$+ \tfrac{1}{2}\sum_P \langle \mathbf{k}_2|\overset{*}{a}{}_P^\dagger \overset{*}{a}{}_I^\dagger a_P a_J|\mathbf{k}_1\rangle g_{PJIP} + \tfrac{1}{2}\sum_P \langle \mathbf{k}_2|a_P^\dagger a_J^\dagger a_J a_P|\mathbf{k}_1\rangle g_{PPIJ} \qquad (1.4.35)$$

Invoking the permutational symmetry (1.4.17) and the elementary anticommutation relations, we arrive at the final expression (1.4.21)

$$\begin{aligned}\langle \mathbf{k}_2|\hat{g}|\mathbf{k}_1\rangle &= \sum_R{}^{\frown} \langle \mathbf{k}_2|a_I^\dagger a_R^\dagger a_R a_J|\mathbf{k}_1\rangle (g_{IJRR} - g_{IRRJ}) \\ &= \sum_R{}^{\frown} \langle \mathbf{k}_2|a_I^\dagger a_J a_R^\dagger a_R|\mathbf{k}_1\rangle (g_{IJRR} - g_{IRRJ}) \\ &= \Gamma_I^{\mathbf{k}_2}\Gamma_J^{\mathbf{k}_1}\sum_R k_R (g_{IJRR} - g_{IRRJ}) \end{aligned} \qquad (1.4.36)$$

It does not matter whether the occupation numbers in this expression refer to $|\mathbf{k}_1\rangle$ or $|\mathbf{k}_2\rangle$ since the contributions vanish whenever the occupations differ. The matrix element between ON vectors differing in two pairs of occupations (1.4.24) can be treated in the same way and is left as an exercise.

The two-electron second-quantization matrix elements (1.4.18), (1.4.21), (1.4.24) and (1.4.25) become identical to the corresponding first-quantization elements obtained from the Slater–Condon rules if we choose

$$g_{PQRS} = \int\int \phi_P^*(\mathbf{x}_1)\phi_R^*(\mathbf{x}_2) g^{\mathrm{c}}(\mathbf{x}_1, \mathbf{x}_2)\phi_Q(\mathbf{x}_1)\phi_S(\mathbf{x}_2)\,\mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2 \qquad (1.4.37)$$

The recipe for constructing a two-electron second-quantization operator is therefore given by expressions (1.4.15) and (1.4.37). For any interaction between identical particles, the operator $g^{\mathrm{c}}(\mathbf{x}_1, \mathbf{x}_2)$ is symmetric in $\mathbf{x}_1$ and $\mathbf{x}_2$. The integrals (1.4.37) therefore automatically exhibit the permutational symmetry in (1.4.17). We also note the following useful permutational symmetries for real spin orbitals:

$$g_{PQRS} = g_{QPRS} = g_{PQSR} = g_{QPSR} \qquad \text{(real spin orbitals)} \qquad (1.4.38)$$

Thus, for real spin orbitals there are a total of eight permutational symmetries (1.4.17) and (1.4.38) present in the two-electron integrals, whereas for complex spin orbitals there is only one such symmetry (1.4.17).

1.4.3 THE MOLECULAR ELECTRONIC HAMILTONIAN

Combining the results of Sections 1.4.1 and 1.4.2, we may now construct the full second-quantization representation of the electronic Hamiltonian operator in the Born–Oppenheimer approximation. Although not strictly needed for the development of the second-quantization theory in this chapter, we present the detailed form of this operator as an example of the construction of operators in second quantization. In the absence of external fields, the second-quantization nonrelativistic and spin-free *molecular electronic Hamiltonian* is given by

$$\hat{H} = \sum_{PQ} h_{PQ} a_P^\dagger a_Q + \tfrac{1}{2}\sum_{PQRS} g_{PQRS}\overset{*}{a}{}_P^\dagger \overset{*}{a}{}_R^\dagger a_S a_Q + h_{\mathrm{nuc}} \qquad (1.4.39)$$

where in atomic units (which are always used in this book unless otherwise stated)

$$h_{PQ} = \int \phi_P^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_I} \right) \phi_Q(\mathbf{x})\, \mathrm{d}\mathbf{x} \tag{1.4.40}$$

$$g_{PQRS} = \iint \frac{\phi_P^*(\mathbf{x}_1)\phi_R^*(\mathbf{x}_2)\phi_Q(\mathbf{x}_1)\phi_S(\mathbf{x}_2)}{r_{12}}\, \mathrm{d}\mathbf{x}_1\, \mathrm{d}\mathbf{x}_2 \tag{1.4.41}$$

$$h_{\mathrm{nuc}} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{R_{IJ}} \tag{1.4.42}$$

Here the Z_I are the nuclear charges, r_I the electron–nuclear separations, r_{12} the electron–electron separation and R_{IJ} the internuclear separations. The summations are over all nuclei. The scalar term (1.4.42) represents the nuclear-repulsion energy – it is simply added to the Hamiltonian and makes the same contribution to matrix elements as in first quantization since the inner product of two ON vectors is identical to the overlap of the determinants. The molecular one- and two-electron integrals (1.4.40) and (1.4.41) may be calculated using the techniques described in Chapter 9.

The form of the second-quantization Hamiltonian (1.4.39) may be interpreted in the following way. Applied to an electronic state, the Hamiltonian produces a linear combination of the original state with states generated by single and double electron excitations from this state. With each such excitation, there is an associated 'amplitude' h_{PQ} or g_{PQRS}, which represents the probability of this event happening. These probability amplitudes are calculated from the spin orbitals and the one- and two-electron operators according to (1.4.40) and (1.4.41).

1.5 Products of operators in second quantization

In the preceding section, we constructed second-quantization operators for one- and two-electron operators in such a way that the same matrix elements and hence the same expectation values are obtained in the first and second quantizations. Since the expectation values are the only observables in quantum mechanics, we have arrived at a new representation of many-electron systems with the same physical contents as the standard first-quantization representation. In the present section, we examine this new tool in greater detail by comparing the first- and second-quantization representations of operators. In particular, we show that, for operator products $A^{\mathrm{c}}B^{\mathrm{c}} = P^{\mathrm{c}}$, the second-quantization representation of P^{c} may differ from the product of the second-quantization representations of A^{c} and B^{c} unless a complete basis is used.

1.5.1 OPERATOR PRODUCTS

Let A^{c} and B^{c} be two one-electron operators in first quantization

$$A^{\mathrm{c}} = \sum_i A^{\mathrm{c}}(\mathbf{x}_i) \tag{1.5.1}$$

$$B^{\mathrm{c}} = \sum_i B^{\mathrm{c}}(\mathbf{x}_i) \tag{1.5.2}$$

and let $\hat{A}$ and $\hat{B}$ be the corresponding second-quantization representations

$$\hat{A} = \sum_{PQ} A_{PQ} a_P^\dagger a_Q \tag{1.5.3}$$

$$\hat{B} = \sum_{PQ} B_{PQ} a_P^\dagger a_Q \tag{1.5.4}$$

From the construction of the second-quantization operators, it is clear that the first-quantization operator $aA^c + bB^c$, where a and b are numbers, is represented by $a\hat{A} + b\hat{B}$. The standard relations

$$\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C} \tag{1.5.5}$$

$$(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger \tag{1.5.6}$$

for linear operators in a linear vector space are also valid.

We now consider the representation of *operator products*. The product of the two first-quantization operators A^cB^c can be separated into one- and two-electron parts

$$P^c = A^c B^c = O^c + T^c \tag{1.5.7}$$

where

$$O^c = \sum_i A^c(\mathbf{x}_i) B^c(\mathbf{x}_i) \tag{1.5.8}$$

$$T^c = \tfrac{1}{2} \sum_{i \neq j} [A^c(\mathbf{x}_i) B^c(\mathbf{x}_j) + A^c(\mathbf{x}_j) B^c(\mathbf{x}_i)] \tag{1.5.9}$$

The two-electron operator is written so that it is symmetric with respect to permutation of the particle indices. This symmetrization is necessary since we know only how to generate the second-quantization representation of two-electron operators that are symmetric in the particles.

The second-quantization representation $\hat{P}$ of P^c is the sum of the second-quantization representations of O^c and T^c:

$$\hat{P} = \sum_{PQ} O_{PQ} a_P^\dagger a_Q + \tfrac{1}{2} \sum_{PQRS} T_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q \tag{1.5.10}$$

where

$$O_{PQ} = \int \phi_P^*(\mathbf{x}) A^c(\mathbf{x}) B^c(\mathbf{x}) \phi_Q(\mathbf{x})\, d\mathbf{x} \tag{1.5.11}$$

$$\begin{aligned} T_{PQRS} &= \iint \phi_P^*(\mathbf{x}) \phi_R^*(\mathbf{x}') [A^c(\mathbf{x}) B^c(\mathbf{x}') + A^c(\mathbf{x}') B^c(\mathbf{x})] \phi_Q(\mathbf{x}) \phi_S(\mathbf{x}')\, d\mathbf{x}\, d\mathbf{x}' \\ &= A_{PQ} B_{RS} + A_{RS} B_{PQ} \end{aligned} \tag{1.5.12}$$

Inserting this expression for the two-electron parameters in the two-electron part of $\hat{P}$, we obtain

$$\hat{T} = \tfrac{1}{2} \sum_{PQRS} (A_{PQ} B_{RS} + A_{RS} B_{PQ}) a_P^\dagger \overset{\circ}{a}_R^\dagger a_S a_Q = \sum_{PQRS} A_{PQ} B_{RS} \overset{\circ}{a}_P^\dagger \overset{\circ}{a}_R^\dagger a_S a_Q \tag{1.5.13}$$

by substitution of dummy indices. Using the anticommutation relations, we may rewrite this expression as

$$\begin{aligned}\hat{T} &= \sum_{PQRS} A_{PQ}B_{RS}(a_P^\dagger a_Q a_R^\dagger a_S - \delta_{RQ}a_P^\dagger a_S) \\ &= \left(\sum_{PQ} A_{PQ}a_P^\dagger a_Q\right)\left(\sum_{RS} B_{RS}a_R^\dagger a_S\right) - \sum_{PS}\left(\sum_R A_{PR}B_{RS}\right)a_P^\dagger a_S \\ &= \hat{A}\hat{B} - \sum_{PQ}\left(\sum_R A_{PR}B_{RQ}\right)a_P^\dagger a_Q \end{aligned} \tag{1.5.14}$$

Inserting (1.5.14) in (1.5.10), we finally arrive at the expression

$$\hat{P} = \hat{A}\hat{B} + \sum_{PQ}\left(O_{PQ} - \sum_R A_{PR}B_{RQ}\right)a_P^\dagger a_Q \tag{1.5.15}$$

which shows that the second-quantization representation of $A^c B^c$ is in general not equal to the product of the representations of A^c and B^c.

We shall now demonstrate that the last term in (1.5.15) vanishes for a complete basis. We use the *Dirac delta function* $\delta(\mathbf{x} - \mathbf{x}')$, defined by the relationship [2,3]

$$\int f(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')\,d\mathbf{x} = f(\mathbf{x}') \tag{1.5.16}$$

For a complete one-electron basis, the delta function may be written in the form

$$\delta(\mathbf{x} - \mathbf{x}') = \sum_{P=1}^{\infty} \phi_P(\mathbf{x})\phi_P^*(\mathbf{x}') \qquad \text{(complete basis)} \tag{1.5.17}$$

Assuming that (1.5.17) holds, we may now write

$$\begin{aligned} O_{PQ} &= \int \phi_P^*(\mathbf{x})A^c(\mathbf{x})B^c(\mathbf{x})\phi_Q(\mathbf{x})\,d\mathbf{x} \\ &= \int\int \phi_P^*(\mathbf{x})A^c(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')B^c(\mathbf{x}')\phi_Q(\mathbf{x}')\,d\mathbf{x}\,d\mathbf{x}' \\ &= \int\int \phi_P^*(\mathbf{x})A^c(\mathbf{x})\left[\sum_{R=1}^{\infty}\phi_R(\mathbf{x})\phi_R^*(\mathbf{x}')\right]B^c(\mathbf{x}')\phi_Q(\mathbf{x}')\,d\mathbf{x}\,d\mathbf{x}' \\ &= \sum_{R\ 1}^{\infty} A_{PR}B_{RQ} \qquad \text{(complete basis)} \end{aligned} \tag{1.5.18}$$

and the last term in (1.5.15) vanishes. We therefore have for a complete one-electron basis

$$P^c = A^c B^c \Rightarrow \hat{P} = \hat{A}\hat{B} \qquad \text{(complete basis)} \tag{1.5.19}$$

but for finite basis sets this expression does not hold.

The second-quantization operators are projections of the exact operators onto a basis of spin orbitals. For an incomplete basis, the second-quantization representation of an operator product therefore depends on when the projection is made. For a complete basis, however, the representation is exact and independent of when the projection is made.

1.5.2 THE CANONICAL COMMUTATORS

The previous discussion suggests that commutation relations that hold for operators in first quantization, do not necessarily hold for their second-quantization counterparts in a finite basis. Consider the *canonical commutators*

$$[r_\alpha^c,\ p_\beta^c] = i\delta_{\alpha\beta}^c \tag{1.5.20}$$

where we have contributions from each of the N electrons

$$r_\alpha^c = \sum_{i=1}^{N} r_\alpha^c(i) \tag{1.5.21}$$

$$p_\nu^c = \sum_{i=1}^{N} p_\alpha^c(i) \tag{1.5.22}$$

$$\delta_{\alpha\beta}^c = \sum_{i\ \ 1}^{N} \delta_{\alpha\beta}(i) \tag{1.5.23}$$

and Greek letters denote Cartesian directions. The relationship (1.5.20) holds exactly for first-quantization operators. Note carefully that the operator (1.5.23) depends on the number of electrons and is not the usual Kronecker delta. The second-quantization representations of the position and momentum operators are

$$\hat{r}_\alpha = \sum_{PQ} [r_\alpha^c]_{PQ} \hat{a_P^\dagger} a_Q \tag{1.5.24}$$

$$\hat{p}_\alpha = \sum_{PQ} [p_\alpha^c]_{PQ} \hat{a_P^\dagger} a_Q \tag{1.5.25}$$

and the commutator of these operators becomes

$$[\hat{r}_\alpha,\ \hat{p}_\beta] = \sum_{PQRS} [r_\alpha^c]_{PQ} [p_\beta^c]_{RS} [\hat{a_P^\dagger} a_Q,\ a_R^\dagger a_S] \tag{1.5.26}$$

In these expressions, square brackets around a first-quantization operator represent the one-electron integral of this operator in the given basis. This somewhat cumbersome notation is adopted for this discussion to make the dependence of the integrals on the first-quantization operators explicit.

In Section 1.8, the commutator between the two excitation operators is shown to be

$$[a_P^\dagger a_Q,\ \hat{a_R^\dagger} a_S] = \delta_{RQ} a_P^\dagger a_S - \delta_{PS} a_R^\dagger a_Q \tag{1.5.27}$$

and the commutator (1.5.26) therefore reduces to

$$[\hat{r}_\alpha,\ \hat{p}_\beta] = \sum_{PQ} \hat{a_P^\dagger} a_Q \sum_R ([r_\alpha^c]_{PR} [p_\beta^c]_{RQ} - [p_\beta^c]_{PR} [r_\alpha^c]_{RQ}) \tag{1.5.28}$$

For a complete basis, we may use (1.5.18) and arrive at the following simplifications:

$$\sum_{R=1}^{\infty} [r_\alpha^c]_{PR} [p_\beta^c]_{RQ} = [r_\alpha^c p_\beta^c]_{PQ} \quad \text{(complete basis)} \tag{1.5.29}$$

$$\sum_{K=1}^{\infty} [p_\beta^c]_{PK}[r_\alpha^c]_{KQ} = [p_\beta^c r_\alpha^c]_{PQ} \quad \text{(complete basis)} \tag{1.5.30}$$

The second-quantization canonical commutator therefore becomes proportional to the number operator in the limit of a complete basis:

$$[\hat{r}_\alpha, \hat{p}_\beta] = \sum_{P,Q=1}^{\infty} [[r_\alpha^c, p_\beta^c]]_{PQ} a_P^\dagger a_Q = \mathrm{i} \sum_{P,Q=1}^{\infty} [\delta_{\alpha\beta}^c]_{PQ} a_P^\dagger a_Q = \mathrm{i}\delta_{\alpha\beta}\hat{N} \quad \text{(complete basis)} \tag{1.5.31}$$

This expression should be compared with its first-quantization counterpart (1.5.20). For finite basis sets, the second-quantization canonical commutator turns into a general one-electron operator (1.5.28).

1.6 First- and second-quantization operators compared

In Box 1.2, we summarize some of the characteristics of operators in the first and second quantizations. The dependence on the spin-orbital basis is different in the two representations. In first quantization, the Slater determinants depend on the spin-orbital basis whereas the operators are independent of the spin orbitals. In the second-quantization formalism, the ON vectors are basis vectors in a linear vector space and contain no reference to the spin-orbital basis. Instead, the reference to the spin-orbital basis is made in the operators. We also note that, whereas the first-quantization operators depend explicitly on the number of electrons, no such dependence is found in the second-quantization operators.

Box 1.2 First- and second-quantization operators compared

First quantization	Second quantization
→ one-electron operator: $\sum_i f^c(\mathbf{x}_i)$	→ one-electron operator: $\sum_{PQ} f_{PQ} a_P^\dagger a_Q$
→ two-electron operator: $\frac{1}{2}\sum_{i\neq j} g^c(\mathbf{x}_i, \mathbf{x}_j)$	→ two-electron operator: $\frac{1}{2}\sum_{PQRS} g_{PQRS} a_P^\dagger a_R^\dagger a_S a_Q$
→ operators are independent of the spin-orbital basis	→ operators depend on the spin-orbital basis
→ operators depend on the number of electrons	→ operators are independent of the number of electrons
→ exact operators	→ projected operators

The fact that the second-quantization operators are projections of the exact operators onto the spin-orbital basis means that a second-quantization operator times an ON vector is just another

vector in the Fock space. By contrast, a first-quantization operator times a determinant cannot be expanded as a sum of Slater determinants in a finite basis. This fact often goes unnoticed since, in the first quantization, we usually work directly with matrix elements.

The projected nature of the second-quantization operators has many ramifications. For example, relations that hold for exact operators such as the canonical commutation properties of the coordinate and momentum operators do not necessarily hold for projected operators. Similarly, the projected coordinate operator does not commute with the projected Coulomb repulsion operator. It should be emphasized, however, that these problems are not peculiar to second quantization but arise whenever a finite basis is employed. They also arise in first quantization, but not until the matrix elements are evaluated.

Second quantization treats operators and wave functions in a unified way – they are all expressed in terms of the elementary creation and annihilation operators. This property of the second-quantization formalism can, for example, be exploited to express modifications to the wave function as changes in the operators. To illustrate the unified description of states and operators afforded by second quantization, we note that any ON vector may be written compactly as a string of creation operators working on the vacuum state (1.2.4)

$$|\mathbf{k}\rangle = \hat{X}_{\mathbf{k}}|\text{vac}\rangle = \left[\prod_{P=1}^{M} (a_P^{\dagger})^{k_P}\right] |\text{vac}\rangle \tag{1.6.1}$$

Matrix elements may therefore be viewed as the *vacuum expectation value* of an operator

$$\langle \mathbf{k}|\hat{O}|\mathbf{m}\rangle = \langle \text{vac}|\hat{X}_{\mathbf{k}}^{\dagger}\hat{O}\hat{X}_{\mathbf{m}}|\text{vac}\rangle \tag{1.6.2}$$

and expectation values become linear combinations of vacuum expectation values. The unified description of states and operators in terms of the elementary creation and annihilation operators enables us to carry out most of our manipulations algebraically based on the anticommutation relations of these operators. Thus, the antisymmetry of the electronic wave function follows automatically from the algebra of the elementary operators without the need to keep track of phase factors.

1.7 Density matrices

Having considered the representation of states and operators in second quantization, let us now turn our attention to expectation values. As in first quantization, the evaluation of expectation values is carried out by means of density matrices [4]. Consider a general one- and two-electron Hermitian operator in the spin-orbital basis

$$\hat{\Omega} = \sum_{PQ} \Omega_{PQ} a_P^{\dagger} a_Q + \tfrac{1}{2} \sum_{PQRS} \Omega_{PQRS} a_P^{\dagger} a_R^{\dagger} a_S a_Q + \Omega_0 \tag{1.7.1}$$

The *expectation value* of this operator with respect to a normalized reference state $|0\rangle$ written as a linear combination of ON vectors,

$$|0\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}}|\mathbf{k}\rangle \tag{1.7.2}$$

$$\langle 0|0\rangle = 1 \tag{1.7.3}$$

is given by the expression

$$\langle 0|\hat{\Omega}|0\rangle = \sum_{PQ} \overline{D}_{PQ}\Omega_{PQ} + \tfrac{1}{2}\sum_{PQRS} d_{PQRS}\Omega_{PQRS} + \Omega_0 \tag{1.7.4}$$

where we have introduced the matrix elements

$$\overline{D}_{PQ} = \langle 0|a_P^\dagger a_Q|0\rangle \tag{1.7.5}$$

$$\overline{d}_{PQRS} = \langle 0|a_P^\dagger a_R^\dagger a_S a_Q|0\rangle \tag{1.7.6}$$

Clearly, all information that is required about the wave function (1.7.2) for the evaluation of expectation values (1.7.4) is embodied in the quantities (1.7.5) and (1.7.6) called the *one- and two-electron density-matrix elements*, respectively. Overbars are used for the spin-orbital densities to distinguish these from those that will be introduced in Chapter 2 for the orbital basis. Since the density elements play such an important role in electronic-structure theory, it is appropriate here to examine their properties within the framework of second quantization.

1.7.1 THE ONE-ELECTRON DENSITY MATRIX

The densities (1.7.5) constitute the elements of an $M \times M$ Hermitian matrix – the *one-electron spin-orbital density matrix* $\overline{\mathbf{D}}$ – since the following relation is satisfied:

$$\overline{D}_{PQ}^* = \langle 0|a_P^\dagger a_Q|0\rangle^* = \langle 0|a_Q^\dagger a_P|0\rangle = \overline{D}_{QP} \tag{1.7.7}$$

For real wave functions, the matrix is symmetric:

$$D_{PQ} = D_{QP} \quad \text{(real wave functions)} \tag{1.7.8}$$

The one-electron density matrix is positive semidefinite since its elements are either trivially equal to zero or inner products of states in the subspace $F(M, N-1)$. The diagonal elements of the spin-orbital density matrix are the expectation values of the occupation-number operators (1.3.1) in $F(M, N)$ and are referred to as the *occupation numbers* ω_P of the electronic state:

$$\omega_P = \overline{D}_{PP} = \langle 0|\hat{N}_P|0\rangle \tag{1.7.9}$$

This terminology is appropriate since the diagonal elements of $\mathbf{D}$ reduce to the usual occupation numbers k_P in (1.3.2) whenever the reference state is an eigenfunction of the ON operators – that is, when the reference state is an ON vector:

$$\langle \mathbf{k}|\hat{N}_P|\mathbf{k}\rangle = k_P \tag{1.7.10}$$

Since the ON operators are projectors (1.3.5), we may write the occupation numbers in the form

$$\overline{\omega}_P = \langle 0|\hat{N}_P\hat{N}_P|0\rangle \tag{1.7.11}$$

where the projected electronic state is given by

$$\hat{N}_P|0\rangle = \sum_{\mathbf{k}} k_P c_{\mathbf{k}}|\mathbf{k}\rangle \tag{1.7.12}$$

The occupation numbers $\overline{\omega}_P$ may now be written in the form

$$\overline{\omega}_P = \sum_{\mathbf{k}} k_P |c_{\mathbf{k}}|^2 \tag{1.7.13}$$

and interpreted as the squared norm of the part of the reference state where spin orbital ϕ_P is occupied in each ON vector. The occupation numbers ω_P thus serve as indicators of the importance of the spin orbitals in the electronic state.

The expansion coefficients satisfy the normalization condition

$$\sum_{\mathbf{k}} |c_{\mathbf{k}}|^2 = 1 \tag{1.7.14}$$

Recalling that the occupation numbers k_P of an ON vector are zero or one, we conclude that the occupation numbers ω_P of an electronic state (1.7.13) are real numbers between zero and one – zero for spin orbitals that are unoccupied in all ON vectors, one for spin orbitals that are occupied in all ON vectors, and nonintegral for spin orbitals that are occupied in some but not all ON vectors:

$$0 \leq \overline{\omega}_P \leq 1 \tag{1.7.15}$$

We also note that the sum of the occupation numbers (i.e. the trace of the density matrix) is equal to the total number of electrons in the system:

$$\mathrm{Tr}\overline{\mathbf{D}} = \sum_P \overline{\omega}_P = \sum_P \langle 0|\hat{N}_P|0\rangle = \langle 0|\hat{N}|0\rangle = N \tag{1.7.16}$$

Here we have used the definition of the particle-number operator (1.3.12).

For a state consisting of a single ON vector, the one-electron spin-orbital density matrix has a simple diagonal structure:

$$D^{\mathbf{k}}_{PQ} = \langle \mathbf{k}|a^{\dagger}_P a_Q|\mathbf{k}\rangle = \delta_{PQ}k_P \tag{1.7.17}$$

By contrast, for an electronic state containing several ON vectors, the density matrix is not diagonal. Applying the Schwarz inequality in the $(N-1)$-electron space, we obtain

$$|\langle 0|a^{\dagger}_P a_Q|0\rangle|^2 \leq \langle 0|a^{\dagger}_P a_P|0\rangle\langle 0|a^{\dagger}_Q a_Q|0\rangle \tag{1.7.18}$$

which gives us an upper bound to the magnitude of the elements of the spin-orbital density matrix equal to the geometric mean of the occupation numbers:

$$|\overline{D}_{PQ}| \leq \sqrt{\overline{\omega}_P \overline{\omega}_Q} \tag{1.7.19}$$

Of course, since $\mathbf{D}$ is a Hermitian matrix, we may eliminate the off-diagonal elements (1.7.19) completely by diagonalization with a unitary matrix:

$$\overline{\mathbf{D}} = \mathbf{U}\overline{\boldsymbol{\eta}}\mathbf{U}^{\dagger} \tag{1.7.20}$$

The eigenvalues are real numbers $0 \leq \overline{\eta}_P \leq 1$, known as *the natural-orbital occupation numbers*. The sum of the natural-orbital occupation numbers is again equal to the number of electrons in the system. From the eigenvectors $\mathbf{U}$ of the density matrix, we obtain a new set of spin orbitals called the *natural spin orbitals* of the system. However, we defer the discussion of unitary orbital transformations to Chapter 3.

1.7.2 THE TWO-ELECTRON DENSITY MATRIX

We now turn our attention to the *two-electron density matrix*. We begin by noting that the two-electron density-matrix elements (1.7.6) are not all independent because of the anticommutation

relations between the creation operators and between the annihilation operators:

$$d_{PQRS} = -d_{RQPS} = -d_{PSRQ} = d_{RSPQ} \tag{1.7.21}$$

The following elements are therefore zero in accordance with the Pauli principle:

$$\overline{d}_{PQPS} = \overline{d}_{PQRQ} = \overline{d}_{PQPQ} = 0 \tag{1.7.22}$$

To avoid these redundancies in our representation, we introduce the two-electron density matrix $\overline{\mathbf{T}}$ with elements given by

$$T_{PQ,RS} = \langle 0|a_P^\dagger a_Q^\dagger a_S a_R|0\rangle, \qquad P > Q, R > S \tag{1.7.23}$$

There are $M(M-1)/2$ rows and columns in this matrix with composite indices PQ such that $P > Q$. The elements of $\overline{\mathbf{T}}$ constitute a subset of the two-electron density elements (1.7.6) and differ from these by a reordering of the middle indices:

$$T_{PQ,RS} = \overline{d}_{PRQS}, \qquad P > Q, R > S \tag{1.7.24}$$

The reason for introducing this reordering is that it allows us to examine the two-electron density matrix by analogy with the discussion of the one-electron density in Section 1.7.1. Thus, as in the one-electron case, we note that the two-electron density matrix $\mathbf{T}$ is Hermitian

$$\overline{T}^*_{PQ,RS} = \langle 0|a_P^\dagger a_Q^\dagger a_S a_R|0\rangle^* = \langle 0|a_R^\dagger a_S^\dagger a_Q a_P|0\rangle = \overline{T}_{RS,PQ} \tag{1.7.25}$$

and therefore symmetric for real wave functions

$$\overline{T}_{PQ,RS} = \overline{T}_{RS,PQ} \qquad \text{(real wave functions)} \tag{1.7.26}$$

Also, the two-electron density matrix $\overline{\mathbf{T}}$ is positive semidefinite since its elements are either trivially equal to zero or inner products of states in $F(M, N-2)$.

We recall that the diagonal elements of $\overline{\mathbf{D}}$ correspond to expectation values of ON operators (1.7.9) and are interpreted as the occupation numbers of the spin orbitals. We now examine the diagonal elements of the two-electron density matrix:

$$\overline{T}_{PQ,PQ} = \langle 0|a_P^\dagger a_Q^\dagger a_Q a_P|0\rangle \tag{1.7.27}$$

Since $P > Q$, we may anticommute a_P from the fourth to the second position, introduce ON operators, and arrive at the following expression analogous to (1.7.9):

$$\omega_{PQ} = \overline{T}_{PQ,PQ} = \langle 0|\hat{N}_P \hat{N}_Q|0\rangle \tag{1.7.28}$$

Since the ON operators are projectors, we may now interpret the diagonal elements $\overline{\omega}_{PQ}$ as *simultaneous occupations of pairs of spin orbitals (pair occupations)*, noting that $\overline{\omega}_{PQ}$ represents the squared amplitude of the part of the wave function where spin orbitals ϕ_P and ϕ_Q are simultaneously occupied:

$$\hat{N}_P \hat{N}_Q|0\rangle = \sum_{\mathbf{k}}{}' k_P k_Q c_{\mathbf{k}}|\mathbf{k}\rangle \tag{1.7.29}$$

The norm of the wave function is successively reduced by the repeated application of ON projectors; compare (1.7.12) and (1.7.29). This observation agrees with the expectation that the

simultaneous occupation of a given spin-orbital pair cannot exceed those of the individual spin orbitals:

$$0 \leq \overline{\omega}_{PQ} \leq \min(\overline{\omega}_P, \overline{\omega}_Q) \leq 1 \tag{1.7.30}$$

The reader may wish to verify that a weaker upper bound to the pair occupations

$$\omega_{PQ} \leq \sqrt{\omega_P \omega_Q} \tag{1.7.31}$$

is arrived at by the application of the Schwarz inequality to (1.7.28). From the trace of the two-electron density matrix

$$\begin{aligned} \mathrm{Tr}\ \mathbf{T} &= \sum_{P>Q} \langle 0|\hat{N}_P \hat{N}_Q|0\rangle = \tfrac{1}{2}\sum_{PQ} \langle 0|\hat{N}_P \hat{N}_Q|0\rangle - \tfrac{1}{2}\sum_{P} \langle 0|\hat{N}_P|0\rangle \\ &= \tfrac{1}{2}\langle 0|\hat{N}^2 - \hat{N}|0\rangle = \tfrac{1}{2}N(N-1) \end{aligned} \tag{1.7.32}$$

we find that the sum of all pair occupations ω_{PQ} is equal to the number of electron pairs in the system in the same way that the sum of all single occupations $\overline{\omega}_P$ is equal to the number of electrons in the system (1.7.16). We may summarize these results by stating that the one-electron density matrix probes the individual occupancies of the spin orbitals and describes how the N electrons are distributed among the M spin orbitals, whereas the two-electron density matrix probes the simultaneous occupations of the spin orbitals and describes how the $N(N-1)/2$ electron pairs are distributed among the $M(M-1)/2$ spin-orbital pairs.

For a state containing a single ON vector, the two-electron density matrix has a particularly simple diagonal structure with the following elements

$$\overline{T}^{\mathbf{k}}_{PQ,RS} = \langle \mathbf{k}|a_P^\dagger a_Q^\dagger a_S a_R|\mathbf{k}\rangle = \delta_{PR}\delta_{QS}k_P k_Q \tag{1.7.33}$$

recalling the conditions $P > Q$ and $R > S$. Indeed, for such electronic states, the two-electron density matrix T may be constructed directly from the one-electron density matrix

$$\overline{T}^{\mathbf{k}}_{PQ,RS} = \overline{D}^{\mathbf{k}}_{PR}\overline{D}^{\mathbf{k}}_{QS} \tag{1.7.34}$$

and likewise the expectation value of any one- and two-electron operator may be obtained directly from the one-electron density matrix. This observation is consistent with our picture of ON vectors (i.e. determinants) as representing an uncorrelated description of the electronic system where the simultaneous occupations of pairs of spin orbitals are just the products of the individual occupations.

For a general electronic state, containing more than one ON vector and providing a correlated treatment of the electronic system, the two-electron density matrix is in general not diagonal and cannot be generated directly from the one-electron density elements. As in the one-electron case (1.7.19), we may invoke the Schwarz inequality to establish an upper bound to the magnitude of the off-diagonal elements

$$|\overline{T}_{PQ,RS}| \leq \sqrt{\omega_{PQ}\omega_{RS}} \tag{1.7.35}$$

and we may in principle diagonalize $\mathbf{T}$ to obtain a more compact representation of the two-electron density, but this is seldom done in practice.

1.7.3 DENSITY MATRICES IN SPIN-ORBITAL AND COORDINATE REPRESENTATIONS

The density matrices we have discussed so far in this section have all been given in the spin-orbital representation. We shall now see how these matrices are represented in the coordinate

representation of quantum mechanics. Since we have not here developed a second-quantization formalism appropriate for the coordinate representation, we shall draw on the equivalence between matrix elements in the first and second quantizations to establish the relationship between density matrices in the spin-orbital and coordinate representations.

We recall that, in the coordinate representation of first quantization, we may write the expectation value of any one-electron operator in the following form

$$\langle \Psi | f^c | \Psi \rangle = \int [f^c(\mathbf{x}_1)\gamma_1(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1' = \mathbf{x}_1} \, d\mathbf{x}_1 \tag{1.7.36}$$

in terms of the *first-order reduced density matrix*

$$\gamma_1(\mathbf{x}_1, \mathbf{x}_1') = N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\Psi^*(\mathbf{x}_1', \mathbf{x}_2, \ldots, \mathbf{x}_N)\, d\mathbf{x}_2 \cdots d\mathbf{x}_N \tag{1.7.37}$$

The density matrix in the spin-orbital representation was introduced in second quantization for the evaluation of one-electron expectation values in the following form

$$\langle 0 | \hat{f} | 0 \rangle = \sum_{PQ} \overline{D}_{PQ} f_{PQ} \tag{1.7.38}$$

where the integrals are those given in (1.4.12):

$$f_{PQ} = \int \phi_P^*(\mathbf{x}_1) f^c(\mathbf{x}_1) \phi_Q(\mathbf{x}_1)\, d\mathbf{x}_1 \tag{1.7.39}$$

Combining (1.7.38) and (1.7.39), we obtain

$$\begin{aligned} \langle 0 | \hat{f} | 0 \rangle &= \sum_{PQ} D_{PQ} \int \phi_P^*(\mathbf{x}_1) f^c(\mathbf{x}_1) \phi_Q(\mathbf{x}_1)\, d\mathbf{x}_1 \\ &= \int \left[f^c(\mathbf{x}_1) \sum_{PQ} D_{PQ} \phi_P^*(\mathbf{x}_1') \phi_Q(\mathbf{x}_1) \right]_{\mathbf{x}_1' = \mathbf{x}_1} d\mathbf{x}_1 \end{aligned} \tag{1.7.40}$$

and we are therefore able to make the identification

$$\gamma_1(\mathbf{x}_1, \mathbf{x}_1') = \sum_{PQ} D_{PQ} \phi_P^*(\mathbf{x}_1') \phi_Q(\mathbf{x}_1) \tag{1.7.41}$$

involving the spin-orbital density matrix $\mathbf{D}$ and the first-order reduced density matrix $\gamma_1(\mathbf{x}_1, \mathbf{x}_1')$. Since the spin orbitals are orthonormal, we obtain the following expression after multiplication by spin orbitals and integration

$$\langle 0 | a_P^\dagger a_Q | 0 \rangle = \int \phi_Q^*(\mathbf{x}_1) \gamma_1(\mathbf{x}_1, \mathbf{x}_1') \phi_P(\mathbf{x}_1')\, d\mathbf{x}_1\, d\mathbf{x}_1' \tag{1.7.42}$$

where we have used (1.7.5). This equation displays the relationship between the density matrices in the spin-orbital representation and in the coordinate representation. We may establish similar relationships for the two-electron densities. Thus, introducing the *second-order reduced density matrix*

$$\gamma_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2') = \frac{N(N-1)}{2} \int \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)\Psi^*(\mathbf{x}_1', \mathbf{x}_2', \mathbf{x}_3, \ldots, \mathbf{x}_N)\, d\mathbf{x}_3 \cdots d\mathbf{x}_N \tag{1.7.43}$$

we obtain the following relationships

$$\gamma_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2') = \tfrac{1}{2} \sum_{PQRS} \overline{d}_{PQRS} \phi_P^*(\mathbf{x}_1') \phi_Q(\mathbf{x}_1) \phi_R^*(\mathbf{x}_2') \phi_S(\mathbf{x}_2) \tag{1.7.44}$$

$$\langle 0 | a_P^\dagger a_R^\dagger a_S a_Q | 0 \rangle = 2 \int \phi_Q^*(\mathbf{x}_1) \phi_S^*(\mathbf{x}_2) \gamma_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_1', \mathbf{x}_2') \phi_P(\mathbf{x}_1') \phi_R(\mathbf{x}_2') \, d\mathbf{x}_1 \, d\mathbf{x}_2 \, d\mathbf{x}_1' \, d\mathbf{x}_2' \tag{1.7.45}$$

analogous to (1.7.41) and (1.7.42). The simple algebraic definitions for the densities in second quantization (as expectation values of excitation operators) should be contrasted with the more complicated expression in terms of the reduced densities.

1.8 Commutators and anticommutators

In the manipulation of operators and matrix elements in second quantization, the *commutator*

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{1.8.1}$$

and the *anticommutator*

$$[\hat{A}, \hat{B}]_+ = \hat{A}\hat{B} + \hat{B}\hat{A} \tag{1.8.2}$$

of two operators are often encountered. The elementary creation and annihilation operators satisfy the anticommutation relations (1.2.27)–(1.2.29). Referring to these basic relations, it is usually possible to simplify the commutators and anticommutators between strings of elementary operators considerably. Since manipulations in second quantization frequently involve complicated operator strings, it is important to establish a good strategy for the evaluation of commutators and anticommutators of such strings.

Before considering the evaluation and simplification of commutators and anticommutators, it is useful to introduce the concepts of operator rank and rank reduction. The *(particle) rank* of a string of creation and annihilation operators is simply the number of elementary operators divided by 2. For example, the rank of a creation operator is 1/2 and the rank of an ON operator is 1. *Rank reduction* is said to occur when the rank of a commutator or anticommutator is lower than the combined rank of the operators commuted or anticommuted. Consider the basic anticommutation relation

$$a_P^\dagger a_P + a_P a_P^\dagger = 1 \tag{1.8.3}$$

Here the combined rank of the creation and annihilation operators is 1 whereas the rank of the anticommutator itself is 0. Anticommutation thus reduces the rank by 1.

Rank reduction is desirable since it simplifies the expression. It would clearly be useful if we were able to distinguish at a glance those commutators and anticommutators that reduce the operator rank from those that do not. The following simple rule is sufficient for this purpose: *Rank reduction follows upon anticommutation of two strings of half-integral rank and upon commutation of all other strings.* In Exercise 1.2, rank reduction is demonstrated for a commutator of two strings of integral rank. The remaining cases may be proved in the same manner. The basic anticommutation relations of the elementary operators (1.2.27)–(1.2.29) are the prototypes of rank reduction for strings of half-integral rank.

We now return to the evaluation of commutators and anticommutators. One useful strategy for the evaluation of such expressions is based on their linear expansion in simpler commutators or

anticommutators according to the operator identities

$$[\hat{A}, \hat{B}_1\hat{B}_2] = [\hat{A}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{A}, \hat{B}_2] \tag{1.8.4}$$

$$[\hat{A}, \hat{B}_1 \cdots \hat{B}_n] = \sum_{k=1}^{n} \hat{B}_1 \cdots \hat{B}_{k-1}[\hat{A}, \hat{B}_k]\hat{B}_{k+1} \cdots \hat{B}_n \tag{1.8.5}$$

$$[\hat{A}, \hat{B}_1\hat{B}_2] = [\hat{A}, \hat{B}_1]_+\hat{B}_2 - \hat{B}_1[\hat{A}, \hat{B}_2]_+ \tag{1.8.6}$$

$$[\hat{A}, \hat{B}_1 \cdots \hat{B}_n] = \sum_{k=1}^{n}(-1)^{k-1}\hat{B}_1 \cdots [\hat{A}, \hat{B}_k]_{\mp} \cdots \hat{B}_n \quad (n \text{ even}) \tag{1.8.7}$$

$$[\hat{A}, \hat{B}_1\hat{B}_2]_{\mp} = [\hat{A}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{A}, \hat{B}_2]_{\mp} = [\hat{A}, \hat{B}_1]_{\mp}\hat{B}_2 - \hat{B}_1[\hat{A}, \hat{B}_2] \tag{1.8.8}$$

$$[\hat{A}, \hat{B}_1 \cdots \hat{B}_n]_- = \sum_{k=1}^{n}(-1)^{k-1}\hat{B}_1 \cdots [\hat{A}, \hat{B}_k]_+ \cdots \hat{B}_n \qquad (n \text{ odd}) \tag{1.8.9}$$

Note that the commutators and anticommutators on the right-hand side of these expressions contain fewer operators than does the commutator or the anticommutator on the left-hand side. For proofs, see Exercise 1.3. In deciding what identity to apply in a given case, we follow the 'principle of rank reduction' – that is, we try to expand the expression in commutators or anticommutators that, to the greatest extent possible, exhibit rank reduction.

Let us consider the simplest nontrivial commutator – $[a_P^{\dagger}, a_Q^{\dagger}a_R]$. Moving one of the operators in $a_Q^{\dagger}a_R$ outside the commutator according to the identities (1.8.4) or (1.8.6), we are left either with commutators or with anticommutators of two elementary operators – strings of half-integral rank. In order to reduce the rank and thus the number of operators, we choose the anticommutator expansion (1.8.6):

$$[a_P^{\dagger}, a_Q^{\dagger}a_R] = [a_P^{\dagger}, a_Q^{\dagger}]_+a_R - a_Q^{\dagger}[a_P^{\dagger}, a_R]_- \tag{1.8.10}$$

The basic anticommutation relations can now be invoked to give

$$[a_P^{\dagger}, a_Q^{\dagger}a_R] = -\delta_{PR}a_Q^{\dagger} \tag{1.8.11}$$

Proceeding in the same manner, we also obtain

$$[a_P, a_Q^{\dagger}a_R] = \delta_{PQ}a_R \tag{1.8.12}$$

but we note that this expression is perhaps more easily obtained by conjugating (1.8.11).

The commutator relations (1.8.11) and (1.8.12) may now be used to simplify more complicated commutators. Invoking (1.8.4), we obtain for the commutator between two excitation operators

$$[a_P^{\dagger}a_Q, a_R^{\dagger}a_S] = [a_P^{\dagger}, a_R^{\dagger}a_S]a_Q + a_P^{\dagger}[a_Q, a_R^{\dagger}a_S] \tag{1.8.13}$$

This commutator is expanded in commutators rather than anticommutators since one of the operators on the right-hand side contains two elementary operators. Inserting (1.8.11) and (1.8.12) in this expression, we obtain

$$[a_P^{\dagger}a_Q, a_R^{\dagger}a_S] = \delta_{QR}a_P^{\dagger}a_S - \delta_{PS}a_R^{\dagger}a_Q \tag{1.8.14}$$

We can now proceed to even more complicated commutators. The proof of the following relationship is left as an exercise:

$$[a_P^{\dagger}a_Q, a_R^{\dagger}a_S a_M^{\dagger}a_N] = \delta_{QR}a_P^{\dagger}a_S a_M^{\dagger}a_N - \delta_{PS}a_R^{\dagger}a_Q a_M^{\dagger}a_N + \delta_{QM}a_R^{\dagger}a_S a_P^{\dagger}a_N - \delta_{PN}a_R^{\dagger}a_S a_M^{\dagger}a_Q \tag{1.8.15}$$

The preceding examples should suffice to illustrate the usefulness of the expansions (1.8.4)–(1.8.9) for evaluating commutators and anticommutators involving elementary operators.

Let us finally consider *nested commutators*. Nested commutators may be simplified by the same techniques as the single commutators, thus giving rise to rank reductions greater than 1. For example, the following *double commutator* is easily evaluated using (1.8.14):

$$[a_P^\dagger a_Q, [a_R^\dagger a_S, a_M^\dagger a_N]] = \delta_{SM}\delta_{QR}a_P^\dagger a_N - \delta_{SM}\delta_{PN}a_R^\dagger a_Q - \delta_{RN}\delta_{QM}a_P^\dagger a_S + \delta_{RN}\delta_{PS}a_M^\dagger a_Q \tag{1.8.16}$$

The particle rank is reduced by 2. In manipulating and simplifying nested commutators, the *Jacobi identity* is often useful:

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{C}, [\hat{A}, \hat{B}]] + [\hat{B}, [\hat{C}, \hat{A}]] = 0 \tag{1.8.17}$$

This identity is easily verified by expansion. Note that the Jacobi identity is different from the expansions (1.8.4)–(1.8.9) in that it relates expressions of the same rank and structure.

1.9 Nonorthogonal spin orbitals

Our discussion so far has been concerned with the development of the second-quantization formalism for an orthonormal basis. Occasionally, however, we shall find it more convenient to work with spin orbitals that are not orthogonal. We therefore extend the formalism of second quantization to deal with such spin orbitals, drawing heavily on the development in the preceding sections.

Consider a set of *nonorthogonal spin orbitals* with overlap

$$S_{PQ} = \int \phi_P^*(\mathbf{x})\phi_Q(\mathbf{x})\,\mathrm{d}\mathbf{x} \tag{1.9.1}$$

A Fock space for these spin orbitals can now be constructed as an abstract vector space using ON vectors as basis vectors in much the same way as for orthonormal spin orbitals. The inner product of the Fock space is defined such that, for vectors with the same number of electrons, it is equal to the overlap between the corresponding Slater determinants. For vectors with different particle numbers, the inner product is zero. The inner product is thus given by

$$\langle \mathbf{k}|\mathbf{m}\rangle = \delta_{N_\mathbf{k}N_\mathbf{m}} \det \mathbf{S}^{\mathbf{km}} \tag{1.9.2}$$

where $N_\mathbf{k}$ and $N_\mathbf{m}$ are the numbers of electrons in the ON vectors. $\mathbf{S}^{\mathbf{km}}$ is the matrix of overlap integrals between the spin orbitals occupied in the ON vectors and $\det \mathbf{S}^{\mathbf{km}}$ represents the determinant of this matrix.

1.9.1 CREATION AND ANNIHILATION OPERATORS

The creation operators $a_P^\dagger$ for nonorthogonal spin orbitals are defined in the same way as for orthonormal spin orbitals (1.2.5). As for orthonormal spin orbitals, the anticommutation relations of the creation operators and the properties of their Hermitian adjoints (the annihilation operators) may be deduced from the definition of the creation operators and from the inner product (1.9.2). However, it is easier to proceed in the following manner. We introduce an auxiliary set of symmetrically orthonormalized spin orbitals

$$\tilde{\boldsymbol{\phi}} = \boldsymbol{\phi}\mathbf{S}^{-1/2} \tag{1.9.3}$$

such that

$$\tilde{S}_{PQ} = \int \tilde{\phi}_P^*(\mathbf{x})\tilde{\phi}_Q(\mathbf{x})\,d\mathbf{x} = [\mathbf{S}^{-1/2}\mathbf{S}\mathbf{S}^{-1/2}]_{PQ} = \delta_{PQ} \tag{1.9.4}$$

For these auxiliary spin orbitals, we next introduce a set of operators that satisfy the usual anticommutation relations for orthonormal spin orbitals. As discussed in Section 3.2, the relationship between the old and new creation operators is similar to the relationship between the old and new orbitals (1.9.3) and becomes

$$\tilde{a}_P^\dagger = \sum_Q a_Q^\dagger [\mathbf{S}^{-1/2}]_{QP} \tag{1.9.5}$$

$$a_P^\dagger = \sum_Q \tilde{a}_Q^\dagger [\mathbf{S}^{1/2}]_{QP} \tag{1.9.6}$$

The relationships between the annihilation operators are found by conjugating these expressions

$$\tilde{a}_P = \sum_Q a_Q [\mathbf{S}^{-1/2}]_{PQ} \tag{1.9.7}$$

$$a_P = \sum_Q \tilde{a}_Q [\mathbf{S}^{1/2}]_{PQ} \tag{1.9.8}$$

We may now evaluate the anticommutators for the nonorthogonal creation operators

$$[a_P^\dagger, a_Q^\dagger]_+ = \sum_{RS} [\tilde{a}_R^\dagger [\mathbf{S}^{1/2}]_{RP}, \tilde{a}_S^\dagger [\mathbf{S}^{1/2}]_{SQ}]_+ = \sum_{RS} [\mathbf{S}^{1/2}]_{RP}[\mathbf{S}^{1/2}]_{SQ}[\tilde{a}_R^\dagger, \tilde{a}_S^\dagger]_+ = 0 \tag{1.9.9}$$

and obtain the annihilation commutation relations by taking the Hermitian conjugate of this anticommutator

$$[a_P, a_Q]_+ = 0 \tag{1.9.10}$$

Clearly, the nonorthogonality does not affect the anticommutators between two creation operators and between two annihilation operators. By contrast, the anticommutator between a creation operator and an annihilation operator becomes

$$\begin{aligned}[a_P^\dagger, a_Q]_+ &= \sum_{RS} [\tilde{a}_R^\dagger [\mathbf{S}^{1/2}]_{RP}, \tilde{a}_S [\mathbf{S}^{1/2}]_{QS}]_+ = \sum_{RS} [\mathbf{S}^{1/2}]_{RP}[\mathbf{S}^{1/2}]_{QS}[\tilde{a}_R^\dagger, \tilde{a}_S]_+ \\ &= \sum_{RS} [\mathbf{S}^{1/2}]_{RP}[\mathbf{S}^{1/2}]_{QS}\delta_{RS} = \sum_R [\mathbf{S}^{1/2}]_{QR}[\mathbf{S}^{1/2}]_{RP}\end{aligned} \tag{1.9.11}$$

We thus have the following anticommutator for nonorthogonal creation and annihilation operators

$$[a_P^\dagger, a_Q]_+ = S_{QP} \tag{1.9.12}$$

which in general is nonzero for all pairs of operators. For orthonormal spin orbitals, this expression reduces to the standard anticommutator (1.2.29).

Since the nonorthogonal annihilation operators are linear combinations of orthonormal annihilation operators, we note that an annihilation operator times the vacuum state vanishes as for orthonormal spin orbitals:

$$a_P|\text{vac}\rangle = 0 \tag{1.9.13}$$

The effect of an annihilation operator a_P on an N-particle ON vector can therefore be written as

$$a_P|\mathbf{k}\rangle = \left[a_P, \prod_{Q=1}^{M} (a_Q^\dagger)^{k_Q}\right]_{(+)} |\text{vac}\rangle \tag{1.9.14}$$

where, in order to reduce the particle rank as discussed in Section 1.8, we introduce a commutator for even N and an anticommutator for odd N. Using (1.8.7) or (1.8.9), we now expand the (anti)commutator in (1.9.14) as a linear combination of elementary anticommutators:

$$\begin{aligned} a_P|\mathbf{k}\rangle &= \sum_{Q=1}^{M} k_Q \Gamma_Q^{\mathbf{k}} (a_1^\dagger)^{k_1} \cdots [a_P, (a_Q^\dagger)^{k_Q}]_+ \cdots (a_M^\dagger)^{k_M} |\text{vac}\rangle \\ &= \sum_{Q=1}^{M} k_Q \Gamma_Q^{\mathbf{k}} S_{PQ} |k_1, \ldots, 0_Q, \ldots, k_M\rangle \end{aligned} \tag{1.9.15}$$

Thus, an annihilation operator working on a single ON vector generates a linear combination of ON vectors, each obtained by removing one electron from the original vector. Again, for an orthonormal basis, (1.9.15) reduces to the usual one-term expression (1.2.16).

It is noteworthy that the corresponding expression for a nonorthogonal creation operator working on an ON vector is identical to the expression for orthonormal spin orbitals (1.2.5)

$$a_P^\dagger|\mathbf{k}\rangle = (1 - k_P)\Gamma_P^{\mathbf{k}} |k_1, \ldots, 1_P, \ldots, k_M\rangle \tag{1.9.16}$$

since the nonorthogonal creation operators anticommute among themselves.

1.9.2 ONE- AND TWO-ELECTRON OPERATORS

The second-quantization one- and two-electron operators in a nonorthogonal basis may be obtained from the corresponding operators in the auxiliary orthonormal basis discussed in Section 1.4. The one-electron operator is given by

$$\hat{f} = \sum_{PQ} \tilde{f}_{PQ} \tilde{a}_P^\dagger \tilde{a}_Q = \sum_{PQ} [\mathbf{S}^{-1/2} \tilde{\mathbf{f}} \mathbf{S}^{-1/2}]_{PQ} a_P^\dagger a_Q \tag{1.9.17}$$

where the first expression is in the auxiliary basis, and the second expression is obtained by expanding the creation and annihilation operators according to (1.9.5) and (1.9.7). The integrals in the auxiliary basis are related to the integrals in the nonorthogonal basis by the equation

$$\tilde{f}_{PQ} = \int \tilde{\phi}_P^*(\mathbf{x}) f(\mathbf{x}) \tilde{\phi}_Q(\mathbf{x})\, d\mathbf{x} = [\mathbf{S}^{-1/2} \mathbf{f} \mathbf{S}^{-1/2}]_{PQ} \tag{1.9.18}$$

Inserting this expression in (1.9.17), we obtain the final expression for one-electron operators in a nonorthogonal basis:

$$\hat{f} = \sum_{PQ} [\mathbf{S}^{-1} \mathbf{f} \mathbf{S}^{-1}]_{PQ} a_P^\dagger a_Q \tag{1.9.19}$$

Two-electron operators may be treated in the same way. We obtain

$$\hat{g} = \tfrac{1}{2} \sum_{PQRS} \left(\sum_{IJKL} [\mathbf{S}^{-1}]_{PI} [\mathbf{S}^{-1}]_{JQ} [\mathbf{S}^{-1}]_{RK} [\mathbf{S}^{-1}]_{LS}\, g_{IJKL} \right) a_P^\dagger a_R^\dagger a_S a_Q \tag{1.9.20}$$

where we have used the indices I, J, K and L for the inner summations. Clearly, the one-electron and two-electron operators both reduce to the standard expression for orthonormal spin orbitals when the overlap matrix becomes the identity matrix.

We now consider the effect of a one-electron operator $\hat{f}$ on an ON vector. Combining equations (1.9.15) and (1.9.16), we obtain

$$\begin{aligned}\hat{f}|\mathbf{k}\rangle &= \sum_{PQ}[\mathbf{S}^{-1}\mathbf{f}\mathbf{S}^{-1}]_{PQ}a_P^\dagger a_Q|\mathbf{k}\rangle \\ &= \sum_{PQR}[\mathbf{S}^{-1}\mathbf{f}\mathbf{S}^{-1}]_{PQ}S_{QR}\varepsilon_{PR}\Gamma_P^{\mathbf{k}}\Gamma_R^{\mathbf{k}}(1-k_P+\delta_{RP})k_R\left|\begin{matrix}k_P\to 1\\ k_R\to\delta_{PR}\end{matrix}\right\rangle \\ &= \sum_{PQ}[\mathbf{S}^{-1}\mathbf{f}]_{PQ}\varepsilon_{PQ}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}(1-k_P+\delta_{PQ})k_Q\left|\begin{matrix}k_P\to 1\\ k_Q\to\delta_{PQ}\end{matrix}\right\rangle\end{aligned} \tag{1.9.21}$$

where ε_{PQ} is defined as in (1.3.18). This expression should be compared with (1.3.17), which gives the result of a single-excitation operator for orthonormal spin orbitals. Although the derivation of the effect of a one-electron operator on an ON vector is more complicated in the nonorthogonal case, the final expressions look much the same since in (1.9.21) we were able to eliminate one summation index by modifying the integrals. Note, however, that the integrals in the final expression of (1.9.21) are not symmetric in the indices.

1.9.3 BIORTHOGONAL OPERATORS

It is possible to arrive at the results of Section 1.9.2 in a different way. We note that all complications due to nonorthogonality arise from the anticommutator (1.9.12). We therefore introduce a transformed set of annihilation operators $\bar{a}_P$ that satisfy the anticommutation relation

$$a_P^\dagger\bar{a}_Q + \bar{a}_Q a_P^\dagger = \delta_{PQ} \tag{1.9.22}$$

To satisfy this relation, the annihilation operators are chosen as

$$\bar{a}_P = \sum_Q a_Q[\mathbf{S}^{-1}]_{PQ} \tag{1.9.23}$$

That these operators indeed satisfy the anticommutation relation (1.9.22) can be verified by substitution and use of (1.9.12). The operators $a_P^\dagger\bar{a}_Q$ behave just like excitation operators in an orthonormal basis:

$$a_P^\dagger\bar{a}_Q|\mathbf{k}\rangle = \varepsilon_{PQ}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}(1-k_P+\delta_{PQ})k_Q\left|\begin{matrix}k_P\to 1\\ k_Q\to\delta_{PQ}\end{matrix}\right\rangle \tag{1.9.24}$$

A general one-electron operator can now be expanded in the excitation operators $a_P^\dagger a_Q$

$$\hat{f} = \sum_{PQ}[\mathbf{S}^{-1}\mathbf{f}\mathbf{S}^{-1}]_{PQ}a_P^\dagger a_Q = \sum_{PQ}[\mathbf{S}^{-1}\mathbf{f}]_{PQ}a_P^\dagger\bar{a}_Q \tag{1.9.25}$$

and we thus obtain (1.9.21) directly from (1.9.24) and (1.9.25). The annihilation operators $\bar{a}_Q$ are said to be *biorthogonal* to the creation operators $a_P^\dagger$ since they fulfill the relation (1.9.22) characteristic of orthonormal spin orbitals [5]. Note, however, that the creation operator $a_P^\dagger$ is not the adjoint of a_P.

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Exercises

EXERCISE 1.1

Show that the effect of an excitation operator on an ON vector can be written as

$$a_P^\dagger a_Q|\mathbf{k}\rangle = \varepsilon_{PQ}\Gamma_P^{\mathbf{k}}\Gamma_Q^{\mathbf{k}}(1 - k_P + \delta_{PQ})k_Q \left\langle \begin{array}{l} k_P \to 1 \\ k_Q \to \delta_{PQ} \end{array} \right\rangle \tag{1E.1.1}$$

where

$$\varepsilon_{PQ} = \begin{cases} 1 & P \le Q \\ -1 & P > Q \end{cases} \tag{1E.1.2}$$

and where the ket on the right-hand side of (1E.1.1) is an ON vector with the same occupation numbers as $|\mathbf{k}\rangle$ except as indicated for spin orbitals P and Q.

EXERCISE 1.2

Let $\hat{I}_n$ and $\hat{I}_m$ be strings that contain n and m elementary (creation or annihilation) operators, respectively. Show by induction that, for even n and m, $[\hat{I}_n, \hat{I}_m]$ can be reduced to a sum of strings, each of which contains at most $n + m - 2$ elementary operators.

EXERCISE 1.3

Verify the following commutation and anticommutation relations:

1. $[\hat{A}, \hat{B}_1\hat{B}_2] = [\hat{A}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{A}, \hat{B}_2]$ (1E.3.1)

2. $[\hat{A}, \hat{B}_1 \cdots \hat{B}_n] = \sum_{k=1}^{n} \hat{B}_1 \cdots \hat{B}_{k-1}[\hat{A}, \hat{B}_k]\hat{B}_{k-1} \cdots \hat{B}_n$ (1E.3.2)

3. $[\hat{A}, \hat{B}_1\hat{B}_2] = [\hat{A}, \hat{B}_1]_+ \hat{B}_2 - \hat{B}_1[\hat{A}, \hat{B}_2]$. (1E.3.3)

$$4.\ [\hat{A}, \hat{B}_1 \cdots \hat{B}_n] = \sum_{k=1}^{n} (-1)^{k-1} \hat{B}_1 \cdots [\hat{A}, \hat{B}_k]_+ \cdots \hat{B}_n \quad (n \text{ even}) \tag{1E.3.4}$$

$$5.\ [\hat{A}, \hat{B}_1 \hat{B}_2]_+ = [\hat{A}, \hat{B}_1]\hat{B}_2 + \hat{B}_1[\hat{A}, \hat{B}_2]_+ = [\hat{A}, \hat{B}_1]_+ \hat{B}_2 - \hat{B}_1[\hat{A}, \hat{B}_2] \tag{1E.3.5}$$

$$6.\ [\hat{A}, \hat{B}_1 \cdots \hat{B}_n]_+ = \sum_{k=1}^{n} (-1)^{k-1} \hat{B}_1 \cdots [\hat{A}, \hat{B}_k]_+ \cdots \hat{B}_n \quad (n \text{ odd}) \tag{1E.3.6}$$

EXERCISE 1.4

Let $\hat{\kappa}$ and $\hat{f}$ be the one-electron operators

$$\hat{\kappa} = \sum_{PQ} \kappa_{PQ} a_P^\dagger a_Q \tag{1E.4.1}$$

$$\hat{f} = \sum_{PQ} f_{PQ} a_P^\dagger a_Q \tag{1E.4.2}$$

Show that the commutator $[\hat{\kappa}, \hat{f}]$ can be written as a one-electron operator

$$[\hat{\kappa}, \hat{f}] = \sum_{PQ} f^{\kappa}_{PQ} a_P^\dagger a_Q \tag{1E.4.3}$$

with the modified integrals

$$f^{\kappa}_{PQ} = \sum_{R} (\kappa_{PR} f_{RQ} - f_{PR} \kappa_{RQ}) \tag{1E.4.4}$$

Solutions

SOLUTION 1.1

We consider first the case $P > Q$. Using (1.2.16) and (1.2.5), we obtain

$$\begin{aligned} a_P^\dagger a_Q |\mathbf{k}\rangle &= a_P^\dagger \delta_{k_Q 1} \Gamma_Q^{\mathbf{k}} |k_1, \cdots, 0_Q, \cdots, k_P, \cdots, k_M\rangle \\ &= \delta_{k_P 0} \delta_{k_Q 1} \Gamma_Q^{\mathbf{k}} \Gamma_P^{\mathbf{k}} \varepsilon_{PQ} \ |k_1, \cdots, 0_Q, \cdots, 1_P, \cdots, k_M\rangle \\ &= \varepsilon_{PQ} \Gamma_Q^{\mathbf{k}} \Gamma_P^{\mathbf{k}} (1 - k_P) k_Q \left| \begin{matrix} k_P \to 1 \\ k_Q \to 0 \end{matrix} \right\rangle \end{aligned} \tag{1S.1.1}$$

in agreement with (1E.1.1). The case $P < Q$ differs from (1S.1.1) only in the interpretation of ε_{PQ}. Finally, the case $P = Q$ is covered by (1.3.2).

SOLUTION 1.2

Assume that the relation

$$[\hat{I}_k, \hat{I}_l] = \sum_i \hat{I}^i_{kl} \tag{1S.2.1}$$

where each $\hat{I}^i_{kl}$ contains at most $k + l - 2$ elementary operators, holds for $m = k$ and $n = l$ where $k \geq 2$ and $l \geq 2$. Introducing

$$\hat{I}_{k\,1\,2} = \hat{I}_k \hat{b} \hat{c} \tag{1S.2.2}$$

where $\hat{b}$ and $\hat{c}$ are elementary operators, we obtain

$$[\hat{I}_{k+2}, \hat{I}_l] = [\hat{I}_k \hat{b}\hat{c}, \hat{I}_l] = [\hat{I}_k, \hat{I}_l]\hat{b}\hat{c} + \hat{I}_k[\hat{b}\hat{c}, \hat{I}_l] \tag{1S.2.3}$$

By assumption, both terms on the right-hand side contain at most $k+l$ elementary operators. Thus, if the assumption holds for $m = k$ and $n = l$, it holds also for $m = k+2$ and $n = l$. By symmetry of k and l in (1S.2.1), the assumption then holds for $m = k$ and $n = l+2$ as well. The proof is completed by noting that the assumption holds for $k = 2$ and $l = 2$, as is easily verified – for example:

$$[a_P^\dagger a_Q^\dagger, a_R a_S] = \delta_{QR} a_P^\dagger a_S - \delta_{PR} a_Q^\dagger a_S + \delta_{QS} a_R a_P^\dagger - \delta_{PS} a_R a_Q^\dagger \tag{1S.2.4}$$

SOLUTION 1.3

1. Relation (1E.3.1) is verified by expanding both sides and comparing terms.
2. Assume that (1E.3.2) holds for $n = m$. Using (1E.3.1), we then obtain for $n = m+1$:

$$\begin{aligned}[\hat{A}, \hat{B}_1 \cdots \hat{B}_m \hat{B}_{m+1}] &= [\hat{A}, \hat{B}_1 \cdots \hat{B}_m]\hat{B}_{m+1} + \hat{B}_1 \cdots \hat{B}_m[\hat{A}, \hat{B}_{m+1}] \\ &= \left(\sum_{k=1}^{m} \hat{B}_1 \cdots \hat{B}_{k-1}[\hat{A}, \hat{B}_k]\hat{B}_{k+1} \cdots \hat{B}_m\right)\hat{B}_{m-1} + \hat{B}_1 \cdots \hat{B}_m[\hat{A}, \hat{B}_{m+1}] \\ &= \sum_{k=1}^{m+1} \hat{B}_1 \cdots \hat{B}_{k-1}[\hat{A}, \hat{B}_k]\hat{B}_{k+1} \cdots \hat{B}_m \hat{B}_{m-1}\end{aligned} \tag{1S.3.1}$$

   Since (1E.3.2) holds for $n = 2$, the induction is complete.
3. Relation (1E.3.3) is verified by expanding both sides and comparing terms.
4. To demonstrate (1E.3.4), we first collect the $\hat{B}_i$ in $n/2$ pairs: $(\hat{B}_1\hat{B}_2)(\hat{B}_3\hat{B}_4)\cdots$. Next, we apply (1E.3.2) to obtain an expansion over the $n/2$ pairs and finally use (1E.3.3) to resolve the two contributions from each pair.
5. Relation (1E.3.5) is verified by expanding both sides and comparing terms.
6. Assume that (1E.3.6) holds for $n = m$ (m odd). Using (1E.3.5), we obtain

$$[\hat{A}, \hat{B}_1 \cdots \hat{B}_m \hat{B}_{m+1} \hat{B}_{m-2}]_+ = [\hat{A}, \hat{B}_1 \cdots \hat{B}_m]_- \hat{B}_{m+1}\hat{B}_{m+2} - \hat{B}_1 \cdots \hat{B}_m[\hat{A}, \hat{B}_{m+1}\hat{B}_{m+2}] \tag{1S.3.2}$$

   Since

$$[\hat{A}, \hat{B}_{m+1}\hat{B}_{m+2}] = [\hat{A}, \hat{B}_{m+1}]_+ \hat{B}_{m+2} - \hat{B}_{m+1}[\hat{A}, \hat{B}_{m+2}]_+ \tag{1S.3.3}$$

   it is easily seen from (1S.3.2) that (1E.3.6) is valid for $n = m+2$. Since it is valid for $n = 1$, we have proved (1E.3.6).

SOLUTION 1.4

Inserting the operators in the commutator and expanding, we obtain

$$\begin{aligned}[\hat{\kappa}, \hat{f}] &= \sum_{PQRS} \kappa_{PQ} f_{RS}[a_P^\dagger a_Q, a_R^\dagger a_S] = \sum_{PQRS} \kappa_{PQ} f_{RS}(\delta_{QR} a_P^\dagger a_S - \delta_{PS} a_R^\dagger a_Q) \\ &= \sum_{PQ}\left(\sum_R f_{RQ}\kappa_{PR} - f_{PR}\kappa_{RQ}\right) a_P^\dagger a_Q = \sum_{PQ} f^{\kappa}_{PQ} a_P^\dagger a_Q\end{aligned} \tag{1S.4.1}$$