# SECOND QUANTIZATION-BASED METHODS IN QUANTUM CHEMISTRY

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In this book we address several modern quantum chemical tools that are presently being applied at the state-of-the-art level to electronic states of atoms and molecules. We have attempted to concentrate on topics for which textbook coverage does not currently exist in an entirely satisfactory form. The emphasis is on quantum chemical methods whose developments and implementations have been presented in the modern literature primarily in the language of second quantization. We do not assess the precision of the numerical results provided by these methods because many of the techniques discussed are relatively new and their precision limits have not yet been established.

There is little mention of specific molecular systems that might be examined using these tools. We have developed an integrated set of problems with detailed answers, all of which can be worked by hand, to illustrate the practical implementation of the techniques developed. These problems appear at the end of each chapter, and we recommend that they be worked as an integral component of the respective chapters. Excellent treatments of the following very important aspects of quantum chemistry already exist in several texts and are therefore not included in this book : questions of basis set choice, efficient evaluation of requisite one- and two-electron integrals, fast and space-efficient methods for transforming integrals from one basis to another and for storing such integral lists, or the use of orbital symmetry correlation concepts in deciding which electronic configurations must be included for specific molecules. The emphasis here is on describing the structure of the various methods rather than on discussing their numerical implementations.

The choice of topics and depth of presentation were guided by our view of the active research workers who are likely to benefit from this book. Many leading theoretical chemistry research groups have only recently begun to make use of second quantization-based techniques. It is not likely that the full potential of these methods will be realized until those quantum chemists who possess the most sophisticated computational tools and experience become more involved in their use. A presentation that is limited to explaining how working equations of these methods are derived and how the equations are implemented in practice should be especially useful and timely. This monograph is intended to be of use both to the research worker in quantum chemistry and to graduate-level students who have already taken introductory courses that cover the fundamentals of quantum mechanics through the Hartree-Fock method as applied to atoms and molecules. The purpose of this book is more to teach than to survey the literature in the research areas covered. We assume that the reader is familiar with linear algebra, matrix representations of operators, Slater- and contracted Gaussian-type basis functions, the Slater-Condon rules for evaluating determinantal matrix elements of one- and two-electron operators, and the construction of Slater determinant wave functions having proper space-spin symmetry.

# List of Abbreviations

ВТ	Brillouin theorem
BWPT	Brillouin-Wigner perturbation theory
CC	coupled cluster
CHF	coupled Hartree-Fock
CI	configuration interaction
CMCHF	coupled multiconfigurational Hartree-Fock
EOM	equations of motion
EP	electron propagator
GBT	generalized Brillouin theorem
GF	Green's function
GUGA	unitary group, graphical approach
HF	Hartree-Fock
INO	iterative natural orbitals
MBPT	many-body perturbation theory
MCSCF	multiconfigurational self-consistent field
MCTDHF	multiconfigurational time-dependent Hartree-Fock
MPPT	Møller-Plesset perturbation theory
PP	polarization propagator
RHF	restricted Hartree-Fock
RPA	random-phase approximation
RSPT	Rayleigh-Schrödinger perturbation theory
SCF	self-consistent field
SCI	superconfiguration interaction
SP	stationary point
TDHF	time-dependent Hartree-Fock
UHF	unrestricted Hartree-Fock

SECOND QUANTIZATION-BASED METHODS IN QUANTUM CHEMISTRY

# Chapter 1 | Introduction to Second-Quantization Methods

In the vast majority of the quantum chemistry literature, Slater determinants have been used to express antisymmetric N-electron wavefunctions, and explicit differential and multiplicative operators have been used to write the electronic Hamiltonian. More recently, it has become quite common to express the operators and state vectors that arise in considering stationary electronic states of atoms and molecules (within the Born-Oppenheimer approximation) in the so-called second quantization notation (Linderberg and Öhrn, 1973). The electron creation  $(r^+, s^+, t^+, u^+)$  and annihilation (r, s, t, u) operators occurring in this language were originally introduced for use in physical problems that actually involved creation or destruction of particles, photons, or excitations (e.g., phonons). In a majority of the applications of the second-quantization techniques to quantum-chemical problems. no electrons or other particles are created or destroyed. Thus, the operators  $\{r^+\}, \{r\}$  usually serve merely as a convenient and operationally useful device in terms of which quantum-mechanical states, operators, commutators, and expectation values can be evaluated. In this chapter, we examine how the electronic Hamiltonian, other quantum-mechanical operators, and state vectors are represented in this second-quantization language. We also show how to describe unitary transformations among orthonormal orbitals in an especially convenient manner. In subsequent chapters we make use of the tools of second quantization to describe many approximation techniques (e.g., Hartree-Fock, perturbation theory, configuration interaction, multiconfigurational Hartree-Fock, cluster methods, Green's functions), which are currently in wide use within the quantum chemistry community. The need for such approximation methods is, of course, motivated by our inability to exactly solve electronic structure problems for more than one electron.

## A. ANTICOMMUTATION PROPERTIES OF CREATION AND ANNIHILATION OPERATORS

Slater determinantal wavefunctions involving orthonormal spin-orbitals  $\phi_k$  can be represented in terms of products of creation operators on the so-called vacuum ket  $|vac\rangle$ ,

$$r^{+}s^{+}\cdots t^{+}|\mathrm{vac}\rangle \leftrightarrow (N!)^{-1/2} \operatorname{det}|\phi_{t}\cdots \phi_{s}\phi_{r}| \equiv |\phi_{t}\cdots \phi_{s}\phi_{r}|$$
 (1.1)

The Fermi statistics present in such wavefunctions can be expressed either in terms of a sign change arising upon permuting columns of the determinant or in terms of the following fundamental relation among the  $r^+$  operators:

$$[r^+, s^+]_+ \equiv r^+ s^+ + s^+ r^+ = 0 \tag{1.2}$$

Note that this equation also states that the state vector cannot contain the same spin-orbital twice (the Pauli principle) since  $r^+r^+ = -r^+r^+ = 0$ . Before we go further, we should stress that Eq. (1.1) does not equate Slater determinants to the product of  $r^+s^+ \cdots$  operating on  $|vac\rangle$ . It simply claims that there is a one-to-one connection between the two objects.

The Fermion annihilation operator r, which is the adjoint of the creation operator  $r^+$ , can be thought of as annihilating an electron in  $\phi_r$  and is defined to yield zero when operating on the vacuum ket

$$r |\text{vac}\rangle = 0 \tag{1.3}$$

The annihilation and creation operators fulfill the following two anticommutation relations (Raimes, 1972):

$$[r,s]_+ \equiv rs + sr = 0 \tag{1.4}$$

$$[r, s^{+}]_{+} \equiv rs^{+} + s^{+}r = \delta_{rs}$$
(1.5)

which together with Eq. (1.2) comprise the essential relationships used in the application of such second quantization operators to quantum chemistry. For nonorthonormal spin-orbitals, Eq. (1.5) is replaced by  $[r, s^+]_+ = \langle \phi_r | \phi_s \rangle$ , where the overlap appears explicitly.

The interpretation of Eq. (1.2) in terms of permutational symmetry of determinants is clear. To make the analogous content of Eqs. (1.4) and (1.5) more transparent, we now examine some of the implications that follow from these equations. Let us first examine Eq. (1.5). For r = s, this reads  $rr^+ + r^+r = 1$ . When operating on a ket in which  $\phi_r$  is "occupied," the first term  $(rr^+)$  clearly gives zero, since according to Eq. (1.2) terms violating the Pauli principle vanish. The second term  $(r^+r)$  yields

$$r^{+}rt^{+}u^{+}\cdots r^{+}\cdots w^{+}|\operatorname{vac}\rangle = (-1)^{k_{r}}r^{+}rr^{+}t^{+}u^{+}\cdots w^{+}|\operatorname{vac}\rangle \quad (1.6)$$

where  $k_r$  is the number of creation operators standing to the left of  $r^+$  in

the original ket. If this is, according to Eq. (1.5), equal to the original ket, then we must have

$$t^{+}u^{+}\cdots r^{+}\cdots w^{+}|\operatorname{vac}\rangle = (-1)^{k_{r}}r^{+}rr^{+}t^{+}u^{+}\cdots w^{+}|\operatorname{vac}\rangle$$
$$= (-1)^{k_{r}}r^{+}t^{+}u^{+}\cdots w^{+}|\operatorname{vac}\rangle \qquad (1.7)$$

The last equality in Eq. (1.7) implies that  $rr^+$ , when operating on a ket that does not contain  $\phi_r$ , leaves that ket unchanged, and that  $r^+r$ , when acting on a ket in which  $\phi_r$  is present, leaves that ket alone. When  $r^+r$  operates on a ket in which  $\phi_r$  is not present, it gives zero. Thus  $r^+r$  tells whether orbital  $\phi_r$  occurs in a ket. For that reason, it is often referred to as the occupation number operator  $n_r = r^+r$ . It is also conventional to introduce the total number operator N as  $N = \sum_r n_r$ , which when operating on any ket gives as its eigenvalue the total number of electrons in that ket.

In the case  $r \neq s$ , Eq. (1.5) implies that r operating on any ket that does not contain  $\phi$ , yields zero, since

$$rs^{+}t^{+}u^{+}\cdots w^{+}|\mathrm{vac}\rangle = -s^{+}rt^{+}u^{+}\cdots w^{+}|\mathrm{vac}\rangle = 0$$
(1.8)

by repeated use of Eqs. (1.5) and (1.3). When the kets contain both  $\phi_r$  and  $\phi_s$ , both the  $rs^+$  and  $s^+r$  terms vanish. For  $s^+r$  operating on a ket that contains  $\phi_r$ ,

$$s^{+}rt^{+}u^{+}\cdots r^{+}w^{+}|\operatorname{vac}\rangle = (-1)^{k_{r}}s^{+}t^{+}u^{+}\cdots w^{+}|\operatorname{vac}\rangle$$
$$= t^{+}u^{+}\cdots s^{+}w^{+}|\operatorname{vac}\rangle \qquad (1.9)$$

which is simply a new ket with  $\phi_r$ , replaced by  $\phi_s$ .

Finally, we should attempt to elaborate on the meaning of Eq. (1.4). Let us consider the action of rs ( $r \neq s$ ) on a ket in which  $\phi_r$  and  $\phi_s$  are present:

$$rst^{+}u^{+}\cdots r^{+}\cdots s^{+}\cdots w^{+}|vac\rangle = (-1)^{k_{r}+k_{s}}rss^{+}r^{+}t^{+}u^{+}\cdots w^{+}|vac\rangle$$

which by Eq. (1.5) reduces to

$$(-1)^{k_r+k_s}r(1-s^+s)r^+t^+u^+\cdots w^+|vac\rangle$$
 (1.10)

The term involving  $s^+s$  vanishes because  $s|vac\rangle = 0$ , and hence we have (again using  $r|vac\rangle = 0$ )

$$(-1)^{k_r+k_s}rr^+t^+u^+\cdots w^+|\operatorname{vac}\rangle = (-1)^{k_r+k_s}t^+u^+\cdots w^+|\operatorname{vac}\rangle \quad (1.11)$$

If instead we consider the action of sr, we obtain

$$srt^{+}u^{+}\cdots r^{+}\cdots s^{+}\cdots w^{+}|\operatorname{vac}\rangle = (-1)^{k_{r}+k_{s}-1}srr^{+}s^{+}t^{+}u^{+}\cdots w^{+}|\operatorname{vac}\rangle$$
$$= (-1)^{k_{r}+k_{s}-1}t^{+}u^{+}\cdots w^{+}|\operatorname{vac}\rangle \qquad (1.12)$$

which is opposite in sign to the result of the rs operation. Thus, the statement rs + sr = 0 simply means that the effect of annihilation displays Fermion

statistics. For r = s, Eq. (1.4) reads rr = -rr = 0, which also expresses the Pauli principle and Fermi statistics.

Although Eqs. (1.2)–(1.5) contain all of the fundamental properties of the Fermion (electron) creation and annihilation operators, it may be useful to make a few additional remarks about how these operators are used in subsequent applications. In treating perturbative expansions of N-electron wavefunctions or when attempting to optimize the spin-orbitals  $\phi_r$  appearing in such wavefunctions, it is often convenient to refer to Slater determinants that have been obtained from some "reference determinant" by replacing certain spin-orbitals by other spin orbitals. In terms of second-quantized operators, these spin-orbital replacements will be achieved by using the replacement operator  $s^+r$  as in Eq. (1.9).

In subsequent chapters, we shall be interested in computing expectation values of one- and two-electron operators. By expressing these operators in terms of the above creation and annihilation operators, the calculation of such expectations values reduces to the evaluation of the elements of the one- and two-electron density matrices  $\langle 0|i^+j|0\rangle$  and  $\langle 0|i^+j^+lk|0\rangle$  (Davidson, 1976). If the wavefunction  $|0\rangle$  is expressed as a linear combination of kets each given in terms of creation operator products  $\prod_{r \in 0} r^+ |vac\rangle$ , the one- and two-electron density matrices can be evaluated in terms of the expansion coefficients of  $|0\rangle$  in these kets. The average occupation of an electron in spin-orbital  $\phi$ , becomes a particular element  $\langle 0|r^+r|0\rangle$  of the one-particle density matrix. If we wish to compute, say,  $\langle 0|t^+u|0\rangle$ , where  $|0\rangle = \prod_{r \in 0} r^+ |vac\rangle$ , we may proceed using the anticommutation algebra obeyed by the creation and annihilation operators, to yield

$$\langle 0|t^{+}u|0\rangle = \prod_{r\in 0} \prod_{r'\in 0} \langle \operatorname{vac}|r't^{+}ur^{+}|\operatorname{vac}\rangle$$

$$= \langle \operatorname{vac}|r_{N}r_{N-1}\cdots r_{1}t^{+}ur_{1}^{+}r_{2}^{+}\cdots r_{N}^{+}|\operatorname{vac}\rangle$$

$$= \delta_{ur_{1}}\langle \operatorname{vac}|r_{N}r_{N-1}\cdots r_{1}t^{+}r_{2}^{+}r_{3}^{+}\cdots r_{N}^{+}|\operatorname{vac}\rangle$$

$$- \langle \operatorname{vac}|r_{N}r_{N-1}\cdots r_{1}t^{+}r_{1}^{+}ur_{2}^{+}r_{3}^{+}\cdots r_{N}^{+}|\operatorname{vac}\rangle$$

$$(1.13)$$

which, by "anticommuting" u through to the right (so as to eventually generate  $u|vac\rangle = 0$ ) and  $t^+$  through to the left (to eventually generate  $\langle vac|t^+ = (t|vac\rangle)^+ = 0$ ), and using  $\langle vac|vac\rangle = 1$ , yields a nonvanishing matrix element only when t = u and u is one of the elements of  $|0\rangle$  (the "occupied" spin orbitals in  $|0\rangle$ ). This result can be summarized as follows:

$$\langle 0|t^+u|0\rangle = \delta_{tu}v_t \tag{1.14}$$

where v, denotes the occupation number of orbital  $\phi_t$  in  $|0\rangle$ .

This expresses a general rule of how to obtain matrix elements of a replacement operator. The rule is the second-quantization analog of the Slater-Condon rule (Condon and Shortley, 1935) for evaluating matrix elements of a one-electron operator. In practical calculations one would, of course, use this rule as well as the other counterparts of the Slater-Condon rules.

# B. EXPRESSING QUANTUM-MECHANICAL OPERATORS IN SECOND QUANTIZATION

Having now seen how state vectors that are in one-to-one correspondence with N-electron Slater determinants can be represented in terms of Fermion creation and annihilation operators, it still remains for us to show how to express one- and two-electron operators in this language. The secondquantized version of any operator is obtained by simply demanding that the operator, when "sandwiched" between ket vectors of the form  $\prod_{i=1}^{N} r^{+} |vac\rangle$ , yield exactly the same result as arises in using the first quantized operator between corresponding Slater determinant wavefunctions. For an arbitrary one-electron operator, which in first-quantized language is  $\sum_{i=1}^{N} f(\mathbf{r}_i)$ , the second quantized equivalent is

$$\sum_{\mathbf{r},s} \langle \phi_{\mathbf{r}} | f | \phi_s \rangle r^+ s \leftrightarrow \sum_{i=1}^{N} f(\mathbf{r}_i)$$
(1.15)

where the sums (r, s) are over a complete set of orthonormal spin-orbitals  $\phi_r$ , and  $\phi_s$ . The analogous expression for any two-electron operator is

$$\frac{1}{2} \sum_{r,s,t,u} \langle \phi_r \phi_s | g | \phi_t \phi_u \rangle r^+ s^+ ut \leftrightarrow \frac{1}{2} \sum_{i,j=1}^N g(\mathbf{r}_i, \mathbf{r}_j)$$
(1.16)

Here  $\langle \phi_r \phi_s | g | \phi_t \phi_u \rangle$  represents the usual two-electron integral involving the operator g:

$$\langle \phi_r \phi_s | g | \phi_t \phi_u \rangle = \int \phi_r^*(1) \phi_s^*(2) g(1,2) \phi_t(1) \phi_u(2) \, d1 \, d2 \tag{1.17}$$

When  $g(1,2) = r_{12}^{-1}$ , we often express these integrals in short-hand notation as  $\langle rs | tu \rangle$ . It should be noted that the order of the creation and annihilation operators appearing in Eq. (1.16) must be as presented in order to guarantee that the proper sign will result when expectation and transition value matrix elements of such operators are formed. These spin orbitals  $\{\phi_r\}$  are, in most practical applications, obtained as linear combinations of atomic orbital basis functions

$$\phi_r = \mathop{}_{\beta}\sum_{a} C_{ra}\chi_a \tag{1.18}$$

where  $\alpha$  and  $\beta$  are the one-electron spin functions. The  $\chi_a$  are usually taken to be Slater-type orbitals or contracted Gaussian orbitals, and the  $C_{ra}$  are the

linear orbital expansion coefficients. In what follows, we assume that the  $\chi_a$  are real orbitals. This means that the Gaussian or Slater orbitals are given in cartesian form rather than in terms of spherical harmonics.

A few clarifying remarks are now in order. First, one should notice that the first-quantized forms of the above operators contain explicit reference to the number of electrons N, whereas the second-quantized operators do not. This means, for example, that the kinetic energy operator

$$\sum_{r,s} \langle \phi_r | - \frac{1}{2} \nabla^2 | \phi_s \rangle r^+ s$$

is independent of N. The kinetic energy operator of the beryllium atom is identical to that of the Be<sup>+</sup>, Be<sup>+</sup>, Be<sup>-</sup>, etc., ions. Of course, nuclear interaction operators  $(-Z_A \sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{R}_A|^{-1})$  do contain reference to nuclear charges in their second-quantized version,

$$\sum_{\mathbf{r},s} \langle \phi_{\mathbf{r}} | - Z_{\mathbf{A}} | \mathbf{r} - \mathbf{R}_{\mathbf{A}} |^{-1} | \phi_{s} \rangle r^{+} s$$

but nowhere does N appear. In second quantization, the only reference to N comes from the ket vectors  $\prod_{r \in 0} r^+ |vac\rangle$ , which contain N creation operators. This property of operators in the second-quantized language plays an important role, for example, in Green's function methods for calculating ionization energies. The fact that the same Hamiltonian can describe neutral and ion states permits the Green's function to be expressed in terms of a single Hamiltonian.

In examining the above expressions for the second-quantized one- and two-electron operators, it should become clear, for example, that the oneelectron operators, which contain  $r^+s$ , can "connect" two N-electron kets (corresponding to N-electron Slater determinants) that differ by at most one spin-orbital label. That is,  $r^+s$  can cause only a single spin-orbital replacement. Similarly, the two-electron operators containing  $r^+s^+ut$  can connect kets differing by at most two spin-orbital labels.

To summarize, we have constructed state vectors that obey Fermi-Dirac statistics through introducing creation and annihilation operators that fulfill the anticommutation relations of Eqs. (1.2), (1.4), and (1.5). The anticommutation relations allow us to build the Slater-Condon rules directly into the operators in the second-quantized language. The operators thereby lose their dependence on the electron number N. The only dependence on N in the second-quantized language appears in the state vectors  $|0\rangle$ . In contrast, in the first-quantized language the dependence on N appears in both the operators and the wavefunctions.

Because it is important that one fully understand how the above forms of arbitrary one- and two-electron operators are related to the Slater-Condon rules, let us now consider an example of how one uses these operators. Let

# B. Expressing Quantum-Mechanical Operators in Second Quantization

us compute the expectation value of the electron-electron interaction operator for the three-electron state  $2s_{\alpha}^+ 1s_{\beta}^+ 1s_{\alpha}^+ |vac\rangle$ . We know from Slater-Condon type rules that we should get  $J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$ , where J and K are the usual coulomb and exchange integrals:

$$J_{ij} = \langle ij | ij \rangle \tag{1.19}$$

$$K_{ij} = \langle ij | ji \rangle \tag{1.20}$$

The second-quantized approach involves evaluating

$$\frac{1}{2} \sum_{r,s,t,u} \langle \operatorname{vac} | 1s_{\alpha} 1s_{\beta} 2s_{\alpha} r^{+} s^{+} u t 2s_{\alpha}^{+} 1s_{\beta}^{+} 1s_{\alpha}^{+} | \operatorname{vac} \rangle \langle \phi_{r} \phi_{s} | \frac{1}{r_{12}} | \phi_{t} \phi_{u} \rangle$$

which involves the two-particle density matrix.

The application of Eq. (1.5) in the form  $rs^+ = \delta_{rs} - s^+ r$  permits the annihilation operators u, t to be anticommuted to the right in the above and the creation operators  $r^+s^+$  to be moved to the left. This strategy permits us to identify all of the nonvanishing contributions (those arising from the  $\delta_{rs}$  terms) and to eventually obtain  $u|vac\rangle$  or  $\langle vac|r^+$ , both of which yield zero. The process of moving ut to the right is carried out as follows:

$$ut2s_{\alpha}^{+}1s_{\beta}^{+}1s_{\alpha}^{+}|vac\rangle = u(\delta_{t2s_{\alpha}} - 2s_{\alpha}^{+}t)1s_{\beta}^{+}1s_{\alpha}^{+}|vac\rangle$$

$$= \left[\delta_{t2s_{\alpha}}(\delta_{u1s_{\beta}} - 1s_{\beta}^{+}u)1s_{\alpha}^{+} - u2s_{\alpha}^{+}(\delta_{t1s_{\beta}} - 1s_{\beta}^{+}t)1s_{\alpha}^{+}\right]|vac\rangle$$

$$= \left[\delta_{t2s_{\alpha}}\delta_{u1s_{\beta}}1s_{\alpha}^{+} - \delta_{t2s_{\alpha}}\delta_{u1s_{\alpha}}1s_{\beta}^{+} - (\delta_{u2s_{\alpha}} - 2s_{\alpha}^{+}u)(\delta_{t1s_{\beta}} - 1s_{\beta}^{+}t)1s_{\alpha}^{+}\right]|vac\rangle$$

$$= \left[\delta_{t2s_{\alpha}}\delta_{u1s_{\beta}}1s_{\alpha}^{+} - \delta_{t2s_{\alpha}}\delta_{u1s_{\alpha}}1s_{\beta}^{+} - \delta_{u2s_{\alpha}}\delta_{t1s_{\beta}}1s_{\alpha}^{+} + \delta_{u2s_{\alpha}}\delta_{t1s_{\alpha}}1s_{\beta}^{+} + \delta_{t1s_{\beta}}\delta_{u1s_{\alpha}}2s_{\alpha}^{+} - \delta_{t1s_{\alpha}}\delta_{u1s_{\beta}}2s_{\alpha}^{+}\right]|vac\rangle$$

$$(1.21)$$

The treatment of  $\langle vac | 1s_{\alpha} 1s_{\beta} 2s_{\alpha} r^+ s^+$  goes through in exactly the same manner and yields the adjoint of the above result, with r replacing t and s replacing u:

$$\langle \operatorname{vac}|1s_{\alpha}1s_{\beta}2s_{\alpha}r^{+}s^{+} = \langle \operatorname{vac}|[\delta_{r2s_{\alpha}}\delta_{s1s_{\beta}}1s_{\alpha} - \delta_{r2s_{\alpha}}\delta_{s1s_{\alpha}}1s_{\beta} - \delta_{s2s_{\alpha}}\delta_{r1s_{\beta}}1s_{\alpha} + \delta_{s2s_{\alpha}}\delta_{r1s_{\alpha}}1s_{\beta} + \delta_{r1s_{\beta}}\delta_{s1s_{\alpha}}2s_{\alpha} - \delta_{r1s_{\alpha}}\delta_{s1s_{\beta}}2s_{\alpha}]$$

$$(1.22)$$

Then by forming the scalar product  $\langle vac | 1s_{\alpha} 1s_{\beta} 2s_{\alpha} r^{+} s^{+} ut 2s_{\alpha}^{+} 1s_{\beta}^{+} 1s_{\alpha}^{+} | vac \rangle$  and using, for example, the fact that  $\langle vac | 1s_{\alpha} 1s_{\alpha}^{+} | vac \rangle = 1$  and  $\langle vac | 1s_{\alpha} 2s_{\alpha}^{+} | vac \rangle = 0$ , one obtains

$$\begin{split} \delta_{tr2s_{\alpha}}\delta_{us1s_{\beta}} + \delta_{tr2s_{\alpha}}\delta_{su1s_{\alpha}} + \delta_{su2s_{\alpha}}\delta_{tr1s_{\beta}} + \delta_{su2s_{\alpha}}\delta_{tr1s_{\alpha}} \\ + \delta_{tr1s_{\beta}}\delta_{su1s_{\alpha}} + \delta_{tr1s_{\alpha}}\delta_{su1s_{\beta}} - \delta_{ur2s_{\alpha}}\delta_{ts1s_{\beta}} - \delta_{ur1s_{\beta}}\delta_{ts2s_{\alpha}} \\ - \delta_{ts2s_{\alpha}}\delta_{ur1s_{\alpha}} - \delta_{ur2s_{\alpha}}\delta_{ts1s_{\alpha}} - \delta_{ts1s_{\alpha}}\delta_{ru1s_{\beta}} - \delta_{ts1s_{\beta}}\delta_{ru1s_{\beta}} \end{split}$$

where the triple-indexed delta function  $\delta_{ijk}$  means  $\delta_{ij}\delta_{jk}$ . This result, when multiplied by  $\frac{1}{2}\langle \phi_r \phi_s | 1/r_{12} | \phi_t \phi_u \rangle$  and summed over r, s, t, u, indeed yields

$$J_{1s,1s} + 2J_{1s,2s} - K_{1s,2s}$$

#### C. TENSOR OPERATORS

To gain further experience and understanding, let us also consider how specific operators that are familiar in first quantization-notation are mapped into their second-quantized analogs. The z projection of the total spin  $S_z$  is given by

$$S_z = \sum_{r,s} \langle \phi_r | S_z | \phi_s \rangle r^+ s \tag{1.23}$$

which, if the  $m_s$  dependence of the spin-orbitals is made explicit ( $\phi_r = {}^a_\beta \overline{\phi}_r$ ), becomes

$$S_{z} = \frac{1}{2}\hbar \sum_{r,s} \langle \bar{\phi}_{r} | \bar{\phi}_{s} \rangle [r_{\alpha}^{+} s_{\alpha} - r_{\beta}^{+} s_{\beta}]$$
(1.24)

Because the orbitals  $\overline{\phi}$ , are assumed to be orthonormal, spatial integration further reduces this to

$$S_{z} = \sum_{r} [r_{\alpha}^{+} r_{\alpha} - r_{\beta}^{+} r_{\beta}] \frac{1}{2} \hbar$$
 (1.25)

where the sum is over the orbitals  $\phi_r$ . The spin-raising and -lowering operators  $S_{\pm} = S_x \pm iS_y$  are, in second quantized form,

$$S_{+} = \sum_{r,s} \langle \phi_r | S_{+} | \phi_s \rangle r^+ s = \sum_r \hbar r_{\alpha}^+ r_{\beta}, \qquad (1.26)$$

$$S_{-} = \sum_{r} \hbar r_{\beta}^{+} r_{\alpha} \tag{1.27}$$

In addition to the operators discussed above, it is often important in quantum-chemical applications to evaluate commutators of pairs of operators. For example, to show that the creation operator  $r_{\alpha}^{+}$  is of doublet spin character (i.e., has the potential to change the total spin eigenvalue of any function upon which it acts by  $\pm \frac{1}{2}\hbar$ ) it is sufficient to demonstrate that  $[S_z, r_{\alpha}^{+}] = \frac{1}{2}\hbar r_{\alpha}^{+}, [S_-, r_{\alpha}^{+}] = \hbar r_{\beta}^{+}, \text{ and } [S_+, r_{\alpha}^{+}] = 0$ . As an example of how to evaluate such commutators, let us compute  $[S_z, r_{\alpha}^{+}]$  and  $[S_-, r_{\alpha}^{+}]$ :

$$[S_z, r_\alpha^+] = \frac{\hbar}{2} \sum_t [t_\alpha^+ t_\alpha - t_\beta^+ t_\beta, r_\alpha^+]$$
(1.28)

$$t_{\alpha}^{+}t_{\alpha}r_{\alpha}^{+} - r_{\alpha}^{+}t_{\alpha}^{+}t_{\alpha} = \delta_{tr}t_{\alpha}^{+} - t_{\alpha}^{+}r_{\alpha}^{+}t_{\alpha} - r_{\alpha}^{+}t_{\alpha}^{+}t_{\alpha} = \delta_{tr}t_{\alpha}^{+}$$
(1.29)

#### C. Tensor Operators

and also

$$t_{\beta}^{+}t_{\beta}r_{\alpha}^{+} - r_{\alpha}^{+}t_{\beta}^{+}t_{\beta} = -t_{\beta}^{+}r_{\alpha}^{+}t_{\beta} - r_{\alpha}^{+}t_{\beta}^{+}t_{\beta} = 0$$
(1.30)

Therefore,

$$[S_{z}, r_{\alpha}^{+}] = \frac{1}{2}\hbar r_{\alpha}^{+} \tag{1.31}$$

Before moving on, we wish to clearly point out an important consequence of performing commutation between operator pairs. For example, notice that although each term in the commutator arising in Eq. (1.29) involves three operators (e.g.,  $t_{\alpha}^{+}t_{\alpha}r_{\alpha}^{+}$ ), the final result contains only one operator. This reduction of the operator "rank" always arises when performing such commutators. We usually say that an operator such as  $r^{+}s$  has one-particle rank, whereas  $r^{+}s^{+}tu$  has two-particle rank. Such rank lowering is an important feature, which is explicitly brought about in the second-quantized language and which is used on numerous occasions in Chapter 2. Because the second-quantized operators contain no reference to N, this cancellation can be achieved at the operator level. The same cancellation occurs in first-quantization calculations but not until determinantal matrix elements are taken.

The commutator involving  $S_{-}$  can be written as

$$\begin{bmatrix} S_{-}, r_{\alpha}^{+} \end{bmatrix} = \hbar \sum_{t} \begin{bmatrix} t_{\beta}^{+} t_{\alpha}, r_{\alpha}^{+} \end{bmatrix} = \hbar \sum_{t} (t_{\beta}^{+} t_{\alpha} r_{\alpha}^{+} - r_{\alpha}^{+} t_{\beta}^{+} t_{\alpha})$$
$$= \hbar \sum_{t} (\delta_{rt} t_{\beta}^{+} - t_{\beta}^{+} r_{\alpha}^{+} t_{\alpha} - r_{\alpha}^{+} t_{\beta}^{+} t_{\alpha})$$
$$= \hbar r_{\beta}^{+}$$
(1.32)

(Again, note the reduction in particle rank.) The importance of this result is that  $r^+$  when operating on any eigenfunction of  $S^2$  (e.g.,  $S^2|0\rangle = \hbar s(s+1)|0\rangle$ ) will yield a function whose  $S_z$  eigenvalue  $m_s\hbar$  is increased by  $\frac{1}{2}\hbar$ 

$$S_z r_a^+ |0\rangle = r_a^+ S_z |0\rangle + \frac{1}{2} \hbar r_a^+ |0\rangle = (m_s + \frac{1}{2}) \hbar r_a^+ |0\rangle$$

As defined in group theory (Tinkham, 1964), general tensor operators of rank L obey  $[J_z, T^L_\mu] = \mu \hbar T^L_\mu$  and  $[J_\pm, T^L_\mu] = \hbar [L(L+1) - \mu(\mu \pm 1)]^{1/2} T^L_{\mu\pm 1}$ , where J refers to angular momentum. Our operators  $r^+_\alpha$ ,  $r^+_\beta$  correspond to  $L = \frac{1}{2}$ ,  $\mu = \pm \frac{1}{2}$ . These operators, together with their corresponding annihilation partners ( $r_\alpha = T^{1/2}_{-1/2}$ ,  $r_\beta = -T^{1/2}_{1/2}$ ), can then be combined, using vectorcoupling coefficients to generate two-or-more-electron creation operators having various total spin values. For example, the two-electron pair creation singlet tensor operator is

$$T_{rs}^{+}(0,0) = \frac{1}{\sqrt{2}} \left[ r_{\alpha}^{+} s_{\beta}^{+} - r_{\beta}^{+} s_{\alpha}^{+} \right]$$
(1.33)

whereas the two-electron triplet (with various  $M_{\star}$ ) tensor operators are

$$T_{rs}^{+}(1,1) = r_{\alpha}^{+} s_{\alpha}^{+}$$

$$T_{rs}^{+}(1,-1) = r_{\beta}^{+} s_{\beta}^{+}$$

$$T_{rs}^{+}(1,0) = \frac{1}{\sqrt{2}} \left[ r_{\alpha}^{+} s_{\beta}^{+} + r_{\beta}^{+} s_{\alpha}^{+} \right]$$
(1.34)

The operators that create singlet and triplet coupled one-electron replacements are

$$q_{rs}^{+}(0,0) = \frac{1}{\sqrt{2}} (r_{\alpha}^{+} s_{\alpha} + r_{\beta}^{+} s_{\beta}), \qquad q_{rs}^{+}(1,1) = -r_{\alpha}^{+} s_{\beta}$$

$$q_{rs}^{+}(1,-1) = r_{\beta}^{+} s_{\alpha}, \qquad q_{rs}^{+}(1,0) = \frac{1}{\sqrt{2}} [r_{\alpha}^{+} s_{\alpha} - r_{\beta}^{+} s_{\beta}]$$
(1.35)

Such tensor operators often occur when one- and two-electron operators are expressed in the second-quantization language. For example, the electronic part of the electric dipole operator  $e\mathscr{E} \cdot \sum_{i=1}^{N} \mathbf{r}_i$  becomes  $\sum_{t,s} e\mathscr{E} \cdot \langle \phi_t | \mathbf{r} | \phi_s \rangle$  $t^+s$ , which after spin integration reduces to

$$\sum_{t,s} e\mathscr{E} \cdot \langle \overline{\phi}_t | \mathbf{r} | \overline{\phi}_s \rangle [t_{\alpha}^+ s_{\alpha} + t_{\beta}^+ s_{\beta}]$$

which contains the singlet-spin tensor operator.

## D. UNITARY TRANSFORMATIONS OF ORBITALS

Having now been introduced to the basic properties of Fermion creation and annihilation operators as they express N-electron wavefunctions and quantum-mechanical operators, as well as to the strategy involved in manipulating these operators, we are nearly ready to consider the efficient use of these tools in expressing wavefunctions as they are actually employed in state-of-the-art quantum-chemical studies. It frequently occurs that we are in possession of a set of orthonormal spin orbitals that, although their construction was straightforwardly achieved, may not represent an optimal choice for the problem under consideration. Hence, it is natural to consider how one can describe unitary transformations among these orbitals within the second-quantization language. We have already shown that the replacement operator  $r^+s$  yields, when operating on a ket in which  $\phi_s$  is occupied, a new ket with  $\phi_s$  replaced by  $\phi_r$ . Now we wish to demonstrate that the exponential operator  $\exp(i\lambda)$  defined as

$$\exp(i\lambda) = 1 + i\lambda + \frac{1}{2!}(i\lambda)(i\lambda) + \cdots$$
(1.36)

#### D. Unitary Transformations of Orbitals

where

$$\lambda = \sum_{r,s} \lambda_{rs} r^+ s \tag{1.37}$$

yields, when operating on *any* ket (and hence when operating on *any* wavefunction that is expressed as a linear combination of kets), a new ket in which each spin-orbital of the original ket  $(\phi_t)$  is transformed into a new spin-orbital  $\tilde{\phi}_t$  (Dalgaard and Jørgensen, 1978). Let us therefore consider the effect of such an exponential transformation  $[\exp(i\lambda)]$  on an arbitrary ket. Using the fact that  $[\exp(i\lambda)]^{-1} = \exp(-i\lambda)$ , we may show the following:

$$\exp(i\lambda)t_1^+t_2^+\cdots t_N^+|\text{vac}\rangle = \exp(i\lambda)t_1^+\exp(-i\lambda)\exp(i\lambda)t_2^+\exp(-i\lambda)$$
$$\cdots \exp(i\lambda)t_N^+\exp(-i\lambda)\exp(i\lambda)|\text{vac}\rangle \qquad (1.38)$$

which because  $\lambda |vac\rangle = 0$  becomes

$$\tilde{t}_1^+ \tilde{t}_2^+ \cdots \tilde{t}_N^+ |\text{vac}\rangle \tag{1.39}$$

with the modified creation operators being defined by

$$\tilde{t}_k^+ \equiv \exp(i\lambda)t_k^+ \exp(-i\lambda) \tag{1.40}$$

By now expanding both of the above exponential operators, we obtain

$$\tilde{t}_{k}^{+} = t_{k}^{+} + i[\lambda, t_{k}^{+}] + \frac{i^{2}}{2!} [\lambda, [\lambda, t_{k}^{+}]] + \cdots \qquad (1.41)$$

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$$[\lambda, t_k^+] = \sum_{r,s} \lambda_{rs}[r^+s, t_k^+] = \sum_r \lambda_{rtk}r^+$$
(1.42)

$$[\lambda, [\lambda, t_k^+]] = \sum_{r,s} \lambda_{sr} \lambda_{rt_k} s^+ = \sum_s (\lambda \lambda)_{st_k} s^+$$
(1.43)

Eq. (1.41) can be rewritten

$$\tilde{t}_{k}^{+} = t_{k}^{+} + i \sum_{s} \lambda_{st_{k}} s^{+} + \frac{i^{2}}{2!} \sum_{s} (\lambda \lambda)_{st_{k}} s^{+} + \frac{i^{3}}{3!} \sum_{s} (\lambda \lambda \lambda)_{st_{k}} s^{+} + \dots = \sum_{s} [\exp(i\lambda)]_{st_{k}} s^{+}$$
(1.44)

The exponential matrix  $\exp(i\lambda)$  appearing in Eq. (1.44) is defined through the power series appearing in that equation. However, as we show below, this matrix can be computed from the  $\lambda$  matrix in a much more straightforward and practical manner.

If we want the transformation described by  $exp(i\lambda)$  to preserve orthonormality of the spin-orbitals or, equivalently, to preserve the anticommutation relations [see discussion following Eq. (1.5)]

$$[t^{+}, s]_{+} = [\tilde{t}^{+}, \tilde{s}]_{+} = \delta_{ts}$$
(1.45)

1 Introduction to Second-Quantization Methods

then certain restrictions must be placed on  $\lambda$ . This restriction, of course, requires the above transformation to be unitary. Using Eq. (1.40) and

$$[\exp(i\lambda)]^+ = \exp(-i\lambda^+)$$
(1.46)

then

$$\tilde{s} = \exp(i\lambda^+) \operatorname{sexp}(-i\lambda^+) \tag{1.47}$$

We therefore have

$$\tilde{t}^{+}\tilde{s} + \tilde{s}\tilde{t}^{+} = \exp(i\lambda)t^{+}\exp(-i\lambda)\exp(i\lambda^{+})s\exp(-i\lambda^{+}) + \exp(i\lambda^{+})s\exp(-i\lambda^{+})\exp(i\lambda)t^{+}\exp(-i\lambda)$$
(1.48)

Now if the operator  $\lambda$  is required to be hermitian, which then makes the elements  $\lambda_{rs}$  form a hermitian matrix

$$\lambda^{+} = \sum_{r,s} (\lambda_{rs}r^{+}s)^{+} = \sum_{r,s} \lambda_{rs}^{*}s^{+}r = \sum_{r,s} \lambda_{sr}s^{+}r = \lambda$$
(1.49)

then Eq. (1.48) will reduce to

$$\tilde{t}^{+}\tilde{s} + \tilde{s}\tilde{t}^{+} = \exp(i\lambda)(t^{+}s + st^{+})\exp(-i\lambda) = \delta_{ts}$$
(1.50)

which means that the above transformation does indeed preserve the anticommutation relations. The fact that the  $\lambda$  matrix is hermitian implies that the transformation matrix exp( $i\lambda$ ) occurring in Eq. (1.44) is unitary since

$$[\exp(i\lambda)]^+ = \exp(-i\lambda^+) = \exp(-i\lambda) = [\exp(i\lambda)]^{-1}$$
(1.51)

This means that the orbital transformation

$$\tilde{\phi}_r \equiv \sum_s [\exp(i\lambda)]_{sr} \phi_s \qquad (1.52)$$

is also unitary and hence preserves orthonomality.

When the matrix  $\lambda$  is hermitian, it can be divided into real and imaginary parts

$$\lambda = \alpha + i\kappa \tag{1.53}$$

where the matrix  $\alpha$  is real and symmetric ( $\alpha_{rs} = \alpha_{sr}$ ) and the matrix  $\kappa$  is real and antisymmetric ( $\kappa_{rs} = -\kappa_{sr}$ , i.e.,  $\kappa_{rr} = 0$ ). The operator  $\lambda$  may also be divided,

$$\lambda = \sum_{rs} \lambda_{rs} r^{+} s = \sum_{rs} (\alpha_{rs} + i\kappa_{rs})r^{+} s$$
$$= \sum_{r} \alpha_{rr} r^{+} r + \sum_{r>s} \alpha_{rs} (r^{+} s + s^{+} r) + i \sum_{r>s} \kappa_{rs} (r^{+} s - s^{+} r) \quad (1.54)$$

into three terms each of which are hermitian. Since we have assumed earlier that the spin-orbitals are real, orbital variations in  $\exp(i\lambda)$  described through the  $\alpha_{rs}$  parameters must vanish identically because these variations would

map the real orbitals into complex orbitals. When the variations described by the  $\alpha_{rs}$  parameters are eliminated, the unitary transformation described by  $\exp(i\lambda)$  becomes an orthogonal transformation  $\exp(-\kappa)$ . In what follows, when we refer to a unitary transformation, it is usually the orthogonal transformation described above.

To see how one can express the  $exp(i\lambda)$  matrix most compactly, let us introduce the unitary transformation u, which diagonalizes  $\lambda$ :

$$udu^{+} = \lambda, uu^{+} = u^{+}u = 1, \quad d_{rr} = \delta_{rr}d_{rr}$$
 (1.55)

Then

e

$$xp(i\lambda) = 1 + i\lambda + \frac{i^2}{2!}\lambda\lambda + \cdots$$
$$= uu^+ + iudu^+ + \frac{i^2}{2!}udu^+udu^+ + \cdots$$
$$= u\left(1 + id + \frac{i^2}{2!}dd + \frac{i^3}{3!}ddd + \cdots\right)u^+$$
$$= u exp(id)u^+$$
(1.56)

Because d is diagonal  $(dd)_{rs} = \delta_{rs}d_r^2$  and hence  $[\exp(id)]_{rs} = \delta_{rs}\exp(id_r)$ . Therefore the elements of  $\exp(i\lambda)$  are easily given by

 $[\exp(i\lambda)]_{rs} = \sum_{t} u_{rt} \exp(id_t) u_{ts}^+$ (1.57)

This equation gives a compact and efficient expression for the orbital transformation matrix appearing in Eq. (1.52).

Having seen how the operators of second quantization can be used to express wavefunctions and quantum-mechanical operators, let us now move on to the problem of choosing wavefunctions that yield optimum descriptions, in an energy optimization sense, of the stationary states of atomic and molecular systems.

#### PROBLEMS

1.1 Show the following identities to be valid for the operators A, B, and C:

$$[AB, C] = A[B, C] + [A, C]B = A[B, C]_{+} - [A, C]_{+}B$$
$$[AB, C]_{+} = [A, C]_{+}B + A[B, C]$$
$$[A_{1}A_{2} \cdots A_{N}, B] = \sum_{j=1}^{N} A_{1}A_{2} \cdots A_{j-1}[A_{j}, B]A_{j+1} \cdots A_{N}$$

1.2

1. Show by performing the following commutators and anticommutators that one achieves a lowering of the particle rank of the operators involved:

$$[i^+j, k^+l], [s, [i^+j^+lk, r^+]]_+, [r^+s, [i^+j, t^+v]]$$

2. By how much (what order) has the rank been lowered in each case?

1.3 Show that the operators  $\{q_r^+, (1, i); i = 1, 0, -1\}$  given in Eq. (1.35) are tensor operators in spin space with S = 1.

1.4 The Fermi contact Hamiltonian may, in first-quantized language, be written as

$$H_{\rm F} = \sum_{i}^{N} \sum_{a} \frac{8\pi}{3} g \cdot \beta \cdot \gamma_{a} \mathbf{S}_{i} \cdot \mathbf{I}^{a} \,\delta(\mathbf{r}_{i} - R_{a})$$

where  $I^a$  is the spin of nucleus *a*, and *g* is the electronic gyromagnetic ratio,  $\beta$  the Bohr magneton,  $\gamma_a$  the nuclear gyromagnetic factor, S the electron spin, and  $\delta(\mathbf{r})$  the Dirac delta function. Show that this Hamiltonian, in second-quantized language, may be written as

$$H_{\rm F} = \sum_{a,r,s} \frac{4\pi}{3} g\beta \gamma_a \bar{\phi}_r^*(R_a) \bar{\phi}_s(R_a) \left[ -q_{rs}^+(1,1)(I_x^a - iI_y^a) + q_{rs}^+(1,-1)(I_x^a + iI_y^a) + \sqrt{2}q_{rs}^+(1,0)I_z^a \right]$$

where  $\overline{\phi}_s(R_a)$  is the amplitude of orbital s at nucleus a and the  $q^+$  operators are defined in Eq. (1.35).

1.5 Given two orthonormal orbitals  $\phi_1$  and  $\phi_2$  expressed as linear combinations of two not necessarily orthonormal basis functions  $\chi_a$  and  $\chi_b$ :

$$\phi_{1,2} = a_{1,2}\chi_a + b_{1,2}\chi_b$$

1. Show that the two-dimensional unitary transformation given in Eq. (1.52), which in this case is described by a  $\kappa$  matrix

$$\boldsymbol{\kappa} = \begin{pmatrix} 0 & -\kappa \\ \kappa & 0 \end{pmatrix}$$

involving one parameter  $\kappa$ , can be expressed as

$$\exp(-\kappa) = \cos\kappa \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sin\kappa \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} \cos\kappa & \sin\kappa \\ -\sin\kappa & \cos\kappa \end{pmatrix}$$

2. Apply this transformation to the orbitals  $\phi_{1,2}$  for  $\kappa = 10^{\circ}$  to obtain new orbitals  $\tilde{\phi}_{1,2}$  and express  $\tilde{\phi}_{1,2}$  explicitly in terms of  $\chi_a, \chi_b, a_{1,2}, b_{1,2}$ .

Solutions

# SOLUTIONS

1.1

$$[AB, C] = ABC - CAB = ABC - ACB - CAB + ACB$$
  
=  $A[B, C] + [A, C]B = A[B, C]_{+} - [A, C]_{+}B$   
 $[AB, C]_{+} = ABC + CAB = ABC - ACB + ACB + CAB$   
=  $[A, C]_{+}B + A[B, C]$   
 $[A_{1}A_{2} \cdots A_{N}, B] = A_{1}A_{2} \cdots A_{N}B - BA_{1}A_{2} \cdots A_{N}$   
=  $A_{1}A_{2} \cdots A_{N}B - A_{1}A_{2} \cdots BA_{N}$   
 $+ A_{1}A_{2} \cdots BA_{N} - BA_{1}A_{2} \cdots A_{N}$   
=  $A_{1}A_{2} \cdots [A_{N}, B] + A_{1}A_{2} \cdots [A_{N-1}, B]A_{N}$   
 $+ A_{1}A_{2} \cdots A_{N-2}BA_{N-1}A_{N} - BA_{1}A_{2} \cdots A_{N}$ 

etc. Clearly, by continuing to move the B to the left, we generate all terms in the series:

1.2 
$$\sum_{j=1}^{N} A_1 \cdots A_{j-1} [A_j, B] A_{j+1} \cdots A_N$$

and the had set of a substant of the set of

$$\begin{split} \begin{bmatrix} i^{+}j, k^{+}l \end{bmatrix} &= i^{+}jk^{+}l - k^{+}li^{+}j \\ &= \delta_{jk}i^{+}l - i^{+}k^{+}jl - \delta_{li}k^{+}j + k^{+}i^{+}lj \\ &= \delta_{jk}i^{+}l - \delta_{li}k^{+}j \\ \begin{bmatrix} i^{+}j^{+}lk, r^{+} \end{bmatrix} &= \delta_{kr}i^{+}j^{+}l - \delta_{lr}i^{+}j^{+}k \end{split}$$

Hence

$$[s, [i^+j^+lk, r^+]]_+ = \delta_{kr}(si^+j^+l + i^+j^+ls) - \delta_{lr}(si^+j^+k + i^+j^+ks)$$
  
$$= \delta_{kr}(\delta_{is}j^+l - \delta_{js}i^+l) - \delta_{lr}(\delta_{is}j^+k - \delta_{js}i^+k)$$
  
$$[i^+j, t^+v] = \delta_{jt}i^+v - \delta_{iv}t^+j$$

Hence

$$[r^{+}s, [i^{+}j, t^{+}v]] = \delta_{jt}[r^{+}s, i^{+}v] - \delta_{iv}[r^{+}s, t^{+}j]$$
  
=  $\delta_{jt}(\delta_{si}r^{+}v - \delta_{rv}i^{+}s) - \delta_{iv}(\delta_{ts}r^{+}j - \delta_{rj}t^{+}s)$ 

2. In the first problem we lowered the rank by one, in the second by two, and in the third by two.

1.3

$$\{q_{rs}^+(1,M_s)\} = \left\{-r_{\alpha}^+ s_{\beta}, \frac{1}{\sqrt{2}}(r_{\alpha}^+ s_{\alpha} - r_{\beta}^+ s_{\beta}), r_{\beta}^+ s_{\alpha}\right\}$$

Consider the  $M_s = 0$  component only (the others are treated in like fashion):

$$\begin{split} \left[S_{x}, q_{rs}^{+}(1,0)\right] &= \sum_{j} \frac{1}{\sqrt{2}} \left[j_{\alpha}^{+} j_{\alpha} - j_{\beta}^{+} j_{\beta}, r_{\alpha}^{+} s_{\alpha} - r_{\beta}^{+} s_{\beta}\right] \hbar/2 \\ &= \frac{\hbar}{2\sqrt{2}} \sum_{j} \left\{\delta_{jr} j_{\alpha}^{+} s_{\alpha} + \delta_{jr} j_{\beta}^{+} s_{\beta} - \delta_{js} r_{\alpha}^{+} j_{\alpha} - \delta_{js} r_{\beta}^{+} j_{\beta}\right\} = 0 \\ \left[S_{+}, q_{rs}^{+}(1,0)\right] &= \sum \frac{\hbar}{\sqrt{2}} \left[j_{\alpha}^{+} j_{\beta}, r_{\alpha}^{+} s_{\alpha} - r_{\beta}^{+} s_{\beta}\right] \\ &= \frac{\hbar}{\sqrt{2}} \sum_{j} \left\{-\delta_{jr} j_{\alpha}^{+} s_{\beta} - \delta_{js} r_{\alpha}^{+} j_{\beta}\right\} \\ &= \frac{\hbar 2}{\sqrt{2}} r_{\alpha}^{+} s_{\beta} = \sqrt{2} \hbar q_{rs}^{+}(1,1) \\ \left[S_{-}, q_{rs}^{+}(1,0)\right] &= \frac{\hbar}{\sqrt{2}} \sum_{j} \left[j_{\beta}^{+} j_{\alpha}, r_{\alpha}^{+} s_{\alpha} - r_{\beta}^{+} s_{\beta}\right] \\ &= \frac{\hbar}{\sqrt{2}} \sum_{j} \left\{\delta_{jr} j_{\beta}^{+} s_{\alpha} + \delta_{js} r_{\beta}^{+} j_{\alpha}\right\} \\ &= \frac{2\hbar}{\sqrt{2}} r_{\beta}^{+} s_{\alpha} = \sqrt{2} \hbar q_{rs}^{+}(1,-1) \end{split}$$

We have thus shown that  $q_{rs}^+(1,0)$  has the properties of a tensor operator of S = 1 with  $M_s = 0$ .

1.4 Using Eq. (1.15), the second-quantized Fermi contact Hamiltonian may be written as

$$\begin{split} H_{\rm F} &= \sum_{a} \sum_{rs} \frac{8\pi}{3} g\beta \gamma_a \langle \phi_r | \mathbf{S} \cdot \mathbf{I}^a \, \delta(\mathbf{r} - R_a) | \phi_s \rangle r^+ s \\ &= \sum_{a} \sum_{rs} \frac{8\pi}{3} g\beta \gamma_a \left\langle \phi_r \right| \begin{bmatrix} \frac{1}{2} (S_+ + S_-) I_x^a + \frac{1}{2i} (S_+ - S_-) I_y^a \\ + S_z I_z^a \end{bmatrix} \delta(\mathbf{r} - R_a) \left| \phi_s \right\rangle r^+ s \\ &= \sum_{a} \sum_{rs} \frac{8\pi}{3} g\beta \gamma_a \overline{\phi}_r^*(R_a) \overline{\phi}_s(R_a) \left( \frac{1}{2} r_\alpha^+ s_\beta I_x^a + \frac{1}{2} r_\beta^+ s_\alpha I_x^a \\ &+ \frac{1}{2i} r_\alpha^+ s_\beta I_y^a - \frac{1}{2i} r_\beta^+ s_\alpha I_y^a + \frac{1}{2} r_\alpha^+ s_\alpha I_z^a - \frac{1}{2} I_z^a r_\beta^+ s_\beta \right) \end{split}$$

#### References

From the definitions of  $\{q^+(1, i), i = 1, 0, -1\}$  in Eq. (1.35), the final results given in the problem follow directly.

1.5

1.

$$\exp(-\kappa) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} 0 & \kappa \\ -\kappa & 0 \end{pmatrix} + \frac{1}{2!} \begin{pmatrix} 0 & \kappa \\ -\kappa & 0 \end{pmatrix} \begin{pmatrix} 0 & \kappa \\ -\kappa & 0 \end{pmatrix} + \cdots$$

Since

$$\begin{pmatrix} 0 & \kappa \\ -\kappa & 0 \end{pmatrix} \begin{pmatrix} 0 & \kappa \\ -\kappa & 0 \end{pmatrix} = -\kappa^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

then

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$$\exp(-\kappa) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \kappa \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} - \frac{\kappa^2}{2!} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - \frac{\kappa^3}{3!} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} + \cdots$$
$$= \cos\kappa \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \sin\kappa \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} \cos\kappa & \sin\kappa \\ -\sin\kappa & \cos\kappa \end{pmatrix}$$

2.

$$\begin{aligned} (\tilde{\phi}_1 \tilde{\phi}_2) &= (\phi_1 \phi_2) \begin{pmatrix} \cos \kappa & \sin \kappa \\ -\sin \kappa & \cos \kappa \end{pmatrix} = (\chi_A \chi_B) \begin{pmatrix} a_1 & a_2 \\ b_1 & b_2 \end{pmatrix} \begin{pmatrix} \cos \kappa & \sin \kappa \\ -\sin \kappa & \cos \kappa \end{pmatrix} \\ \kappa &= 10^\circ = 0.174 \text{ rad}, \quad \cos \kappa = 0.985, \quad \sin \kappa = 0.174 \\ (\tilde{\phi}_1 \tilde{\phi}_2) &= (\chi_a \chi_b) \begin{pmatrix} 0.985a_1 - 0.174a_2 & 0.174a_1 + 0.985a_2 \\ 0.985b_1 - 0.174b_2 & 0.174b_1 + 0.985b_2 \end{pmatrix} \end{aligned}$$

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