Chapter 4

Atomic Multiplets

In this chapter, we extend the study of atomic structure from atoms with one valence electron to those with two or more valence electrons. As illustrated in the two previous chapters, excited states of one valence electron atoms having a given angular momentum and parity can be described in the independent-particle model using a single Slater determinant. For atoms with two or more electrons, a linear combination of two or more Slater determinants are typically needed to describe a particular state. In addition to the state of interest, this linear combination describes one or more closely related states; the collection of states given by the linear combination of Slater determinants is referred to as a multiplet. To study multiplets, it is convenient to replace the description of states using Slater determinants by the equivalent second-quantization description of the following section. The rules of second-quantization rules are familiar from studies of the harmonic oscillator in quantum mechanics. A more complete discussion may be found in Lindgren and Morrison (1985).

4.1 Second-Quantization

We start our discussion of second quantization by examining the description of one- and two-electron states. As in the previous chapters, we let a single index \( k \) designate the set of one-particle quantum numbers \((n_k l_k m_k \mu_k)\). The one-electron state \(| j_k i \rangle\), described by its wave function \( \Psi_k(r) \) previously, is represented in second quantization by an operator \( a_k^\dagger \) acting on the vacuum state \(| 0 \rangle\):

\[
| k \rangle = a_k^\dagger | 0 \rangle .
\]  
(4.1)

The vacuum state is the state in which there are no electrons; it is assumed to be normalized

\[
\langle 0 | 0 \rangle = 1 .
\]  
(4.2)

The adjoint to the state \(| k \rangle\) is given by

\[
\langle k | = \langle 0 | a_k .
\]  
(4.3)
We assume that \( a_k \) operating on the vacuum state vanishes; therefore,
\[
a_k |0\rangle = 0 \quad \text{and} \quad (0|a_k^\dagger = 0. \quad (4.4)
\]
The operators \( a_k^\dagger \) and \( a_k \) are called creation and annihilation operators, respectively. The creation and annihilation operators are assumed to satisfy the following anticommutation relations:
\[
\begin{align*}
\{a_j^\dagger, a_k^\dagger\} &= a_j^\dagger a_k^\dagger + a_k^\dagger a_j^\dagger = 0, \quad (4.5) \\
\{a_j, a_k\} &= a_j a_k + a_k a_j = 0, \quad (4.6) \\
\{a_j, a_k^\dagger\} &= a_j a_k^\dagger + a_k a_j^\dagger = \delta_{jk}. \quad (4.7)
\end{align*}
\]
The third of these relations (4.7) can be used to prove the orthonormality of the one-electron states \( |j\rangle \) and \( |k\rangle \):
\[
\langle j|k \rangle = \langle 0|a_j a_k^\dagger |0\rangle = \langle 0|\delta_{jk} - a_k^\dagger a_j |0\rangle = \delta_{jk} \langle 0|0\rangle = \delta_{jk}. \quad (4.8)
\]
The antisymmetric two-electron state, represented previously by a Slater determinant \( \Psi_{jk}(r_1, r_2) \), is represented in second quantization by
\[
|jk \rangle = a_j^\dagger a_k^\dagger |0\rangle. \quad (4.9)
\]
The anticommutation relations (4.5) insure the antisymmetry of the state \( |jk \rangle \). Similarly, the antisymmetry of the adjoint state follows from the relation (4.6).
The normalization condition for a two-electron state \( |jk \rangle \) can be written:
\[
\langle jk|jk \rangle = \langle 0|a_k a_j a_j^\dagger a_k^\dagger |0\rangle = \langle 0|a_k^\dagger a_j a_j^\dagger a_k |0\rangle = \langle 0|0 - a_k^\dagger a_k - a_j^\dagger a_j + a_j^\dagger a_k a_k a_j |0\rangle = 1. \quad (4.10)
\]
If we define the number operator for a state \( |k\rangle \) by \( \mathcal{N}_k = a_k^\dagger a_k \), then, by virtue of the anticommutation relations, we obtain
\[
\mathcal{N}_k^2 = a_k^\dagger a_k a_k^\dagger a_k = a_k^\dagger a_k - a_k^\dagger a_k a_k a_k = a_k^\dagger a_k = \mathcal{N}_k. \quad (4.11)
\]
Therefore, the number operator satisfies the identity \( \mathcal{N}_k^2 - \mathcal{N}_k = 0 \). If \( n_k \) is an eigenvalue of \( \mathcal{N}_k \), then \( n_k \) satisfies the same equation, \( n_k^2 - n_k = 0 \). From this, it follows that the possible eigenvalues of \( \mathcal{N}_k \) are 0 and 1. The one-electron state \( |k\rangle \) is an eigenstate of \( \mathcal{N}_k \) with eigenvalue 1,
\[
\mathcal{N}_k |k\rangle = a_k^\dagger a_k a_k^\dagger |0\rangle = (a_k^\dagger - a_k a_k^\dagger) |0\rangle = a_k^\dagger |0\rangle = |k\rangle. \quad (4.12)
\]
A general \( N \)-particle state described by a Slater determinant wave function formed from a product of the orbitals \( \psi_a \psi_b \cdots \psi_n \) is represented in second quantization as
\[
|ab \cdots n \rangle = a_n^\dagger a_{n-1}^\dagger \cdots a_1^\dagger |0\rangle. \quad (4.13)
\]
This state is antisymmetric with respect to the interchange of any two indices; moreover, it is normalized to 1. Defining the number operator $N$ by

$$ N = \sum_k N_k = \sum_k a_k^\dagger a_k, \quad (4.14) $$

where the sum extends over all single-particle quantum numbers, it can easily be shown that $|ab\cdots n\rangle$ is an eigenstate of $N$ with eigenvalue $N$. In a similar way, we see that the state $|ab\cdots n\rangle$ is an eigenstate of the unperturbed Hamiltonian operator $H_0$ defined by

$$ H_0 = \sum_k \epsilon_k a_k^\dagger a_k, \quad (4.15) $$

with eigenvalue

$$ E^{(0)} = \epsilon_a + \epsilon_b + \cdots + \epsilon_n. \quad (4.16) $$

Here $\epsilon_k$ is the eigenvalue of the one-electron Hamiltonian $h(r)$ belonging to the eigenfunction $\psi_k(r)$:

$$ h\psi_k(r) = \epsilon_k \psi_k(r). $$

Equation (4.15) gives the representation of the unperturbed Hamiltonian $H_0$ in second quantization. This equation can be rewritten

$$ H_0 = \sum_k \langle k|h|k \rangle a_k^\dagger a_k. \quad (4.17) $$

A general single-particle operator $F = \sum_{i=1}^N f(r_i)$ is represented in second quantization as

$$ F = \sum_{kl} \langle k|f|l \rangle a_l^\dagger a_k. \quad (4.18) $$

This operator acting on the state $|ab\cdots n\rangle$ gives

$$ F |ab\cdots n\rangle = \sum_{kc} \langle k|f|c \rangle |ab\cdots c \rightarrow k\cdots n\rangle, \quad (4.19) $$

where $|ab\cdots c \rightarrow k\cdots n\rangle$ is identical to the state $|ab\cdots n\rangle$ with the operator $a_k^\dagger$ replaced by $a_k^\dagger$. In this expression, $c$ is a state occupied in $|ab\cdots n\rangle$ and the sum extends over all such states. The state $k$ is either identical to $c$ or is a state not occupied in $|ab\cdots n\rangle$. The matrix element of $F$ between a state $|ab'b'\cdots n'\rangle$ and $|ab\cdots n\rangle$ is nonvanishing only if the sets $\{ab\cdots n\}$ and $\{ab'b'\cdots n'\}$ differ in at most one place. Thus

$$ \langle ab\cdots c'\cdots n|F|ab\cdots c\cdots n\rangle = \langle c'|f|c \rangle. \quad (4.20) $$

Furthermore,

$$ \langle ab\cdots n|F|ab\cdots n\rangle = \sum_c \langle c|f|c \rangle. \quad (4.21) $$

These rules are precisely the same as those developed in Chapter 2 to calculate matrix-elements of single-particle operators between Slater determinant wave functions.
The two-particle operator,

\[ G = \frac{1}{2} \sum_{i \neq j} g(r_{ij}) , \]

is represented in second quantization by:

\[ G = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_i^\dagger a_j a_k , \quad (4.22) \]

where, as before,

\[ g_{ijkl} = Z \delta_{d_3}^3 r_1 \delta_{d_3}^3 r_2 \psi_i^\dagger (r_1) \psi_j^\dagger (r_2) g(r_{12}) \psi_k (r_1) \psi_l (r_2) . \]

Again, it is simple to verify that matrix elements of \( G \) satisfy precisely the rules written down in the previous chapter for calculating matrix elements of two-particle operators between determinant wave functions. As an example, let us consider the expectation value of \( G \) in the two-particle state \( |ab\rangle \). We have

\[ \langle ab | G | ab \rangle = \frac{1}{2} \sum_{ijkl} g_{ijkl} (\delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja}) (\delta_{ka} \delta_{lb} - \delta_{lb} \delta_{ka}) |0\rangle . \quad (4.23) \]

With the aid of the anticommutation relations, the product \( a_b a_a a_i^\dagger a_j^\dagger \) on the left in Eq.(4.23) can be rearranged to give

\[ a_b a_a a_i^\dagger a_j^\dagger = \delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja} - \delta_{ia} a_j^\dagger a_b + \delta_{ia} a_j^\dagger a_a + a_i^\dagger a_j^\dagger a_a a_a . \quad (4.24) \]

Since \( \langle 0 | a_j^\dagger = 0 \), only the first two terms on the right-hand side of this equation contribute in (4.23). Similarly, the product of operators \( a_i a_k a_b^\dagger a_a^\dagger \) can be written

\[ a_i a_k a_b^\dagger a_a^\dagger = \delta_{ka} \delta_{lb} - \delta_{ka} \delta_{lb} + \delta_{ki} a_k^\dagger a_l + \delta_{ka} a_k^\dagger a_l - \delta_{ka} a_k^\dagger a_l + a_a^\dagger a_i^\dagger a_k . \quad (4.25) \]

Only the first two terms in this expression contribute to (4.23) since \( a_k |0\rangle = 0 \). Therefore,

\[ \langle ab | G | ab \rangle = \frac{1}{2} \sum_{ijkl} g_{ijkl} (\delta_{ia} \delta_{jb} - \delta_{ib} \delta_{ja}) (\delta_{ka} \delta_{lb} - \delta_{lb} \delta_{ka}) |0\rangle = g_{abab} - g_{abba} . \quad (4.26) \]

This is precisely the result that we obtain in configuration space using a Slater determinant wave function.
4.2 ANGULAR MOMENTUM COUPLING SCHEMES

Schrödinger Hamiltonian: With the aid of the second quantization expressions for one- and two-body operators, we write the expression for the Hamiltonian in second quantization as \( H = H_0 + V \), where

\[
H_0 = \sum_k \epsilon_k a_k^\dagger a_k, \quad \text{(4.27)}
\]

\[
V = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - \sum_{ik} U_{ik} a_i^\dagger a_k. \quad \text{(4.28)}
\]

Here, \( \epsilon_k \) is the eigenvalue of the one-electron Schrödinger equation in a potential \(-Z/r + U(r)\), the quantity \( g_{ijkl} \) is a two-electron matrix element of the Coulomb potential \( g(r_{12}) = 1/r_{12} \) and \( U_{ik} \) is the one-electron matrix element of the background potential \( U(r) \):

\[
U_{ik} = \int d^3r \psi_i^\dagger(r) U(r) \psi_k(r). \quad \text{(4.29)}
\]

No-Pair Hamiltonian: The Dirac-Coulomb Hamiltonian of the previous chapter can also be cast in second-quantized form. Again, \( H = H_0 + V \), where \( H_0 \) and \( V \) are given by the formulas (4.27-4.28). For the Dirac case, \( \epsilon_k \) in (4.27) is an eigenvalue of the one-electron Dirac Hamiltonian in a potential \(-Z/r + U(r)\), and \( g_{ijkl} \) is a two-electron Coulomb integral evaluated with Dirac orbitals. In the expression for the Hamiltonian, the operators are restricted to be creation and annihilation operators for positive-energy solutions to the Dirac equation. These are the solutions associated with electron states. Contributions from negative-energy (positron) states are omitted from the Hamiltonian entirely. The resulting Hamiltonian is called the no-pair Hamiltonian. Since positron states are not present in the no-pair Hamiltonian, effects of virtual electron-positron pairs on atomic structure are omitted. To account for these small effects, we must carry out a separate QED calculation. The no-pair Hamiltonian is free from the problems mentioned in the previous chapter in connection with the Dirac-Coulomb Hamiltonian; it can be used in higher-order perturbation theory calculations. The no-pair Hamiltonian was introduced in a slightly different form by Brown and Ravenhall (1951) and has been discussed in great detail by Mittleman (1971, 1972, 1981) and Sucher (1980).

4.2 Angular Momentum Coupling Schemes

Before continuing our discussion of many-body techniques, it is necessary to make a short digression into angular momentum theory to discuss coupling of three or four angular momentum vectors.

4.2.1 6-j Symbols

The Wigner 6-j symbols arise when we consider the coupling of three angular momentum vectors quantum mechanically. We can couple three single-particle
states with angular momenta \( j_1, j_2 \) and \( j_3 \) to a total angular momentum \( J \) in various ways. For example, we can first couple \( j_1 \) and \( j_2 \) to an intermediate angular momentum \( J_{12} \), and then couple \( J_{12} \) and \( j_3 \) to \( J \) and \( M \), leading to the state

\[
|j_1(\j_1 \j_2 \j_3) \rangle = \sum_{m_1, m_2, m_3} |j_1 \rangle |j_2 \rangle |j_3 \rangle \langle j_1 \rangle |j_2 \rangle |j_3 \rangle = \sum_{m_1, m_2, m_3} \frac{1}{\sqrt{\delta_{j_1m_1, j_2m_2} \delta_{j_3m_3}}} |j_1 \rangle |j_2 \rangle |j_3 \rangle .
\]

(4.30)

Alternatively, we can couple \( j_2 \) and \( j_3 \) to \( J_{23} \), and then couple \( j_1 \) to \( J_{23} \) to give the resulting value of \( J \) and \( M \). This order of coupling leads to the state

\[
|j_1(j_2j_3) \rangle = \sum_{m_1, m_2, m_3} |j_1 \rangle |j_2 \rangle |j_3 \rangle \langle j_1 \rangle |j_2 \rangle |j_3 \rangle = \sum_{m_1, m_2, m_3} \frac{1}{\sqrt{\delta_{j_1m_1, j_2m_2} \delta_{j_3m_3}}} |j_1 \rangle |j_2 \rangle |j_3 \rangle .
\]

(4.31)

States obtained from either of these two coupling schemes can be expressed as linear combinations of states obtained using the other scheme. Thus, for example, we may write

\[
|j_1(j_2j_3) \rangle = \sum_{J_{12}} |j_1(j_2j_3) \rangle |j_1 \rangle \langle j_1 \rangle |j_2 \rangle |j_3 \rangle = \sum_{J_{12}} \frac{1}{\sqrt{\delta_{j_1m_1, j_2m_2} \delta_{j_3m_3}}} |j_1 \rangle |j_2 \rangle |j_3 \rangle .
\]

(4.32)

The resulting recoupling coefficient \( \langle j_1(j_2j_3), J_{12}, J_{23}, J, M \rangle \) is independent of \( M \). We evaluate this coefficient by connecting the lines corresponding to \( j_1, j_2 \) and \( j_3 \) in the graphs from (4.30) and (4.31) above. The resulting graph has two free ends, both labeled by \( J, M \). Since the recoupling coefficient is independent of \( M \), we may obtain the coefficient by averaging over \( M \). This is done by connecting the free ends and dividing by \( |J| \). The resulting coefficient can be expressed as

\[
\langle j_1(j_2j_3), J_{12}, J_{23}, J, M \rangle = \langle j_1(j_2j_3), J_{12}, J_{23}, J \rangle / |J|,
\]

(4.33)

where the expression in curly brackets can be brought into the graphical form

\[
\left\{ \begin{array}{ccc} j_1 & j_2 & J_{12} \\ j_3 & J_{23} \end{array} \right\} = \frac{1}{|J|} \left( \begin{array}{ccc} j_1 & j_2 & J_{12} \\ J_{12} & J_{23} & j_3 \end{array} \right).
\]

(4.34)
The quantity
\[
\left\{ \begin{array}{ccc} j_1 & j_2 & j_{12} \\ j_3 & J & J_{23} \end{array} \right\}
\]
is a 6-j symbol. This quantity vanishes unless angular momentum triangle inequalities are satisfied by the triples \( j_1 j_2 J_{12}, j_3 J J_{12}, j_3 J_{23}, j_1 J_{23} \). Moreover, the 6-j symbols satisfy the symmetry relations
\[
\frac{1}{2} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ l_a & l_b & l_c \end{array} \right\} = \frac{1}{2} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ l_b & l_a & l_c \right\} = \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ l_a & l_b & l_c \right\}.
\]
(4.35)

In other words, the 6-j symbol is invariant with respect to a permutation (even or odd) of columns. Further, the 6-j symbol satisfies the symmetry relations
\[
\frac{1}{2} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ l_a & l_b & l_c \end{array} \right\} = \frac{1}{2} \left\{ \begin{array}{ccc} j_a & l_b & l_c \\ l_a & j_b & j_c \right\} = \left\{ \begin{array}{ccc} l_a & j_b & j_c \\ l_a & l_b & l_c \right\};
\]
(4.36)
i.e., the 6-j symbol is invariant under inversion of the arguments in any two columns.

The graphical representation of the 6-j symbol leads to its analytical expression in terms of 3-j symbols
\[
\frac{1}{2} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\} = \sum_{m's} (-1)^K \times
\left( \begin{array}{ccc} j_a & j_b & j_c \\ -m_a & -m_b & -m_c \end{array} \right) \left( \begin{array}{ccc} j_a & j_e & j_f \\ m_a & -m_e & m_f \end{array} \right) \times
\left( \begin{array}{ccc} j_b & j_f & j_d \\ m_b & m_f & m_d \end{array} \right) \left( \begin{array}{ccc} j_c & j_d & j_e \\ m_c & -m_d & m_e \end{array} \right),
\]
(4.37)
with
\[ K = j_a - m_a + j_b - m_b + j_c - m_c + j_d - m_d + j_e - m_e + j_f - m_f \]

A useful formula (Edmonds, 1974) for calculating 6-j symbols is
\[
\left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\} = \Delta(j_a j_b j_c) \Delta(j_d j_e j_f) \Delta(j_d j_b j_f) \Delta(j_d j_e j_c) \times
\sum_k \left[ \frac{(-1)^k (k + 1)!}{(k - j_a - j_b - j_c)! (k - j_a - j_e - j_f)!} \times \frac{1}{(k - j_d - j_b - j_f)! (k - j_d - j_e - j_c)! (j_a + j_b + j_d + j_e - k)!} \times \frac{1}{(j_b + j_c + j_e + j_f - k)! (j_c + j_a + j_f + j_d - k)!} \right],
\]
(4.38)
where
\[
\Delta(j_a j_b j_c) = \sqrt{\frac{(j_a + j_b + j_c)! (j_a - j_b + j_c)! (-j_a + j_b + j_c)!}{(j_a + j_b + j_c + 1)!}}.
\]
(4.39)
The 6-j symbols satisfy the following orthogonality relation

$$\sum_{j_f} [j_c][j_f] \frac{1}{\sqrt{S(S+1)}} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\} \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\} = \delta_{j_c,j_f}. \quad (4.40)$$

Additionally, they satisfy the following two sum rules: (Racah)

$$\sum_{j_f} (-1)^{s+k+|j_f|} [j_f] \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\} = \left\{ \begin{array}{ccc} j_a & j_b & j_c \\ j_d & j_e & j_f \end{array} \right\}, \quad (4.41)$$

and (Biedenharn, 1953; Elliott, 1953)

$$\sum_{k} (-1)^{s+k}[k] \left\{ \begin{array}{ccc} l_1 & l_2 & l_3 \\ l_1' & l_2' & l_3' \end{array} \right\} \left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ j_1' & j_2' & j_3' \end{array} \right\} = \left\{ \begin{array}{ccc} l_1 & l_2 & l_3 \\ l_1' & l_2' & l_3' \end{array} \right\}, \quad (4.42)$$

where $S = j_1 + j_2 + j_3 + l_1 + l_2 + l_3 + l_1' + l_2' + l_3'$. The following special case is often useful

$$\left\{ \begin{array}{ccc} j_1 & j_2 & j_3 \\ l_1 & l_2 & 0 \end{array} \right\} = \delta_{j_1,j_2} \delta_{j_2,l_1} \frac{(-1)^{j_1+j_2+j_3}}{\sqrt{|j_1||j_2|}}. \quad (4.43)$$

### 4.2.2 9-j Symbols

Let us consider the problem of coupling spin and orbital angular momenta of two electrons to total angular momentum $J$. This problem requires us to consider ways of coupling four angular momentum vectors, which can be done in several ways. For example, we may couple the orbital angular momenta $l_1$ and $l_2$ of the electrons to $L$, the spin angular momenta $s_1$ and $s_2$ to $S$, then couple the resulting $L$ and $S$ to a final $J$. This method of coupling the angular momenta of two electrons is referred to as $LS$ coupling. The angular part of the two-electron wave function for an $LS$-coupled state is

$$\langle (l_1 l_2) | (s_1 s_2) S | J M \rangle = \sum_{m_1 m_2 \mu_1 \mu_2} \frac{(-1)^{l_1 m_1 + l_2 m_2}}{\sqrt{S(S+1)}} \frac{J M}{S M_S} \langle l_1 m_1 | l_2 m_2 | s_1 \mu_1 \rangle \langle l_2 m_2 | s_2 \mu_2 \rangle. \quad (4.44)$$

As an alternative to $LS$ coupling, we can first couple $l_1$ and $s_1$ to $j_1$, then couple $l_2$ and $s_2$ to $j_2$, and finally couple the resulting $j_1$ and $j_2$ to $J$. This is referred to as the $jj$ coupling scheme. The angular parts of the one-electron wave function that results from coupling $l_i$ and $s_i$ to $j_i$ are just the spherical spinors $\Omega_{\kappa_i m_i}$. 
4.2. ANGULAR MOMENTUM COUPLING SCHEMES

The angular part of the two-electron wave function in the \( jj \) coupling scheme is

\[
\langle |(l_1s_1)_{j_1} \rangle |(l_2s_2)_{j_2} \rangle JM = \sum_{m_1m_2} \frac{\epsilon_{j_1j_2M_1j_2M_2}}{\epsilon_{j_1j_2M_1j_2M_2}} |(l_1m_1)_{s_1\mu_1} \rangle |(l_2m_2)_{s_2\mu_2} \rangle |s_1\mu_1 \rangle |s_2\mu_2 \rangle. \tag{4.45}
\]

Either scheme can be used to describe possible two-electron wave functions; the \( LS \) scheme is a more convenient starting point for describing states in atoms with low nuclear charge where relativistic (spin-orbit) effects are negligible, while the \( jj \) scheme is more convenient for atoms with high nuclear charge where relativistic effects are important. The natural starting point for relativistic calculations of two electron systems, where single-particle orbitals are taken from the Dirac equation, is the \( jj \)-scheme.

We may write each \( jj \) coupled wave functions as a linear combinations of \( LS \) wave functions:

\[
\langle |(l_1s_1)_{j_1} \rangle |(l_2s_2)_{j_2} \rangle JM = \sum_{LS} \langle LS J \mid j_1 j_2 J \rangle \langle |(l_1l_2)_{L} \rangle |(s_1s_2)_{S} \rangle JM \rangle, \tag{4.46}
\]

where the orthogonal matrix \( \langle LS J \mid j_1 j_2 J \rangle \) is given diagrammatically by

\[
\langle LS J \mid j_1 j_2 J \rangle = (-1)^R \sqrt{|L| |S| |j_1| |j_2|} + \sum_{LS} \langle LS J \mid j_1 j_2 J \rangle \langle |(l_1l_2)_{L} \rangle |(s_1s_2)_{S} \rangle JM \rangle, \tag{4.47}
\]

The phase factor \( R = l_1 + l_2 + s_1 + s_2 + j_1 + j_2 + L + S + J \) is the sum of all 9 angular momentum quantum numbers. The hexagonal diagram above serves to define the 9-j symbol:

\[
\{ L \ S \ J \} = \sum_{LS} \langle LS J \mid j_1 j_2 J \rangle \langle |(l_1l_2)_{L} \rangle |(s_1s_2)_{S} \rangle JM \rangle, \tag{4.48}
\]

The 9-j symbol can be expressed conveniently as a product of 3-j symbols:

\[
\{ a \ b \ c \} \{ d \ e \ f \} \{ g \ h \ j \} = \sum_{x} (-1)^{2x} [x] \{ a \ b \ c \} \{ d \ e \ f \} \{ g \ h \ j \}. \tag{4.49}
\]

The 9-j symbol is invariant under an even permutation of rows or columns. An odd permutation of rows or columns gives rise to a phase factor \((-1)^R\), where
$R$ is the previously defined sum of nine angular momenta. The $9$-j symbol is also symmetric with respect to a transposition of rows and columns. Thus, for example

$$
\begin{pmatrix}
a & b & c \\
d & e & f \\
g & h & j
\end{pmatrix}
= (-1)^R
\begin{pmatrix}
a & d & g \\
b & e & h \\
c & f & j
\end{pmatrix}
$$

With the aid of the symmetry relations, we may write the transformation matrix from the $LS$ to $jj$ scheme as

$$
\begin{pmatrix} L \\ S \end{pmatrix}
\begin{pmatrix}
I_1 & S_1 & J_1 \\
I_2 & S_2 & J_2
\end{pmatrix}
= \frac{\delta_{c,f} \delta_{gh}}{\sqrt{|c||g|}}
\begin{pmatrix}
a & b & c \\
d & e & f \\
g & h & 0
\end{pmatrix}
\begin{pmatrix}
I_1 & S_1 & J_1 \\
I_2 & S_2 & J_2
\end{pmatrix}.
$$

A useful special case to bear in mind is that in which one angular momentum is zero. In that case, one finds:

$$
\begin{pmatrix}
a & b & c \\
d & e & f \\
g & h & 0
\end{pmatrix}
= \delta_{c,f} \delta_{gh}
\begin{pmatrix}
a & b & c \\
e & d & g
\end{pmatrix}.
$$

### 4.3 Two-Electron Atoms

In this Section, we use second quantization to study the excited states of two-electron atoms and ions. We start our discussion by considering a two-electron state $|ab\rangle$. This is an eigenstate of $H_0$, with eigenvalue $E_{ab}^{(0)} = \epsilon_a + \epsilon_b$:

$$
H_0 |ab\rangle = (\epsilon_a + \epsilon_b) |ab\rangle.
$$

The state $|ab\rangle$ is $2|l_a\rangle \times 2|l_b\rangle$-fold degenerate. It is not necessarily an angular momentum eigenstate. We make use of the degeneracy to construct eigenstates of $L^2$, $L_z$, $S^2$ and $S_z$ from $|ab\rangle$. To this end, we first couple $l_a$ and $l_b$ to give an eigenstate of $L^2$ and $L_z$, then we couple $s_a$ ($s_a = 1/2$) and $s_b$ ($s_b = 1/2$) to give an eigenstate of $S^2$ and $S_z$. The possible eigenvalues of $S^2$ are $S(S + 1)$, where $S = 0$ or 1. States with $S = 0$ are referred to as singlet states, since there is only one such state with $M_S = 0$. States with $S = 1$ are called triplet states. The resulting eigenstates of $L^2$, $L_z$, $S^2$ and $S_z$ are called $LS$-coupled states. Singlet states are also eigenstates of $J$ ($J = L + S$) with $J = L$. Triplet states can be further combined to give eigenstates of $J$ having eigenvalues $J = L - 1$, $L$, $L + 1$. Nonrelativistically, the triplet states with different values of $J$ are degenerate. This degeneracy is lifted in relativistic calculations. The observed spectrum of helium consists of singlets and triplets of various angular symmetries $S$, $P$, ... corresponding to $L = 0$, 1, .... The triplets are slightly split by relativistic effects. $LS$-coupled states with orbital angular momentum $L$, spin angular momentum $S$, and total angular momentum $J$ are designated by the spectroscopic notation $^{2S+1}L_J$. In Fig. 4.1, we show the
4.3. TWO-ELECTRON ATOMS

<table>
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<tr>
<th>1S</th>
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Figure 4.1: Energy level diagram for helium

approximate ordering of the low-lying singlet and triplet levels of helium in an energy level (or Grotrian) diagram.

To form the $LS$-coupled states, we combine the degenerate states according to

$$
|ab, LM_L, SM_S\rangle = \eta \sum_{m_a,m_b,\mu_a,\mu_b} \begin{pmatrix} \frac{1}{2\mu_a} & \frac{1}{2\mu_b} \\ \frac{LM_L}{L} & \frac{SM_S}{S} \end{pmatrix} \hat{a}_{\mu a}^\dagger \hat{a}_{\mu b}^\dagger |0\rangle.
$$

Here, $\eta$ is a normalization factor. The norm of this coupled state is easily shown to be

$$
\langle ab, LM_L, SM_S|ab, LM_L, SM_S\rangle = \eta^2 (1 + (-1)^{S+L}\delta_{n_bn_a}\delta_{l_a l_b})).
$$

For states with $n_b \neq n_a$ or $l_b \neq l_a$, we obtain a normalized state by choosing $\eta = 1$. For states formed from identical orbitals ($n_b = n_a$ and $l_b = l_a$), the sum $L + S$ must be even in order to have a normalizable state. To normalize such a state, we choose $\eta = 1/\sqrt{2}$. An example of a state formed from identical orbitals is the $(1s)^2$ ground state. This state has $L = 0$ and $S = 0$; it is a $1S_0$ state.

The first-order correction to the energy of an $LS$-coupled state is given by

$$
E_{ab,LS}^{(1)} = \langle ab, LM_L, SM_S|V|ab, LM_L, SM_S\rangle.
$$

This result can be written

$$
E_{ab,LS}^{(1)} = \eta^2 \sum_{m'm'\mu'\mu} \begin{pmatrix} \frac{1}{2\mu_a} & \frac{1}{2\mu_b} \\ \frac{LM_L}{L} & \frac{SM_S}{S} \end{pmatrix} \begin{pmatrix} \frac{1}{2\mu'_a} & \frac{1}{2\mu'_b} \\ \frac{LM_L}{L} & \frac{SM_S}{S} \end{pmatrix} \begin{pmatrix} g_{a'\nu a'\mu} \delta_{\mu'\mu-a} \delta_{\nu'\nu} & -g_{a'\nu a'\mu} \delta_{\mu'\mu-a} \delta_{\nu'\nu} \\ -g_{a'\nu a'\mu} \delta_{\mu'\mu-a} \delta_{\nu'\nu} & g_{a'\nu a'\mu} \delta_{\mu'\mu-a} \delta_{\nu'\nu} \end{pmatrix} (U_{aa} + U_{bb})
$$

.$$
We make use of the identity
\[
g_{abcd} = \sum_k \begin{vmatrix} l_a & m_a \\ k & l_b \end{vmatrix} \begin{vmatrix} l_m & l_m \\ l_a & l_b \end{vmatrix} X_k(abcd),
\]
where
\[
X_k(abcd) = (-1)^k |l_a||C^k||l_b||C^l| R_k(abcd).
\]
Substituting this into the expression for the first-order energy, we find
\[
E^{(1)}_{ab,LS} = \eta^2 \sum_k \left[ (-1)^{L+k+l_a+l_b} \begin{vmatrix} l_a & l_b \\ l_b & l_a \end{vmatrix} L \begin{vmatrix} l_m & l_m \\ l_a & l_b \end{vmatrix} X_k(abab) \right.
\]
\[
+ (-1)^{S+k+l_a+l_b} \begin{vmatrix} l_a & l_b \\ l_b & l_a \end{vmatrix} L \begin{vmatrix} l_m & l_m \\ l_a & l_b \end{vmatrix} X_k(abbab) \left. - U_{aa} - U_{bb} \right].
\]
Let us consider the special case where \(a\) is a \(1s\) state and \(b\) is an \(nl\) excited state. Such states are single-particle excitations of the helium ground state. All of the bound levels of helium are of this type; doubly-excited states of helium are not bound! We, therefore, set \(l_a = 0\) and \(l_b = l\) in Eq.(4.59). In the first term, \(k = 0\) so the sum reduces to
\[
R_0(1s, nl, 1s, nl).
\]
Here, we have made use of Eq.(4.43) and the fact that \(\langle s||C^k||s\rangle = \delta_{k0}\) and \(\langle l||C^0||l\rangle = \sqrt{l}\). In the second term, we find from Eq.(4.43) that \(k = L = l\). Furthermore, \(\langle l||C^l||s\rangle = 1\), and \(\langle s||C^l||l\rangle = (-1)^l\). Therefore, the second term reduces to
\[
(-1)^S \frac{1}{|l|} R_l(1s, nl, nl, 1s) \delta_{LL}.
\]
Combining these results, we obtain for \((1snl)\) states
\[
E^{(1)}_{1snl,LS} = \eta^2 \left[ R_0(1s, nl, 1s, nl) + (-1)^S \frac{1}{|l|} R_l(1s, nl, nl, 1s) \right.
\]
\[
- U_{1s1s} - U_{nlnl} \left. \delta_{LL} \right].
\]
First, let us consider the case \(nl = 1s\). In this case, as discussed above, \(S = 0\) and \(\eta = 1/\sqrt{2}\), leading to the result
\[
E^{(1)}_{1s1s,00} = R_0(1s, 1s, 1s, 1s) - 2U_{1s1s}.
\]
This is precisely the expression obtained in the previous section for the first-order correction to the ground-state energy of a heliumlike ion. For states with \(nl \neq 1s\), \(\eta = 1\) and we find
\[
E^{(1)}_{1snl,LS} = \left( R_0(1s, nl, 1s, nl) + (-1)^S \frac{1}{|l|} R_l(1s, nl, nl, 1s) \right.
\]
\[
- U_{1s1s} - U_{nlnl} \left. \delta_{LL} \right].
\]
Table 4.1: Energies of \((1s_{nl})\) singlet and triplet states of helium (a.u.). Comparison of a model-potential calculation with experiment (Moore).

| \(nl\) | \(2s\) | \(2s\) | \(3s\) | \(3s\) | \(4s\) | \(4s\) | \(5s\) | \(5s\) | \(2p\) | \(2p\) | \(3p\) | \(3p\) | \(4p\) | \(4p\) | \(5p\) | \(5p\) | \(3d\) | \(3d\) | \(4d\) | \(4d\) | \(5d\) | \(5d\) | \(4f\) | \(4f\) | \(5f\) | \(5f\) |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 2s    | -.153734 | -.145954 | -.172019 | -.175212 | .018285 | .029258 |
| 3s    | -.063228 | -.061264 | -.068014 | -.068682 | .004785 | .007418 |
| 4s    | -.034363 | -.033582 | -.036265 | -.036508 | .001902 | .002925 |
| 5s    | -.021562 | -.021174 | -.022502 | -.022616 | .000940 | .001442 |
| 2p    | -.121827 | -.123823 | -.130465 | -.133154 | .008638 | .009331 |
| 3p    | -.054552 | -.055126 | -.057337 | -.058075 | .002785 | .002939 |
| 4p    | -.030820 | -.031065 | -.032022 | -.032321 | .001202 | .001258 |
| 5p    | -.019779 | -.019903 | -.020400 | -.020549 | .000621 | .000645 |
| 3d    | -.055546 | -.055614 | -.055572 | -.055592 | .000026 | .000015 |
| 4d    | -.031244 | -.031276 | -.031260 | -.031285 | .000015 | .000008 |
| 5d    | -.019997 | -.020014 | -.020006 | -.020018 | .000009 | .000005 |
| 4f    | -.031250 | -.031246 | -.031250 | -.031249 | .000000 | .000003 |
| 5f    | -.020000 | -.020005 | -.020000 | -.019999 | .000000 | .000007 |

The lowest-order energy of these states, \(\epsilon_{1s} + \epsilon_{nl}\), is independent of \(S\). The separation between the singlet and triplet states is, therefore, given by

\[
\Delta E = E_{1s_{nl}, S=0} - E_{1s_{nl}, S=1} = \frac{2}{|l|} R_{l}(1s, nl, nl, 1s) .
\]

In Table 4.1, we compare a first-order perturbation theory calculation of the energies of the singlet and triplet states, \(S\), \(P\), \(D\), and \(F\) of helium with experiment. For the purposes of this calculation, we assume that the \(1s\) electron moves in the unscreened potential of the nucleus, but that the excited \(nl\) electrons move in the field of the nucleus screened by the monopole potential \(v_0(1s, r)\) of the \(1s\) electron. This somewhat exotic potential can be formally described in terms of projection operators. We let \(P = \langle 1s | 1s \rangle\) be the projection operator onto the \(1s\) state, and \(Q\) be the projection operator onto the complement to the \(1s\) state:

\[
Q = \sum_{nl\neq 1s} |nl \rangle \langle nl| .
\]

It follows that \(P + Q = 1\). We represent the screening potential by

\[
U = Q v_0 Q = v_0 - P v_0 - v_0 P + P v_0 P .
\]
Note that
\[ U_{1s} = v_0 |1s\rangle - |1s\rangle \langle 1s| v_0 |1s\rangle - v_0 |1s\rangle + |1s\rangle \langle 1s| v_0 |1s\rangle = 0, \quad (4.64) \]
while for \( nl \neq 1s \) we find,
\[ U_{nl} = v_0 |nl\rangle - |1s\rangle \langle 1s| v_0 |nl\rangle. \quad (4.65) \]
For states with \( l \neq 0 \), the second term in the above expression vanishes and \( U = v_0 (1s, r) \). For states with \( l = 0 \), the second term ensures that the resulting radial wave function is orthogonal to the \( 1s \) wave function. Notice that \( U_{1s1s} = 0 \) for this potential, and that \( U_{nl} = R_0 (1s, nl, 1s, nl) \). For comparison with experiment, we evaluate the energy relative to that of the hydrogenlike ion formed when the \( nl \) electron is removed. The energy of the hydrogenic ion is precisely \( \epsilon_{1s} \). The energy relative to the ion in this model potential is, therefore, given by
\[ E_{1snl,LS} - E_{\text{ion}} = \epsilon_{nl} + (-1)^s \frac{1}{[l]} R_l (1s, nl, nl, 1s). \quad (4.66) \]
Values obtained from this formula are tabulated in Table 4.1. As seen from this Table, this simple model potential suffices to predict the multiplet structure in helium at the few-percent level of accuracy.

### 4.4 Atoms with One or Two Valence Electrons

In this section, we study states of atoms that have one or two valence electrons beyond closed shells. For atoms with one valence electron, the present section is an extension of our previous discussion using the \( V_{\text{HF}}^{N-1} \) potential. For atoms with two valence electrons, the material here is an extension of the discussion of excited states of helium given in the previous section.

We let \( |0_c\rangle \) represent the ionic core, which is assumed to consists of filled subshells,
\[ |0_c\rangle = a_0^d a_1^d \cdots |0\rangle. \quad (4.67) \]
The states of interest can then be described as
\[ |v\rangle = a_v^d |0_c\rangle, \quad (4.68) \]
\[ |vw\rangle = a_v^d a_w^d |0_c\rangle, \quad (4.69) \]
where the indices \( v \) and \( w \) designate orbitals that are different from any of those occupied in the core. Here and later, we adopt the notation that letters at the beginning of the alphabet \( a, b, \cdots \), designate core orbitals, letters in the middle of the alphabet \( i, j, \cdots \), designate either core or excited (outside of the core) orbitals, letters \( m, n, \cdots \), represent excited orbitals, and letters at the end of the alphabet \( v, w, \cdots \), represent valence orbitals. Valence orbitals are, of course, special cases of excited orbitals.

It is useful to introduce the normal product of operators here. The normal product of two operators is defined as the product rearranged so that core
creation operators are always put to the right of core annihilation operators and excited state annihilation operators are always put to the right of excited state creation operators. In carrying out that rearrangement, a sign change is made for each operator transposition. Normal products are designated by enclosing the operators between pairs of colons; thus : a\textsuperscript{†}_{m} a_{n} : represents the normal product of the operators a\textsuperscript{†}_{m} and a_{n}. Normal products of two creation operators or two annihilation operators are just the product of the two operators. Moreover,

\begin{align*}
: a_{m}^\dagger a_{n} : &= a_{m}^\dagger a_{n} , \\
: a_{n} a_{m} : &= - a_{n}^\dagger a_{m} , \\
: a_{a}^\dagger a_{b} : &= - a_{b} a_{a}^\dagger , \\
: a_{b} a_{a}^\dagger : &= a_{b} a_{a}^\dagger .
\end{align*}

This definition can be extended to arbitrary products of operators. The normal product of \( N \) operators is the product of the \( N \) operators rearranged so that core creation operators are to the right of core annihilation operators and excited state annihilation operators are to the right of excited state creation operators with a sign change for each transposition of two operators. With this definition, it follows that the expectation value of the normal product of two operators calculated in the core state vanishes:

\begin{equation}
\langle 0_{c} | : a_{0} a_{1} \cdots a_{l} : | 0_{c} \rangle = 0 .
\end{equation}

Here \( o_{i} \) designates either a creation operator \( a_{i}^\dagger \) or an annihilation operator \( a_{i} \).

The Hamiltonian \( H \) can be expressed in terms of normal products by

\begin{align*}
H &= H_{0} + V , \\
H_{0} &= E_{0} + \sum_{k} \epsilon_{k} : a_{k}^\dagger a_{k} : , \\
V &= \frac{1}{2} \sum_{ijkl} g_{ijkl} : a_{i}^\dagger a_{j}^\dagger a_{l} a_{k} : + \sum_{ij} (V_{HF} - U)_{ij} : a_{i}^\dagger a_{j} : \\
&\quad + V_{0} .
\end{align*}

Here

\[ E_{0} = \sum_{a} \epsilon_{a} , \]

and

\[ V_{0} = \sum_{a} \left[ \frac{1}{2} (V_{HF})_{aa} - U_{aa} \right] . \]

In the above equations we have used the notation

\[ (V_{HF})_{ij} = \sum_{b} (g_{ibjb} - g_{ibbj}) . \]
The quantity $V_{\text{HF}}$ is just the Hartree-Fock potential of the closed core. We should notice that 
\[ E_{\text{core}} = \langle 0_c | H | 0_c \rangle = E_0 + V_0 = \sum_a \epsilon_a + \frac{1}{2} \sum_{ab} (g_{abab} - g_{abba}) - \sum_a U_{aa}. \] 
(4.75)

This result was derived previously by manipulating Slater determinants.

**One valence electron:** Let us first consider an atom with one valence electron in a state $v$. To help evaluate the expectation value of $H_0$, we make use of the easily established identity
\[ a_v : a_k^\dagger a_k : a_v^\dagger : = a_v a_k a_k a_v : + \delta_{kv} : a_k a_v^\dagger : + \delta_{kv} : a_v a_k^\dagger : + \delta_{kv}. \] 
(4.76)

From this identity, it follows that 
\[ \langle v | a_k^\dagger a_k : | v \rangle = \langle 0_c | a_v : a_k^\dagger a_k : a_v^\dagger | 0_c \rangle = \delta_{kv}. \] 
(4.77)

Therefore, from Eq.(4.72) it follows that,
\[ E_v^{(0)} = \langle v | H_0 | v \rangle = E_0 + \epsilon_v. \] 
(4.78)

To evaluate the first-order energy, we make use of the identities
\[ \langle 0_c | a_v : a_k^\dagger a_j a_k : a_v^\dagger | 0_c \rangle = 0, \] 
(4.79)
\[ \langle 0_c | a_v : a_j^\dagger a_v : a_v^\dagger | 0_c \rangle = \delta_{iv} \delta_{jv}. \] 
(4.80)

Combining these relations with the expression for $V$ given in Eq.(4.73), we find
\[ E_v^{(1)} = \langle v | V | v \rangle = V_0 + (V_{\text{HF}} - U)_{vv}. \] 
(4.81)

To first order, we therefore have
\[ E_v = E_{\text{core}} + \epsilon_v + (V_{\text{HF}} - U)_{vv}. \] 
(4.82)

If we let $U$ be the Hartree-Fock potential of the core, then the valence orbital is just the $V_{\text{HF}}^{-1}$ orbital discussed in the previous section. As we found previously, $\epsilon_v$ is the difference between the energy of the atom and ion. This rule will, of course, be modified when we consider corrections from higher-order perturbation theory. For atoms with one valence electron, the second-quantization approach leads easily to results obtained previously by evaluating matrix elements using Slater determinants.

**Two valence electrons:** Now, let us turn to atoms having two valence electrons. As an aid to evaluating the energy for such atoms, we make use of the identities
\[ \langle 0_c | a_w a_v : a_j^\dagger a_i^\dagger a_k a_j : a_i^\dagger a_w^\dagger | 0_c \rangle = (\delta_{iv} \delta_{jw} - \delta_{iv} \delta_{iw} ) \times (\delta_{kw} \delta_{lw} - \delta_{kv} \delta_{lw} ), \] 
(4.83)
\[ \langle 0_c | a_w a_v : a_i^\dagger a_j : a_i^\dagger a_w^\dagger | 0_c \rangle = \delta_{iw} \delta_{jv} + \delta_{iw} \delta_{jw}. \] 
(4.84)
4.4. ATOMS WITH ONE OR TWO VALENCE ELECTRONS

From these identities, we find for the lowest-order energy,

$$ E_{vw}^{(0)} = \langle vw|H_0|vw \rangle = E_0 + \epsilon_v + \epsilon_w, \quad (4.85) $$

and for the first-order energy,

$$ E_{vw}^{(1)} = \langle vw|V|vw \rangle $$

$$ = V_0 + (V_{HF} - U)_{vw} + (V_{HF} - U)_{ww} + g_{vwvw} - g_{wvwv}. \quad (4.86) $$

Combining, we find to first order

$$ E_{vw} = E_{\text{core}} + \epsilon_v + \epsilon_w + (V_{HF} - U)_{vw} + (V_{HF} - U)_{ww} + g_{vwvw} - g_{wvwv}. \quad (4.87) $$

For the purpose of illustration, we assume that $U = V_{HF}$ in Eq.(4.87), and we measure energies relative to the closed core. We then have $E_{vw}^{(0)} = \epsilon_v + \epsilon_w$ and $E_{vw}^{(1)} = g_{vwvw} - g_{wvwv}$. As in the case of helium, the degenerate states $v$ and $w$ can be combined to form eigenstates of $L^2$, $L_z$, $S^2$ and $S_z$. The expression for $E^{(1)}$ in an $LS$ basis is found from (4.59) to be:

$$ E_{vw,LS}^{(1)} = \eta^2 \sum_k \left[ (-1)^{L+k+l_v+l_w} \left\{ \frac{l_v}{l_w} \frac{l_w}{l_v} \frac{L}{k} \right\} X_k(vvw) ight. $$

$$ \left. + (-1)^{S+k+l_v+l_w} \left\{ \frac{l_v}{l_w} \frac{l_w}{l_v} \frac{L}{k} \right\} X_k(vww) \right]. \quad (4.88) $$

Here $\eta = 1/\sqrt{2}$ for the case of identical particles ($n_v = n_w$ and $l_v = l_w$), and $\eta = 1$ otherwise. For the identical-particle case, the sum $L + S$ must be an even integer.

As specific examples, let us consider the atoms such as beryllium or magnesium which, in the ground state, have two $s$ electrons outside closed shells. In the ground state, beryllium ($Z = 4$) has two 2$s$ electrons outside a heliumlike core and magnesium ($Z = 12$) has two 3$s$ electrons outside of a neonlike core. Other such atoms are calcium, zinc, mercury and radium. The low-lying excited states of these atoms are $(2snl)$ singlet or triplet states for beryllium, $(3snl)$ singlet or triplet states for magnesium, etc. For such states, the expression for the first-order energy simplifies to a form similar to that obtained for helium:

$$ E_{klsn,LS}^{(1)} = \eta^2 \left( R_0(ks, nl, ks, nl) + (-1)^S \frac{1}{[l]} R_l(ks, nl, nl, ks) \right) \delta_{ll}. \quad (4.89) $$

Combining this with the lowest-order energy, we find for the $(ks)^2$ ground-state energy,

$$ E_{kks,00} = 2\epsilon_{ks} + R_0(ks, ks, ks, ks), \quad (4.90) $$

and for $(knl)$ excited states,

$$ E_{knsn,LS} = \epsilon_{ks} + \epsilon_{nl} + \left( R_0(ks, nl, ks, nl) + (-1)^S \frac{1}{[l]} R_l(ks, nl, nl, ks) \right) \delta_{ll}. \quad (4.91) $$
For beryllium, magnesium and calcium, doubly excited \(|(2p)^2, LS|\), \(|(3p)^2, LS|\) and \(|(4p)^2, LS|\) states, respectively, are also observed in the bound state spectrum. Furthermore, doubly-excited \(|3d4p, LS|\) states are observed in the spectrum of calcium.

For \((kp)^2\) configurations, the sum \(L+S\) must be even. Therefore, the possible states are \(1S\), \(3P\) and \(1D\). The first-order energy for these states is given by

\[
E_{kpkp,00}^{(1)} = R_0(kp, kp, kp, kp) + \frac{2}{5} R_2(kp, kp, kp, kp),
\]
(4.92)

\[
E_{kpkp,11}^{(1)} = R_0(kp, kp, kp, kp) - \frac{1}{5} R_2(kp, kp, kp, kp),
\]
(4.93)

\[
E_{kpkp,20}^{(1)} = R_0(kp, kp, kp, kp) + \frac{1}{25} R_2(kp, kp, kp, kp).
\]
(4.94)

From this, it is predicted in first-order that the \(3P\) state has the lowest energy and that the \(1S\) state has the highest energy.

Both carbon \((Z = 6)\) and silicon \((Z = 14)\) have two \(kp\) electrons beyond closed \((ks)^2\) shells in their ground states. We therefore expect the ground states of these atoms to be \(3P\) state and we expect the next two excited states to be \(1D\) and \(1S\) states, respectively. The collection of states from the \((kp)^2\) configuration is called the ground-state multiplet.

The lowest state in the observed spectrum of both carbon and silicon is a \(3P\) state as predicted, and the next two states are \(1D\) and \(1S\) states, as expected. From Eqs.(4.92-4.94), we predict that

\[
R = \frac{E(kpkp,00) - E(kpkp, 20)}{E(kpkp, 00) - E(kpkp, 11)} = \frac{3}{5}.
\]

For carbon the observed ratio is \(R = 0.529\), while for silicon \(R = 0.591\).

Another interesting example is titanium \((Z = 24)\) which has a ground-state configuration \((3d)^2\). For this case, the ground-state multiplet consists of the \(1S\), \(3P\), \(1D\), \(3F\) and \(1G\) states. The first-order energy is given by

\[
E_{3d3d,00}^{(1)} = R_0 + \frac{2}{7} R_2 + \frac{2}{7} R_4,
\]
(4.95)

\[
E_{3d3d,11}^{(1)} = R_0 + \frac{1}{7} R_2 - \frac{4}{21} R_4,
\]
(4.96)

\[
E_{3d3d,20}^{(1)} = R_0 - \frac{3}{49} R_2 + \frac{4}{49} R_4,
\]
(4.97)

\[
E_{3d3d,31}^{(1)} = R_0 - \frac{8}{49} R_2 - \frac{1}{49} R_4,
\]
(4.98)

\[
E_{3d3d,40}^{(1)} = R_0 + \frac{4}{49} R_2 + \frac{1}{441} R_4,
\]
(4.99)

where \(R_k \equiv R_k(3d, 3d, 3d, 3d)\). From Eqs.(4.95-4.99), we expect the order of the levels in the ground-state multiplet of titanium to be (from lowest to highest): \(3F\), \(1D\), \(3P\), \(1G\) and \(1S\). This ordering of levels is indeed observed in the ground-state multiplet.
4.5 Particle-Hole Excited States

The low-lying excited states of noble gas atoms are those in which an outer-shell electron is promoted to a single-particle state outside of the core, leaving a vacancy (or hole) in the closed shell. The particle-hole state in which a core electron with quantum numbers $a$ is excited to a state with quantum numbers $v$ is represented by the state vector $|va\rangle$:

$$|va\rangle = a^\dagger_v a^\dagger_a |0_c\rangle$$

This state is an eigenstate of $H_0$ with eigenvalue

$$E^{(0)}_{va} = E_0 + \epsilon_v - \epsilon_a .$$

The state is $2|l_a\rangle \times 2|l_v\rangle$-fold degenerate. Again, we make use of the degeneracy to form $LS$-coupled angular momentum states. Here, some caution is required. A state with a hole in substate $\cdots m_a, \mu_a$, has angular momentum properties of a particle with angular momentum components $\cdots -m_a, -\mu_a$. Moreover, if the state $|0_c\rangle$ is formed by applying creation operators to the vacuum in descending order; namely,

$$|0_c\rangle = \cdots a^\dagger_{n_a} l_a, \cdots, 1/2 a^\dagger_{n_a} l_a, -1/2 a^\dagger_{n_a} l_a, l_{a-1}, -1/2 \cdots a^\dagger_{n_a} l_a, -1/2 |0\rangle ,$$

then an extra factor of

$$(-1)^{l_a-m_a} \times (-1)^{1/2-\mu_a}$$

is obtained in transposing the operator $a^\dagger_a$ to the position to the left of $a^\dagger_a$ in the wave function, where we can replace the product $a^\dagger_a a^\dagger_a$ by 1. Thus, the state vector corresponding to a particle with angular momentum $l_v, m_v, \mu_v$ and hole with angular momentum $l_a, -m_a, -\mu_a$ is

$$(-1)^{l_a-m_a} (-1)^{1/2-\mu_a} a^\dagger_v a^\dagger_a |0_c\rangle .$$

States of this type can be combined to form an $LS$ state. We find,

$$|va, LS\rangle = \sum_{m_v m_a \mu_v \mu_a} (-1)^{l_a-m_a} LML (-1)^{1/2-\mu_a} S_{MS} a^\dagger_v a^\dagger_a |0_c\rangle$$

$$= \sum_{m_v m_a \mu_v \mu_a} LML a^\dagger_v a^\dagger_a |0_c\rangle .$$

These states are properly normalized:

$$\langle va | va \rangle = 1 .$$
Table 4.2: Comparison of $V_{\text{HF}}^{N-1}$ energies of (3s2p) and (3p2p) particle-hole excited states of neon and neonlike ions with measurements.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$V_{\text{HF}}^{N-1}$ (3s2p) $^3P$</th>
<th>Exp.</th>
<th>$V_{\text{HF}}^{N-1}$ (3s2p) $^1P$</th>
<th>Exp.</th>
<th>$V_{\text{HF}}^{N-1}$ (3p2p) $^3S$</th>
<th>Exp.</th>
<th>$V_{\text{HF}}^{N-1}$ (3p2p) $^1S$</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>1.9942</td>
<td>1.9424</td>
<td>2.0234</td>
<td>1.9662</td>
<td>2.1778</td>
<td>2.1296</td>
<td>2.4162</td>
<td>2.2073</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.2602</td>
<td>1.2089</td>
<td>1.2814</td>
<td>1.2246</td>
<td>1.3840</td>
<td>1.3360</td>
<td>1.5416</td>
<td>1.4073</td>
</tr>
<tr>
<td>Ne</td>
<td>0.6638</td>
<td>0.6118</td>
<td>0.6757</td>
<td>0.6192</td>
<td>0.7263</td>
<td>0.6755</td>
<td>0.7927</td>
<td>0.6970</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>2.2300</td>
<td>2.1830</td>
<td>2.2300</td>
<td>2.1797</td>
<td>2.2091</td>
<td>2.1622</td>
<td>2.2275</td>
<td>2.1754</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1.4178</td>
<td>1.3681</td>
<td>1.4178</td>
<td>1.3664</td>
<td>1.4043</td>
<td>1.3558</td>
<td>1.4160</td>
<td>1.3632</td>
</tr>
<tr>
<td>Ne</td>
<td>0.7404</td>
<td>0.6877</td>
<td>0.7404</td>
<td>0.6870</td>
<td>0.7348</td>
<td>0.6826</td>
<td>0.7394</td>
<td>0.6849</td>
</tr>
</tbody>
</table>

The first-order energy for the state $\left|va, LS\right>$ is evaluated using the relations

$$
\langle 0_c|a_i^l a_w : a_j^l a_j : a_k^l a_a |0_c\rangle = \delta_{ij} \delta_{lw} \delta_{ac} - \delta_{ij} \delta_{ia} \delta_{vw},
$$

\hspace{1cm} (4.102)

$$
\langle 0_c|a_i^l a_w : a_j^l a_j : a_k^l a_k : a_l^l a_a |0_c\rangle = (\delta_{lw} \delta_{kc} - \delta_{vk} \delta_{lc})
\times (\delta_{ja} \delta_{lw} - \delta_{ia} \delta_{jw}).
$$

\hspace{1cm} (4.103)

From these relations, we conclude that the matrix element of $V$ between uncoupled particle-hole states is

$$
\langle wc|V|va\rangle = g_{wacv} - g_{wvac} + (V_{\text{HF}} - U)_{wc} \delta_{ac} - (V_{\text{HF}} - U)_{ac} \delta_{vw}.
$$

\hspace{1cm} (4.104)

For coupled states, we obtain

$$
E_{va, LS}^{(1)} = \sum_{m_v, l_v, m_w, l_w, m_c, l_c} \left[ \delta_{lm_v} - \frac{1}{2} \delta_{l_{m_w}} - \delta_{l_{m_c}} \right] \frac{1}{2 \mu_v} \frac{1}{2 \mu_w} \frac{1}{2 \mu_c}
$$

$$
\left[ g_{wacv} - g_{wvac} + (V_{\text{HF}} - U)_{wc} \delta_{ac} - (V_{\text{HF}} - U)_{ac} \delta_{vw} \right],
$$

\hspace{1cm} (4.105)

where $(n_w, l_w) = (n_v, l_v)$ and $(n_c, l_c) = (n_a, l_a)$. Carrying out the sums over magnetic substates, we obtain

$$
E_{va, LS}^{(1)} = \langle -1 \rangle_{L_v}^{l_v} a_{l_w}^{l_v} \left( \frac{2}{L} \delta_{Sl_v} X_L(vava) - \sum_k L a_{l_v}^{l_v} a_{l_k}^{l_v} \right) X_L(vava)
$$

$$
+ (V_{\text{HF}} - U)_{vw} - (V_{\text{HF}} - U)_{aa}.
$$

\hspace{1cm} (4.106)
This expression is simplified by choosing the potential $U$ to be the $V_{HF}^{N-1}$ potential, defined for closed shells as

$$V_{HF}^{N-1} \overset{\text{def}}{=} V_{HF} + Q\Delta VQ.$$  \hfill (4.107)

The term $Q\Delta VQ$ subtracts the contribution of one core electron (assumed to have quantum numbers $h$) from the HF potential, when it acts on an excited-state orbital:

$$\Delta VP_n = -v_0(h,r)P_n + \sum_k \Lambda_{hkl_n} v_k(h,n,r)P_h.$$  \hfill (4.108)

In Eq.(4.107), $Q = 1 - P$ is the projection operator onto excited states:

$$P = \sum_a \langle a | a \rangle,$$  \hfill (4.109)

$$Q = \sum_n \langle n | n \rangle.$$  \hfill (4.110)

Setting $U = V_{HF}^{N-1}$, we obtain

$$UP_a = V_{HF}P_a,$$  \hfill (4.111)

$$UP_n = (V_{HF} + \Delta V)P_n - \sum_a \langle a | \Delta V | n \rangle P_a.$$  \hfill (4.112)

It follows that $(V_{HF} - U)_{aa} = 0$ and $(V_{HF} - U)_{vv} = -(\Delta V)_{vv}$.

As an example, let us consider the excited states of Ne (Z=10) and the neonlike ions Na$^+$ (Z=11) and Mg$^{2+}$ (Z=12). The low-lying states of these systems are the odd parity ($\chi = 3s^2p$), $3p$, and $1P$ states. Just above these states are the even parity ($3p^2s$), $3d$, $1D$, $3P$, $1P$ and $1S$ states. In Table 4.2, we show the results of calculations of the energies of these states using Eq.(4.106) with a $V_{HF}^{N-1}$ potential. This model for the excited states of closed-shell systems leads to energies that agree with observation at the 10% level of accuracy. To improve the agreement, it is necessary to consider corrections from higher-order perturbation theory.

### 4.6 Relativity and Fine Structure

In the preceding (nonrelativistic) discussion of excited-state energy levels, we found that on transforming to $LS$-coupled states, the interaction Hamiltonian $V$ became diagonal. Each of the resulting $LS$ states is still $[L] \times [S]$-fold degenerate. We can, of course, combine these degenerate $LS$ states into eigenstates of $J^2$ and $J_z$, but the degeneracy of the resulting $[LS, JM]$ states (designated by the spectroscopic notation $^{2S+1}L_J$) remains. In the case of one-electron atoms, where the eigenstates of orbital angular momentum split into eigenstates of $J^2$ with $j = \ell \pm 1/2$, the $2\ell$ fold degeneracy of the orbital angular momentum
eigenstates is removed. The splitting between the states with a given value of \( l \) but different values of \( j \) is referred to as the "fine-structure" splitting. In a similar way, nonrelativistic many-particle \( LS \) states split into fine-structure components having different \( J \) values when relativistic effects are introduced.

**Two-Electron Ions:** Let us consider the relativistic two-particle state \(|ab\rangle = a_a^\dagger a_b^\dagger |0\rangle\), where the single-particle indices \(a = (n_a\kappa_a m_a)\) and \(b = (n_b\kappa_b m_b)\) refer to quantum numbers of Dirac orbitals. This state is an eigenstate of the unperturbed part, \(H_0\), of the no-pair Hamiltonian with eigenvalue \(E(0) = \epsilon_a + \epsilon_b\):

\[
H_0|ab\rangle = (\epsilon_a + \epsilon_b)|ab\rangle. \tag{4.113}
\]

The states \(|ab\rangle\) are \([j_a]|j_b\rangle\)-fold degenerate. They can be combined to form eigenstates of \(J^2\) and \(J_z\) \((|ab, JM\rangle\) using Clebsch-Gordan coefficients. The resulting states are referred to as \(jj\)-coupled states. We have

\[
|ab, JM\rangle = \eta \sum_{m_a m_b} |j_a m_a\rangle \frac{JM J a a^\dagger b b^\dagger}{j_h m_b} |0\rangle. \tag{4.114}
\]

These states are also eigenstates of parity with eigenvalue \(P = (-1)^{J_a + J_b}\). The norm of the \(jj\) state in Eq.(4.114) is

\[
\langle ab, JM | ab, JM \rangle = 1 + (-1)^J \delta_{ab}. \tag{4.115}
\]

Thus, identical-particle states \((n_b = n_a \text{ and } \kappa_b = \kappa_a)\) couple to even values of \( J \) only. It follows that we must introduce a normalization factor \(\eta = 1/\sqrt{2}\) for identical-particle states, and \(\eta = 1\) for other states. With this normalization, we obtain the following expression for the first-order energy:

\[
E^{(1)}_{ab, J} = \eta^2 \sum_k \left[ (-1)^{J + k + j_a + j_b} \left\{ \begin{array}{ccc} j_a & j_b & J \\ j_b & j_a & k \end{array} \right\} X_k(abab) \\
+ (-1)^{J + k + j_a + j_b} \left\{ \begin{array}{ccc} j_a & j_b & J \\ j_a & j_b & k \end{array} \right\} X_k(abba) \right] - U_{aa} - U_{bb}, \tag{4.116}
\]

where the quantities \(X_k(abcd)\) are given by the Dirac counterpart of Eq.(4.58),

\[
X_k(abcd) = (-1)^l \langle \kappa_a || C^k || \kappa_b \rangle \langle \kappa_b || C^k || \kappa_d \rangle \langle \kappa_b || \kappa_a \rangle R_k(abcd). \tag{4.117}
\]

For heliumlike ions, the ground state is a \((1s1s)_{J=0}\). Although it is possible to couple two \(j = 1/2\) states to form a \(J = 1\) state, the above rule \((J = \text{even for identical-particle states})\) prohibits \(J = 1\) in the \((1s)^2\) configuration. The lowest excited state nonrelativistically is the \((1s2s)\) \(^3S_1\) state. Relativistically, this is the \((1s2s)_{J=1}\) state. The \((1s2s)\) \(^3S_0\) state has the \((1s2s)_{J=0}\) state as its relativistic counterpart. The relativistic \((1s2p_{1/2})_{J=0}\) and \((1s2p_{3/2})_{J=2}\) states correspond to the nonrelativistic \(^3P_0\) and \(^3P_2\), respectively. The correspondence
4.6. RELATIVITY AND FINE STRUCTURE

between nonrelativistic and relativistic \((1s2p)\) states is ambiguous for the case
\(J = 1\). Relativistically, we have two such states \((1s2p_{1/2})_1\) and \((1s2p_{3/2})_1\),
while in the nonrelativistic case, we have the two states \(^3P_1\) and \(^1P_1\). On general
grounds, we expect to be able to express the relativistic states that have \(^3P_1\) and
\(^1P_1\) states as their nonrelativistic limits as linear combinations of the \((1s2p_{1/2})_1\)
and \((1s2p_{3/2})_1\) states. Thus, we are led to consider the linear combination of
relativistic states

\[
|1s2p, 1\rangle = c_1|1s2p_{1/2}, 1\rangle + c_2|1s2p_{3/2}, 1\rangle ,
\]

with \(c_1^2 + c_2^2 = 1\). The lowest-order energy in this state is given by

\[
E^{(0)}_{1s2p} = c_1^2 \epsilon_{1p/2} + c_2^2 \epsilon_{2p_{3/2}} ,
\]

and the corresponding interaction energy is given by

\[
E^{(1)}_{1s2p} = c_1^2 \beta_{1p/2} + c_2^2 \beta_{2p_{3/2}} + \left[ (1s2p_{1/2}, 1) - U_{1s, 1s} \right]
\]

In the first of these two equations we have dropped a term \(\epsilon_{1s}\) which is inde-
pendent of the expansion coefficients \(c_1\) and \(c_2\), and, in the second equation, we
have dropped a similar \(c\)-independent term \(-U_{1s, 1s}\). Diagonalizing the energy
\(E^{(0)}_{1s2p} + E^{(1)}_{1s2p}\) leads to the \(2 \times 2\) eigenvalue equation:

\[
\begin{pmatrix}
\epsilon_{1p/2} + V_{3/2, 1/2} - U_{1/2, 1/2} & V_{1/2, 3/2} \\
V_{3/2, 1/2} & \epsilon_{2p_{3/2}} + V_{3/2, 3/2} - U_{3/2, 3/2}
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix}
= E
\begin{pmatrix}
c_1 \\
c_2
\end{pmatrix},
\]

where

\[
U_{j,j'} = U_{2p_j, 2p_{j'}} \delta_{jj'},
\]

\[
V_{j,j'} = \langle 1s2p_j | V | 1s2p_{j'} \rangle = R_0(1s, 2p_j, 1s, 2p_{j'}) \delta_{jj'}
\]

We must add \(\epsilon_{1s} - U_{1s, 1s}\) to the eigenvalues of Eq.(4.121) to obtain the energies of
the two relativistic \(J = 1\) states. This additive term is, of course, just the energy
of the one-electron ion formed when the two-electron system is ionized and must
be omitted if energies are calculated relative to the ionization threshold.

As an example, let us consider heliumlike neon (\(Z = 10\)). For simplicity, we
choose \(U = 0\), and calculate the energies of the two \((1s2s)\) states and the four
\((1s2p)\) states. In Table 4.3, we show the lowest-order and first-order energies
\(E^{(0)}\) and \(E^{(1)}\) together with the resulting sum. These energies are all given
relative to the one-electron ion. The energies of the \(^3P_1\) and \(^1P_1\) states were
Table 4.3: First-order relativistic calculations of the \( (1s^2s) \) and \( (1s^2p) \) states of heliumlike neon \((Z = 10)\), illustrating the fine-structure of the \( ^3P \) multiplet.

<table>
<thead>
<tr>
<th>Term</th>
<th>(^3S_1)</th>
<th>(^1S_0)</th>
<th>(^3P_0)</th>
<th>(^3P_1)</th>
<th>(^3P_2)</th>
<th>(^1P_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E^{(0)})</td>
<td>-12.5209</td>
<td>-12.5209</td>
<td>-12.5209</td>
<td>-12.5125</td>
<td>-12.5042</td>
<td>-12.5125</td>
</tr>
<tr>
<td>(E^{(1)})</td>
<td>1.8834</td>
<td>2.3247</td>
<td>2.2641</td>
<td>2.2596</td>
<td>2.2592</td>
<td>2.6049</td>
</tr>
<tr>
<td>(E_{\text{tot}})</td>
<td>-10.6375</td>
<td>-10.1962</td>
<td>-10.2568</td>
<td>-10.2529</td>
<td>-10.2450</td>
<td>-9.9076</td>
</tr>
</tbody>
</table>

Figure 4.2: Variation with nuclear charge of the energies of \( 1s2p \) states in heliumlike ions. At low \( Z \) the states are \( LS \)-coupled states, while at high \( Z \), they become \( jj \)-coupled states. Solid circles \(^1P_1\); Hollow circles \(^3P_0\); Hollow squares \(^3P_1\); Hollow diamonds \(^3P_2\).

obtained by solving the \( 2 \times 2 \) eigenvalue problem in Eq. (4.121). The degeneracy between the \(^3P\) substates is removed in this relativistic calculation, giving rise to the \( J \)-dependent fine structure of the state seen in the table.

In Fig. 4.2, we illustrate the transition from \( LS \) to \( jj \) coupling as \( Z \) increases along the helium isoelectronic sequence by presenting the results of a series of first-order calculations of the energies of \( (1s2p) \) states in two electron ions with nuclear charges ranging from \( Z = 4 \) to \( Z = 90 \). We plot the ratio of the energy of each of the four substates to the average energy of the states. For low values of \( Z \), near the nonrelativistic limit, the states divide into a singlet state and a triplet state. As \( Z \) increases the triplet state splits apart into \( J \) dependent fine-structure components. For large \( Z \), the states come together again to form the two \( jj \) states \((1s_{1/2}2p_{1/2})\) and \((1s_{1/2}2p_{3/2})\).

**Atoms with Two Valence Electrons:** The fine-structure of atoms with two valence electrons beyond closed shells can be treated in much the same way as the fine structure of heliumlike ions. Let us consider the nonrelativistic \( LS-\)
coupled state $^{2S+1}L$ (with $S = 0$ or $S = 1$) made up from the configurations $(n_v l_v, n_w l_w)$. A single nonrelativistic two-electron configuration $(n_v l_v n_w l_w)$ corresponds to four relativistic configurations $(n_v l_v n_w l_w)$ with $j_v = l_v \pm 1/2$ and $j_w = l_w \pm 1/2$. A $jj$-coupled state having the state $^{2S+1}L_J$ as its nonrelativistic limit is generally made up as a linear combination

$$\langle JM \rangle = \sum_{vw} c_{vw} |vw, J \rangle.$$  

Here $|vw, J \rangle$ are normalized $jj$-coupled and $c_{vw}$ are expansion coefficients satisfying

$$\sum_{vw} c_{vw}^2 = 1.$$  

As a specific example, let us consider the even-parity $^3D_2$ state obtained nonrelativistically from the configuration $(2p^3p)$. There are three relativistic configurations contributing to this state; $(2p_{1/2} 3p_{3/2})_{J=2}$, $(2p_{3/2} 3p_{1/2})_{J=2}$ and $(2p_{3/2} 3p_{3/2})_{J=2}$. The configuration $(2p_{1/2} 3p_{1/2})$ can not contribute since two single-particle states with $j = 1/2$ cannot couple to $J = 2$.

The lowest-order energy for the state $|JM \rangle$ in Eq.(4.124) is

$$E_j^{(0)} = \sum_{vw} c_{vw}^2 (\epsilon_v + \epsilon_w).$$  

The first-order energy is given by the quadratic form

$$E_j^{(1)} = \sum_{vw, xy} c_{vw} c_{xy} V_{vw, xy} + \sum_{vw} c_{vw}^2 [(V_{HF} - U)_{vv} + (V_{HF} - U)_{ww}].$$  

The interaction potential $V_{vw, xy}$ in Eq.(4.127) is given by

$$V_{vw, xy} = \eta_{vw} \eta_{xy} \sum_k \left[ (-1)^{j_v + j_y + J + k} \binom{j_v}{j_x} \binom{j_y}{j_y} \binom{J}{J + k} X_k(vwxy) ight] + (-1)^{j_v + j_y + k} \binom{j_v}{j_x} \binom{j_y}{j_y} \binom{J}{J + k} X_k(vwxy),$$  

where, as usual, the normalization factor $\eta_{vw} = 1/\sqrt{2}$ for identical particle configurations ($n_w = n_v$ and $\kappa_w = \kappa_v$) and $\eta_{vw} = 1$ otherwise. It can be easily seen that $V_{vw, xy} = V_{xy, vw}$.

As in the mixed-configuration case described previously for heliumlike ions, diagonalizing the quadratic form in Eq.(4.127) leads to the algebraic eigenvalue equation for the energy:

$$\sum_{xy} \left( [\epsilon_x + (V_{HF} - U)_{xx} + \epsilon_y + (V_{HF} - U)_{yy}] \delta_{vw, xy} + V_{vw, xy} \right) c_{xy} = E c_{vw}.$$  

(4.129)
Particle-Hole States  Because of the relatively large separation between energies of subshells with a given value of \( l \) and different values of \( j \) in closed shell atoms (even an atom as light as neon), the fine-structure splitting of particle-hole states is particularly important. The arguments in the preceding paragraphs apply with obvious modifications to the particle-hole states as well.

First, we construct an angular momentum eigenstate as a linear combination of those relativistic particle-hole configurations \((n_v l_v n_a l_a)\) with \( j_v = l_v \pm 1/2 \) and \( j_a = l_a \pm 1/2 \) that couple to a given value of \( J \):

\[
|JM\rangle = \sum_{va} c_{va}|va, JM\rangle ,
\]

where the expansion coefficients satisfy the normalization constraint \( \sum_{va} c_{va}^2 = 1 \). Again, the first-order energy is a quadratic form in the expansion coefficients. Diagonalizing this quadratic form leads to an algebraic eigenvalue problem for the energy and the expansion coefficients. In the particle-hole case, the eigenvalue problem takes the form

\[
\sum_{va} \left( [\varepsilon_v + (V_{\text{HF}} - U)_{vv} - \varepsilon_a - (V_{\text{HF}} - U)_{aa}] \delta_{v\alpha} \delta_{ab} + V_{wb,v\alpha} \right) c_{va} = E c_{wb} ,
\]

where the (symmetric) interaction matrix is given by

\[
V_{wb,v\alpha} = (-1)^{J+w-j_b+J} \frac{1}{[J]} X_J(wabv) + \sum_{k} (-1)^{J+w-j_b} \left\{ \begin{array}{ccc} j_w & j_b & J \\ j_a & j_v & k \end{array} \right\} X_k(wavb). \tag{4.132}
\]

4.7 Hyperfine Structure

The interaction of atomic electrons with the multipole moments of the nucleus leads to a nuclear spin-dependence of atomic energy levels referred to as the atomic hyperfine structure. The moments of a nucleus with angular momentum \( I \) are limited by angular momentum selection rules to those with multipolarity \( k \leq 2I \). Parity selection rules further limit the moments to even-order electric moments and odd-order magnetic moments. Thus a nucleus with \( I = 0 \) can have only an electric monopole moment, the nuclear charge \( |e|Z \). A nucleus with angular momentum \( I = 1/2 \) can also have a magnetic dipole moment, while a nucleus with \( I = 1 \) can have a magnetic dipole moment and an electric quadrupole moment in addition to its charge. Low-order nuclear moments give the most significant contributions to the hyperfine interaction. Here, we concentrate on the dominant interactions, those of the magnetic dipole and electric quadrupole moments.

The hyperfine interaction of a (relativistic) electron with the nucleus is just the electromagnetic interaction with the scalar and vector potentials generated
4.7. HYPERFINE STRUCTURE

by the nuclear moments

\[ h_{\text{hfs}}(\mathbf{r}) = e\phi(\mathbf{r}) - ee\mathbf{\alpha} \cdot \mathbf{A}(\mathbf{r}). \] (4.133)

Nonrelativistic limits can be worked out as needed.

If we let \( \mu \) designate the nuclear magnetic moment, then the corresponding magnetic vector potential is given by

\[ A(\mathbf{r}) = \frac{\mu_0}{4\pi} \frac{[\mu \times \mathbf{r}]}{r^3}. \]

It is convenient to express the interaction \(-ee\mathbf{\alpha} \cdot \mathbf{A}(\mathbf{r})\) in a spherical basis. For this purpose, we rewrite

\[ \alpha \cdot [\mu \times \mathbf{r}] = [\mathbf{r} \times \alpha] \cdot \mu = \sum_{\lambda} (-1)^\lambda [\mathbf{r} \times \alpha]_\lambda \mu_{-\lambda}. \]

For an arbitrary vector \( \mathbf{v} \), one may show,

\[ [\mathbf{r} \times \mathbf{v}]_\lambda = -i\sqrt{2} r C^{(0)}_{1 \lambda}(\hat{r}) \cdot \mathbf{v}, \]

where \( C^{(0)}_{1 \lambda}(\hat{r}) \) is a normalized vector spherical harmonic defined by

\[ C^{(0)}_{kq}(\hat{r}) = \sqrt{\frac{4\pi}{2k+1}} Y^{(0)}_{kq}(\hat{r}). \]

Using this relation, we can write the magnetic hyperfine interaction as:

\[ \frac{e}{4\pi\epsilon_0} \sum_{\lambda} (-1)^\lambda \frac{i\sqrt{2} [\alpha \cdot C^{(0)}_{1 \lambda}(\hat{r})]}{e\gamma^2} \mu_{-\lambda}. \]

The quantity \( [\alpha \cdot C^{(0)}_{1 \lambda}(\hat{r})] \) is an irreducible tensor operator of rank 1 acting in the space of electron coordinates and spin. Quantum mechanically, \( \mu_\lambda \) is an irreducible tensor operator of rank 1 acting in the space of nuclear coordinates and spin. The c-number magnetic moment \( \mu \) is the expectation value of the operator \( \mu_0 \) in the “extended” state of the nucleus, \( M_I = I \):

\[ \mu \overset{\text{def}}{=} (II|\mu_0|II). \] (4.134)

The nuclear magnetic moment \( \mu \) is measured in units of the nuclear magneton \( \mu_N \):

\[ \mu_N = \frac{|e|\hbar}{2M_p}, \]

where \( M_p \) is the mass of the proton. We write \( \mu \) in terms of the angular momentum quantum number \( I \) as:

\[ \mu = g_I I \mu_N. \] (4.135)
The dimensionless factor $g_I$ is called the gyromagnetic ratio. For the proton, the gyromagnetic ratio has the numerical value $g_I = 5.5856948(1)$.

If we let $Q_{ij}$ represent the nuclear quadrupole moment tensor, then the scalar potential is given by

$$\phi(r) = \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{x_i x_j}{2r^3} Q_{ij}.$$

The quadrupole tensor $Q_{ij}$ is a traceless symmetric tensor of rank 2; it therefore has 5 independent components. For a classical charge distribution $\rho(r)$ the Cartesian components of the quadrupole tensor are given by

$$Q_{ij} = \int d^3r (3x_i x_j - r^2 \delta_{ij}) \rho(r).$$

The components of this tensor can be transformed to a spherical basis and expressed in terms of the five components of the second-rank spherical tensor $Q_\lambda$ defined by,

$$Q_\lambda = \int d^3r r^2 C_2^0(\hat{r}) \rho(r),$$

where $C_2^0(\hat{r})$ is a normalized spherical tensor of rank 2. In particular, $Q_{33} = 2Q_0$. The potential due to the quadrupole, expressed in a spherical basis, is

$$\phi(r) = \frac{1}{4\pi\varepsilon_0} \sum_{\lambda} (-1)^\lambda \frac{C_2^0(\hat{r})}{r^3} Q_{-\lambda}.$$

Here, $Q_\lambda$ is an irreducible tensor operator of rank 2 acting in the space of nucleon coordinates and spins. The c-number quadrupole moment of the nucleus $Q$ is given in terms of the expectation value of the operator $Q_0$ in the extended state:

$$Q \overset{\text{def}}{=} 2\langle II|Q_0|II\rangle.$$

The nuclear quadrupole moment $Q$ is dimensionally a charge times a length squared. It is commonly written in units of $|e| \times$ barn.

The hyperfine interaction Hamiltonian for a relativistic electron with the nuclear magnetic dipole and electric quadrupole moments becomes

$$h_{\text{hfs}}(r) = \frac{e}{4\pi\varepsilon_0} \left\{ \sum_{\lambda} (-1)^\lambda \frac{i\sqrt{2}}{c\eta} \alpha \cdot \mathbf{C}_1^{(0)}(\hat{r}) \mu_{-\lambda} + \sum_{\lambda} (-1)^\lambda \frac{C_2^0(\hat{r})}{r^3} Q_{-\lambda} \right\},$$

Both the electric and magnetic interactions are thereby expressed in terms of tensor operators and the hyperfine interaction Hamiltonian takes the form

$$h_{\text{hfs}}(r) = \sum_{k\lambda} (-1)^\lambda t^k_\lambda(\hat{r}) T^k_{-\lambda},$$

where $t^k_\lambda(\hat{r})$ is an irreducible tensor operator of rank $k$ that acts on electron coordinates and spin, and $T^k_{\lambda}$ is a rank $k$ irreducible tensor operator that acts
on nuclear coordinates and spin. Here, \( k = 1 \) for the magnetic dipole interaction and \( k = 2 \) for the electric quadrupole interaction. Specifically,

\[
t_{\lambda \lambda}(r) = -\frac{|e|}{4\pi\epsilon_0} \frac{i\sqrt{2} \alpha \cdot C_{\lambda \lambda}^{(0)}(\hat{r})}{cr^2},
\]

\[
t_{\lambda \lambda}^2(r) = -\frac{|e|}{4\pi\epsilon_0} \frac{C_{\lambda \lambda}^{(2)}(\hat{r})}{r^3},
\]

and

\[
T_{\lambda}^1 = \mu_{\lambda},
\]

\[
T_{\lambda}^2 = Q_{\lambda}.
\]

For a collection of \( N \) electrons \( h_{\text{hfs}}(r) \) is replaced by the single-particle operator

\[
H_{\text{hfs}} = \sum_{i=1}^{N} h_{\text{hfs}}(r_i) = \sum_{\lambda} (-1)^{\lambda} T_{\lambda}^k T_{-\lambda}^k,
\]

with

\[
 T_{\lambda}^k = \left\{ \begin{array}{ll}
 \sum_{i=1}^{N} t_{\lambda \lambda}^k(r_i) & \text{in first quantization}, \\
 \sum_{ij} \langle i | t_{\lambda \lambda}^k(j) | a_i a_j \rangle & \text{in second quantization}.
\end{array} \right.
\]

Let us consider an atomic angular momentum eigenstate \( |J, M_J\rangle \) and a nuclear angular momentum eigenstate \( |I, M_I\rangle \). These states are coupled to give a eigenstate of total angular momentum \( F = I + J \),

\[
|IJ, FM_F\rangle = \sum_{M_I, M_J} \left[ \begin{array}{c}
 M_I \\
 F \\
 M_J \\
 J M_J
\end{array} \right] |I, M_I\rangle |J, M_J\rangle.
\]

The first-order correction to the energy in this state is just the expectation value of \( H_{\text{hfs}} \), which is easily shown to be

\[
W_F = \langle (IJ), FM_F | H_{\text{hfs}} | (IJ), FM_F \rangle
\]

\[
= \sum_k (-1)^{I+J+F} \left\{ \begin{array}{ccc}
 I & J & F \\
 J & I & k
\end{array} \right\} \langle J || T_{\lambda}^k || I \rangle \langle J || T_{\lambda}^k || I \rangle.
\]

We can write this equation in a somewhat more convenient way by introducing

\[
(-1)^{I+J+F} \left\{ \begin{array}{ccc}
 I & J & F \\
 J & I & k
\end{array} \right\}
\]

\[
= \frac{(2I)!(2J)!}{\sqrt{(2I-k)!(2I+k+1)!(2J-k)!(2J+k+1)!}} M(IJ, Fk),
\]
where
\[ M(IJ, Fk) = \begin{cases} 
\frac{K}{2IJ}, & \text{for } k = 1, \\
\frac{6K(K+1)-8J(J+1)J(J+1)}{2I(2I-1)2J(2J-1)}, & \text{for } k = 2,
\end{cases} \]
with \( K = F(F+1) - I(I+1) - J(J+1) \). With the aid of the identity
\[ \binom{J}{J-k} = \frac{(2J)!}{(2J-k)!(2J+k+1)!}, \]  
(4.145)
it follows that
\[ \langle JJ|T^k_0|JJ\rangle = \frac{(2J)!}{(2J-k)!(2J+k+1)!}\langle JJ|T^k||J\rangle. \]  
(4.146)
Combining Eqs. (4.144) and (4.146), we obtain for the energy the expression
\[ W_F = \sum_k M(IJ, Fk)\langle JJ|T^k_0|JJ\rangle\langle JJ|T^k_0|II\rangle. \]  
(4.147)
The two terms in this sum can be written out explicitly as
\[ W_F = \frac{1}{2}Ka + \frac{1}{2} \frac{3K(K+1) - 4J(J+1)I(I+1)}{2I(2I-1)2J(2J-1)}b, \]  
(4.148)
where
\[ a = \frac{1}{IJ} \langle JJ|T^0_0|JJ\rangle\langle II|T^0_0|II\rangle = \frac{\mu}{IJ} \langle JJ|T^0_0|JJ\rangle, \]  
(4.149)
\[ b = 4\langle JJ|T^2_0|JJ\rangle\langle II|T^2_0|II\rangle = 2Q \langle JJ|T^2_0|JJ\rangle. \]  
(4.150)
The problem of evaluating the energy shift due to the atomic hyperfine interaction is now reduced to that of determining the expectation values of the tensor operators \( T^k_0 \) in atomic states.

Let us suppose that \( b = 0 \). The interaction energy then reduces to \( W_F = Ka/2 \), with \( K = F(F+1) - I(I+1) - J(J+1) \). This is precisely the energy that would have been obtained from an effective Hamiltonian of the form
\[ H_{\text{eff}} = a \mathbf{I} \cdot \mathbf{J}. \]

We find that an eigenstate of \( J \) breaks up into \( 2J + 1 \) sublevels for the case \( I \geq J \) or \( 2I + 1 \) sublevels for \( J < I \). Let us consider the case \( I \geq J = 1/2 \). In this case, an eigenstate of \( J \) breaks up into 2 sublevels,
\[ W_F = \begin{cases} 
Ia/2 & \text{for } F = I + 1/2, \\
-(I+1)a/2 & \text{for } F = I - 1/2.
\end{cases} \]
The splitting between the two sublevels is \( \Delta W = (I + 1/2)a \). For \( I \geq J = 1 \), an eigenstate of \( J \) splits into three components separated by \( (I + 1)a \) and \( Ia \), respectively. Generally, for the case \( I \geq J \), the hyperfine pattern has \( 2J + 1 \) components; the splitting between two adjacent sublevels being \( W_{F+1} - W_F = Fa \). By counting the hyperfine components in the case \( J > I \) we can determine the nuclear angular momentum \( I \), while measurements of the separation between sublevels permits us to evaluate the nuclear gyromagnetic ratio \( g_I \).
4.7. HYPERFINE STRUCTURE

**Units:** Dimensionally, the magnetic hyperfine interaction energy is given by

\[
[W^{\text{m.d.}}] = \frac{|e|}{4\pi \epsilon_0} \frac{|e| \hbar}{2M_p c a_0^2} = \frac{1}{2M_p c} = 1.987131 \times 10^{-6} \text{ a.u.} \\
= 0.4361249 \text{ cm}^{-1} \\
= 13074.69 \text{ MHz}.
\]

Similarly, the electric quadrupole hyperfine interaction energy is, dimensionally,

\[
[W^{\text{e.q.}}] = \frac{|e|}{4\pi \epsilon_0} |e| \times \text{barn} \frac{1}{a_0^3} = 3.571064 \times 10^{-8} \text{ a.u.} \\
= 7.837580 \times 10^{-3} \text{ cm}^{-1} \\
= 234.965 \text{ MHz}.
\]

In the following, we express the nuclear magnetic moment in units of \( \mu_N \), the quadrupole moment in terms of \( |e| \times \text{barn} \), and omit the constants \( e/4\pi \epsilon_0 \) and \( c \) in expressions given previously for the interaction. The results will then be in terms of the units given in this paragraph.

**4.7.1 Atoms with One Valence Electron**

We now turn to the problem of determining \( W_F \) for an atom having a single valence electron in the state \( v = (n_v, \kappa_v, m_v) \),

\[
|v\rangle = a_v^\dagger |O_c\rangle.
\]

The atomic angular momentum components \( J \) and \( M_J \) are given by \( J = j_v \) and \( M_J = m_v \) for this state, and the many-body expectation value of the tensor operator \( T^k_\lambda \) is given by

\[
\langle v|T^k_\lambda|v\rangle = \langle v|t^k_\lambda(\mathbf{r})|v\rangle + \sum_a \langle a|t^k_\lambda(\mathbf{r})|a\rangle,
\]

where the sum over \( a \) extends over all core states. The core sum is easily shown to vanish:

\[
\sum_a \langle a|t^k_\lambda(\mathbf{r})|a\rangle = \sum_a -\frac{k\lambda}{j_a} \langle a||t^k||a\rangle = \sum_{n_a \kappa_a} \sum_{j_a} \frac{k\lambda}{j_a} \langle a||t^k||a\rangle = \sum_{n_a \kappa_a} \delta_{k\lambda} \delta_{\lambda 0} \sqrt{j_a} \langle a||t^k||a\rangle = 0.
\]
The expectation value of $T^k$, therefore reduces to the valence electron expectation value of $t^k_\lambda(r)$. For a one valence electron atom, we therefore have,

\[ a = \frac{g_\mu}{j_v} \langle n_v\kappa_v m_v = j_v|t^1_0|n_v\kappa_v m_v = j_v \rangle \times 13074.7 \text{ MHz}, \quad (4.151) \]

\[ b = 2Q \langle n_v\kappa_v m_v = j_v|t^2_0|n_v\kappa_v m_v = j_v \rangle \times 234.965 \text{ MHz}. \quad (4.152) \]

In the magnetic case, $\kappa = 1$, we obtain from Eq.(4.138)

\[ \langle w|t^1_\lambda(r)|v \rangle = -i\sqrt{2} \int \frac{dr}{r^2} \left( -iP_{n_v\kappa_v}(r)Q_{n_v\kappa_v}(r) \langle \kappa_v m_w|\sigma \cdot C_{kq}^{(0)}(\hat{r})\rangle - \kappa_v m_v \right) \]

\[ + iQ_{n_v\kappa_v}(r)P_{n_v\kappa_v}(r) \langle -\kappa_v m_w|\sigma \cdot C_{kq}^{(0)}(\hat{r})|\kappa_v m_v \rangle, \quad (4.153) \]

where, for example,

\[ \langle \kappa_v m_w|\sigma \cdot C_{kq}^{(0)} - \kappa_v m_v \rangle = \int d\Omega \Omega^\dagger_{\kappa_v m_w}(\hat{r}) \sigma \cdot C_{kq}^{(0)}(\hat{r}) \Omega_{-\kappa_v m_v}(\hat{r}). \]

Often in relativistic calculations, one encounters angular matrix elements, such as those in the above equation, of $\sigma$ times a normalized vector spherical harmonic $C_{kq}^{(\nu)}$. Such matrix elements are easily reduced to matrix elements of normalized spherical harmonics. We find:

\[ \langle \kappa_b m_b|\sigma \cdot C_{kq}^{(-1)}|\kappa_a m_a \rangle = -\langle \kappa_b m_b|C_{kq}^{(1)}|\kappa_a m_a \rangle, \quad (4.154) \]

\[ \langle \kappa_b m_b|\sigma \cdot C_{kq}^{(0)}|\kappa_a m_a \rangle = \frac{\kappa_a - \kappa_b}{\sqrt{k(k + 1)}} \langle \kappa_b m_b|C_{kq}^{(1)}|\kappa_a m_a \rangle, \quad (4.155) \]

\[ \langle \kappa_b m_b|\sigma \cdot C_{kq}^{(1)}|\kappa_a m_a \rangle = \frac{\kappa_a + \kappa_b}{\sqrt{k(k + 1)}} \langle \kappa_b m_b|C_{kq}^{(1)}|\kappa_a m_a \rangle. \quad (4.156) \]

With the aid of Eq.(4.155), we obtain

\[ \langle w|t^1_\lambda(r)|v \rangle = (\kappa_v + \kappa_w) \langle -\kappa_v m_w|C_{kq}^{(1)}|\kappa_v m_v \rangle \left( \frac{1}{r^2} \right)_{wv}, \quad (4.157) \]

where

\[ \left( \frac{1}{r^2} \right)_{wv} = \int_0^\infty \frac{dr}{r^2} \left( P_{n_v\kappa_v}(r)Q_{n_v\kappa_v}(r) + Q_{n_v\kappa_v}(r)P_{n_v\kappa_v}(r) \right). \quad (4.158) \]

Here we have used the symmetry relation

\[ \langle -\kappa_v m_w|C_{kq}^{(1)}|\kappa_v m_v \rangle = \langle \kappa_w m_w|C_{kq}^{(0)}|\kappa_v m_v \rangle \cdot \quad (4.159) \]

Therefore, we have in the case $k = 1$,

\[ \langle n_v\kappa_v j_v|t^1_0|n_v\kappa_v j_v \rangle = 2\kappa_v \langle -\kappa_v j_v|C_{kq}^{(1)}|\kappa_v j_v \rangle \left( \frac{1}{r^2} \right)_{v} \cdot \quad (4.160) \]
A similar, but simpler calculation for \( k = 2 \) gives

\[
\langle n_\nu \kappa_e j_e | l_0^2 | n_\nu \kappa_e j_e \rangle = -\langle \kappa_e j_e | C_0^2 | \kappa_e j_e \rangle \left\langle \frac{1}{r^3} \right\rangle_{vv},
\]

where

\[
\left\langle \frac{1}{r^3} \right\rangle_{vv} = \int_0^\infty \frac{dr}{r^3} (P_{n_\nu \kappa_e}(r) P_{n_\nu \kappa_e}(r) + Q_{n_\nu \kappa_e}(r) Q_{n_\nu \kappa_e}(r)).
\]

The angular matrix elements in Eqs.(4.160) and (4.161) are evaluated to give

\[
\langle -\kappa_e j_e | C_0^1 | \kappa_e j_e \rangle = -\frac{1}{2j_e + 2},
\]

\[
\langle \kappa_e j_e | C_0^2 | \kappa_e j_e \rangle = -\frac{2j_e - 1}{4j_e + 4},
\]

from which it follows that

\[
a = -\frac{g_i \kappa_e}{2j_e + 1} \left( \frac{1}{r^3} \right)_{vv} \times 13074.7 \text{ MHz},
\]

\[
b = Q \frac{2j_e - 1}{2j_e + 2} \left( \frac{1}{r^3} \right)_{vv} \times 234.965 \text{ MHz}.
\]

**Pauli Approximation:** To obtain the nonrelativistic limit of the expression for the dipole hyperfine constant \( a \) in Eq.(4.163), we consider an approximation to the radial Dirac equation referred to as the Pauli approximation. We set \( W_{n_\kappa} = E_{n_\kappa} - c^2 \) and write the radial Dirac equations as

\[
c \left( \frac{d}{dr} - \frac{\kappa}{r} \right) Q_{n_\kappa} = (W_{n_\kappa} - V) P_{n_\kappa},
\]

\[
(2c^2 + W_{n_\kappa} - V)Q_{n_\kappa} = -c \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_{n_\kappa}.
\]

The Pauli approximation consists of neglecting \( W_{n_\kappa} - V \) compared to \( 2c^2 \) in Eq.(4.166), leading to the relation

\[
Q_{n_\kappa} \approx -\frac{1}{2c} \left( \frac{d}{dr} + \frac{\kappa}{r} \right) P_{n_\kappa}.
\]

Substituting this approximation into Eq.(4.166), gives the differential equation

\[
\frac{1}{2} \frac{d^2 P_{n_\kappa}}{dr^2} + \left( W_{n_\kappa} - V - \frac{\kappa(\kappa + 1)}{2r^2} \right) P_{n_\kappa} = 0,
\]

for the large component radial function \( P_{n_\kappa} \). This is just the radial Schrödinger equation for orbital angular momentum \( l \), since \( \kappa(\kappa + 1) = l(l + 1) \) for the two possible \( \kappa \) values associated with a given value of \( l \) (\( \kappa = l \) and \( \kappa = -l - 1 \)).
Therefore, in the Pauli approximation, the large component radial function $P_{nl}$ goes over to the corresponding nonrelativistic radial function $P_{nl}$. The small component radial function in the Pauli approximation is found from Eq.(4.167) with $P_{nl}$ replaced by $P_{nl}$. With the aid of the Pauli approximation, we therefore obtain

$$
\left( \frac{1}{r^2} \right)_{vw} = -\frac{1}{2c} \int_0^\infty \frac{dr}{r^2} \left[ P_{n\ell_v} \left( \frac{d}{dr} + \frac{\kappa_v}{r} \right) P_{n\ell_w} + P_{n\ell_v} \left( \frac{d}{dr} + \frac{\kappa_w}{r} \right) P_{n\ell_w} \right]
$$

$$
= -\frac{1}{2c} \int_0^\infty dr \left[ \frac{d}{dr} \left( \frac{P_{n\ell_v} P_{n\ell_w}}{r^2} \right) + \frac{\kappa_v + \kappa_w + 2}{r^3} P_{n\ell_v} P_{n\ell_w} \right]
$$

$$
= \frac{1}{2c} \left( \frac{P_{n\ell_v} P_{n\ell_w}}{r^2} \right)_{r=0} - \frac{\kappa_v + \kappa_w + 2}{2c} \left( \frac{1}{r^3} \right)_{vw},
$$

where the radial matrix element of $1/r^3$ on the last line is to be evaluated using nonrelativistic wave functions. The first term on the last line of Eq.(4.169) contributes if, and only if, both states $v$ and $w$ are $s$ states, since the nonrelativistic radial wave functions $P_{nl}(r)$ are proportional to $r^{l+1}$. Indeed, if we let $\lim_{r \to 0} \left( \frac{P_{n\ell_v}(r)}{r} \right) = N_v \delta_{\ell,0}$,

then we obtain the following nonrelativistic limiting values for the dipole hyperfine constant:

$$
a_{NR} = \frac{2}{3} g_i N_v^2 \times 95.4016 \text{ MHz}, \quad \text{for } \ell_v = 0,
$$

$$
a_{NR} = \frac{\ell_v(\ell_v + 1)}{j_v(j_v + 1)} g_i \left( \frac{1}{r^3} \right)_{vw} \times 95.4016 \text{ MHz}, \quad \text{for } \ell_v \neq 0.
$$

The overall scale here is set by the constant $13074.69 \times \alpha = 95.4106 \text{ MHz}$. For the ground state of hydrogen, $N_{1s} = 2$, and Eq.(4.170) leads to the result

$$
a_{NR} = \frac{2}{3} \times 5.5856948 \times 2^2 \times 95.4016 \text{ MHz} = 1421.16 \text{ MHz}.
$$

This number is to be compared with the experimental value $a_{\text{Exp.}} = 1420.406 \text{ MHz}$. The difference between these values arises from radiative, reduced-mass and relativistic corrections. These corrections are discussed, for example, in Bethe and Salpeter (1957).

In Table 4.4, we compare results of HF calculations of the hyperfine constants for the ground states of alkali-metal atoms with measurements. These values are seen to be in only qualitative agreement with experiment. The agreement between theory and experiment can be improved to the level of 5% or better by including corrections from first-order and second-order perturbation theory. For the heavier alkali atoms, a significant part of the difference between calculation and measurement is due to the use of the nonrelativistic approximation. For example, if we use the relativistic expression Eq.(4.163) rather than Eq.(4.170) to evaluate $a$ for rubidium, we obtain $a = 643.9 \text{ MHz}$ instead of the value $a = 542.0 \text{ MHz}$ given in the table.
### Table 4.4: Nonrelativistic HF calculations of the magnetic dipole hyperfine constants $a$ (MHz) for ground states of alkali-metal atoms compared with measurements.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$Z$</th>
<th>$A$</th>
<th>$I$</th>
<th>State</th>
<th>$g_I$</th>
<th>$a_{NR}$</th>
<th>$a_{Exp.}$</th>
</tr>
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<tr>
<td>Li</td>
<td>3</td>
<td>7</td>
<td>3/2</td>
<td>$2s_{1/2}$</td>
<td>2.17065</td>
<td>284.2</td>
<td>401.752</td>
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<tr>
<td>Na</td>
<td>11</td>
<td>23</td>
<td>3/2</td>
<td>$3s_{1/2}$</td>
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<td>615.9</td>
<td>885.813</td>
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<tr>
<td>K</td>
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<td>39</td>
<td>3/2</td>
<td>$4s_{1/2}$</td>
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<td>140.8</td>
<td>230.860</td>
</tr>
<tr>
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<td>37</td>
<td>85</td>
<td>5/2</td>
<td>$5s_{1/2}$</td>
<td>0.54121</td>
<td>542.0</td>
<td>1011.911</td>
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Bibliography


