The multi-electron, central force problem is one that does not have an exact solution. Approximations must be applied, and some aspects of these approximations are common to all multi-particle problems, particularly those of nuclear physics. Atoms can rightly be thought of as the building blocks of our material world. Understanding how quantum mechanics describes atoms, which justifies so much that you have been taught in chemistry and modern physics courses, is the goal for the rest of this text. In this chapter, the hardest part of that broad effort will be attempted which is trying to understand the energy-level structure of an isolated, multi-electron atom. That will be what is meant by the “solution” to the problem at hand. The problem, as presented, will rapidly grow in complexity and seem to be impossible to handle. But then the complexity will shrink as so many terms of interest are shown to be equal to others or zero.

The problem being considered is to find the total energy of all of the electrons of a multi-electron atom under the influence of the Coulomb attraction of the electrons to the nucleus and the mutual repulsion of each of the other electrons. Solving the Schrödinger equation is not the approach to take. Rather one starts by evaluating the energy assuming that you know the wave functions. The variational procedure tells you that if you then modify the assumed wave functions in any way at all that lowers the energy, both the wave functions and energy are closer to the “correct” ones. Interestingly, how one performs this procedure is not really very important. The optimum method is the Hartree–Fock procedure which will be briefly described in the last section of this chapter. What is important is understanding how one evaluates the energy, what approximations are used in making that evaluation, and which quantum numbers can be used to describe the states available to the atom. After all, when doing atomic physics research, the atom is often in an excited state, so these are every bit as important to understand as the ground state of the atom.
2.1 Shell Model of the Atom

Consider forming a system of several electrons electrostatically bound to an infinitely heavy nucleus of charge $Ze$. The electrons also electrostatically repel each other, so a Hamiltonian for the system can be written that, in atomic units, looks like

$$H = \sum_{i=1}^{N} \left( \frac{-\nabla_{i}^{2}}{2} - \frac{Z}{|\vec{r}_{i}|} \right) + \sum_{i>j=1}^{N} \frac{1}{|\vec{r}_{i} - \vec{r}_{j}|}$$

or

$$H = \sum_{i=1}^{N} \left( \frac{-\nabla_{i}^{2}}{2} - \frac{Z}{r_{i}} \right) + \sum_{i>j=1}^{N} \frac{1}{r_{ij}} \quad (2.1)$$

where $\vec{r}_{i}$ is the position of electron $i$ with respect to the nucleus. $r_{i}$ and $r_{ij}$ are defined by the corresponding expression in the equation above. While the Hamiltonian is not complete, all additional terms can quite successfully be treated as perturbations.

The Schrödinger equation for this Hamiltonian is hopelessly complicated to solve using even the largest computer presently imaginable. The starting point for calculations is then taken to be the assumption of a central potential, $V(r_{i})$, for each of the electrons. Various approximations differ by what is chosen for $V(r_{i})$. Very often $V$ is chosen iteratively: assume a $V$, calculate the wave functions, find a new $V$, and calculate new wave functions until the procedure converges, called the self-consistent field approximation. This treatment doesn’t take that approach. Our potential really will be the one given above. However, the overall form of the wave functions, taken to be obtained as products of one-electron wave functions, is justified by looking at the form the wave functions would have if the potential were central.

Using a central potential $H$ may be written as

$$H = \sum_{i=1}^{N} \frac{-\nabla_{i}^{2}}{2} + V(r_{i}). \quad (2.2)$$

The Schrödinger equation is

$$Hu = Eu$$

where

$$u = \prod_{i=1}^{N} u_{i}(a_{i}) = u_{1}(a_{1})u_{2}(a_{2}) \ldots u_{N}(A_{N}) \quad (2.3)$$

and

$$E = \sum_{i=1}^{N} E_{i}(a_{i}) \quad (2.4)$$
Here \( u_i(a_i) \) is the wave function of the \( i \)th electron having a set of quantum numbers \( a_i \).

**Problem 2.1**
Show that the above product wave function is a solution of the Schrödinger equation.

The separation of the wave function into a product of one-electron wave functions is a direct consequence of the central potential assumption and is the cornerstone of the atomic theory of complex atoms. In fact our potential is not a central potential, so how can such a separation be justified? The answer is that the largest part of the potential, attraction to the nucleus, is rigorously central and the electron–electron repulsion, which is not central, appears to average out enough to let this crucial approximation work amazingly well. Keep in mind that no change to the potential is being made here. This is an assumption relating to the overall form of the solution. Hence it will be assumed that the form of the wave function can be taken as a product of one-electron wave functions.

It follows then that each \( u_i \) is a solution of the one-electron central force problem and must be of the form

\[
 u_i(a_i) = R_{n_i\ell_i}(r_i)Y_{\ell_i}^{m_i}(\theta_i, \phi_i)\chi_{s_i}(i) \tag{2.5}
\]

which is a one-electron spin orbital. The form of the \( R_{n_i\ell_i}(r_i) \) is unspecified and depends on the particular choice of central potential. So \( a_i \) must represent the set of four quantum numbers:

\[
 a_i \equiv n_i \ell_i m_{\ell_i} m_{s_i} \tag{2.6}
\]

which could also be written as

\[
 u_i(a_i) = |n_i \ell_i m_{\ell_i} m_{s_i} \rangle. \tag{2.7}
\]

What if the positions of the \( i \)th and \( j \)th electron were exchanged? The expression would be

\[
 u_j(a_i) = R_{n_i\ell_i}(r_j)Y_{\ell_i}^{m_i}(\theta_j, \phi_j)\chi_{s_i}(j) \nonumber
\]

So something is wrong with our solution, (2.3). It has erroneously assigned a given set of quantum numbers to a given electron when the electrons cannot be distinguished.

For brevity consider a 2-electron system. (2.3) might be more properly written as

\[
 u^s = u_1(a_1)u_2(a_2) + u_2(a_1)u_1(a_2) \tag{2.8}
\]

\[
 u^a = u_1(a_1)u_2(a_2) - u_2(a_1)u_1(a_2). \tag{2.9}
\]

\( u^s \) is symmetric under exchange of electrons, while \( u^a \) is antisymmetric (changes sign) under such an interchange. Both solutions satisfy the indistinguishability of electrons.
To explain the building-up of the periodic table of elements, Pauli postulated that no two electrons could have the same set of quantum numbers. Using this criterion the solution \( u^a \) is chosen over \( u^s \) since the former vanishes whenever the two electrons have the same quantum numbers. The correct generalization of the Pauli principle is that a system composed of fermions (spin \( \frac{1}{2} \) odd integer) has a wave function which is antisymmetric against exchange of any two particles.

One could now define a symmetrization operator and an antisymmetrization operator which would form the necessary linear combinations to account for indistinguishability of particles. Since in atomic physics only the latter needs to be considered, there is a particularly elegant way to perform this. It is known as the Slater determinant. Let

\[
\begin{vmatrix}
  u_1(a_1) & u_1(a_2) & u_1(a_3) & \ldots & u_1(a_N) \\
  u_2(a_1) & u_2(a_2) & u_2(a_3) & \ldots & u_2(a_N) \\
  \vdots & \vdots & \vdots & \ddots & \vdots \\
  u_N(a_1) & u_N(a_2) & u_N(a_3) & \ldots & u_N(a_N)
\end{vmatrix}
\]

Note that this reduces to (2.9) for two particles. Also note that our first attempt as a solution, (2.3), is represented by the diagonal entries.

A more compact notation for \( |u(a)\rangle \) is

\[
|u(a)\rangle = \mathcal{A}|n_1 \ell_1 m_{\ell_1} m_{s_1}\rangle n_2 \ell_2 m_{\ell_2} m_{s_2}\rangle \ldots |n_N \ell_N m_{\ell_N} m_{s_N}\rangle
\]

where \( \mathcal{A} \) means antisymmetrical product or Slater determinant. Let us write

\[
n = 3 \quad \ell = 2 \quad m_{\ell} = 1 \quad m_s = \frac{1}{2} \quad \text{as} \quad |3d^{1+}\rangle
\]

\[
n = 3 \quad \ell = 2 \quad m_{\ell} = -2 \quad m_s = -\frac{1}{2} \quad \text{as} \quad |3d^{-2-}\rangle
\]

which shall define our notation.

If there were four electrons in a \( 1s^22p^3d \) configuration, what might the wave function be? Four electrons require the specification of 16 quantum numbers whereas \( 1s^22p^3d \) specifies only eight of them. There must be a whole host of states permitted by the classification \( 1s^22p^3d \). One of them could look like

\[
|u(a)\rangle = \mathcal{A}|1s^{0+}\rangle |1s^{0-}\rangle |2p^{1+}\rangle |3d^{-2+}\rangle
\]

\[
= \frac{1}{\sqrt{4!}} \begin{vmatrix}
  |1s^{0+}\rangle_1 & |1s^{0-}\rangle_1 & |2p^{1+}\rangle_1 & |3d^{-2+}\rangle_1 \\
  |1s^{0+}\rangle_2 & |1s^{0-}\rangle_2 & |2p^{1+}\rangle_2 & |3d^{-2+}\rangle_2 \\
  |1s^{0+}\rangle_3 & |1s^{0-}\rangle_3 & |2p^{1+}\rangle_3 & |3d^{-2+}\rangle_3 \\
  |1s^{0+}\rangle_4 & |1s^{0-}\rangle_4 & |2p^{1+}\rangle_4 & |3d^{-2+}\rangle_4
\end{vmatrix}
\]

The subscript to the right of each ket indicates the electron number. Each electron takes a turn getting each set of quantum numbers. There are four electrons and four specified sets of QN’s, but one cannot say which electron has which set. Therefore
\[ |u(a)\rangle \] specified above is one state allowed to the configuration \(1s^22p3d\). How many different states are there?

If a determinant were formed in which two of the states were \(|1s\,0^+\rangle|1s\,0^+\rangle\) or \(|1s\,0^-\rangle|1s\,0^-\rangle\), then two columns of the Slater determinant would be identical, and the state would be zero. Also, if the state \(|1s\,0^-\rangle|1s\,0^+\rangle\) were formed, it would be the determinant previously written with the first two columns interchanged, yielding precisely the same state. So the specification \(|1s\,0^+\rangle|1s\,0^-\rangle\) for \(1s^2\) is unique.

Six different kets could be formed using a \(2p\) configuration. They would be
\[ |2p\,1^+\rangle, |2p\,1^-\rangle, |2p\,0^+\rangle, |2p\,0^-\rangle, |2p\,-1^+\rangle, |2p\,-1^-\rangle \]

Similarly, ten different kets could be formed using \(3d\). All in all 60 different Slater determinants could be formed from the configuration \(1s^22p3d\). Do these 60 different states yield 60 different energies, the same energy 60 times, or what?

The answer is that if the central potential were \(Z/r_i\), all 60 states would be degenerate. The occurrence of \(1/r_{ij}\) in the Hamiltonian partially lifts the degeneracy. (There are six different energies for these 60 states using the Hamiltonian of \((2.1)\). This point will be returned to later.)

The shell structure of an atom should now be understandable. Only one state can be formed from the configuration \(1s^2\). Similarly the configuration \(1s^22s^2\) has only one state. It is formed by the determinant
\[ |u(a)\rangle = \mathcal{A}|1s\,0^+\rangle|1s\,0^-\rangle|2s\,0^+\rangle|2s\,0^-\rangle \]

In this way all shells (those having the same value of \(n\)) when filled have only one state. \(2n^2\) electrons fill a shell. The following are closed shells:

\[1s^2\]
\[2s^22p^6\]
\[3s^23p^63d^{10}\]

etc.

It is equally clear, however, that whenever \(2(2\ell + 1)\) electrons are assigned to an \(n\ell\) subshell, there is only one state:

\[2s^2\]
\[3s^2\text{ or } 3p^6\]
\[4d^{10}\]

etc.
Multiple states for a single configuration arise only with partially filled subshells. All filled shells (given \( n \) value) or subshells (given \( n \) and \( \ell \) values) have a total angular momentum of zero and are completely defined by the configuration specifications.

**Problem 2.2**
Consider all different filled subshells in the periodic table up to \( {}^{54}\text{Xe} \). Which ones yield chemically nonreactive substances? Which are chemically reactive? Why?

### 2.2 Angular Momentum for Complex Atoms

In Chap. 1, the general rules for coupling two angular momenta were presented. One always couples angular momenta in pairs, usually starting from the innermost to the outermost electron in a partially filled subshell. (Filled subshells have zero total angular momentum.) The most common coupling scheme for atoms is called Russell–Saunders or \( LS \) coupling. In this scheme all of the orbital angular momenta are coupled together, all of the spin angular momenta are coupled together, and the two sums are then coupled together to form the total angular momentum, \( \vec{J} \):

\[
\vec{L} = \sum_{i=1}^{N} \vec{\ell}_i
\]

\[
\vec{S} = \sum_{i=1}^{N} \vec{s}_i
\]

\[
\vec{J} = \vec{L} + \vec{S}
\]

For two electrons, everything carries over from the coupling of two angular momenta. So,

\[
|\ell_1 - \ell_2| \leq L \leq |\ell_1 + \ell_2|
\]

\[
|s_1 - s_2| \leq S \leq |s_1 + s_2|
\]

\[
|L - S| \leq J \leq |L + S|
\]

Even for more than two electrons, one can write

\[
M_L = \sum_{i=1}^{N} m_{\ell_i}
\]

\[
M_S = \sum_{i=1}^{N} m_{s_i}
\]

\[
M_J = M_L + M_S
\]
For two electrons in the configuration \(2p3p\), the possible values for the total orbital angular momentum are \(L = 0, 1,\) or \(2\) whose symbols are \(S, P,\) or \(D\). Since the spin for each is \(s = \frac{1}{2}\), the total spin can be \(S = 1\) or \(0\). These possibilities are expressed as
\[ 1S, \ 3S, \ 1P, \ 3P, \ 1D, \ 3D \] called terms.

The rule is
\[ 2^{S+1}L_J \]
where \((2S + 1)\) is called the multiplicity. The levels can then be
\[ 1S_0, \ 3S_1, \ 1P_1, \ 3P_{0,1,2}, \ 1D_2, \ 3D_{1,2,3} \]
where \(3P_{0,1,2}\) means \(3P_0\) and \(3P_1\) and \(3P_2\) pronounced “triplet pee two.”

Proceeding as before, remember that the configuration \(2p3p\) has 36 states, each with its own Slater determinant. The coupling done above effectively changes the basis from these 36 states to another set of 36 states, each of which is a linear combination of one or more of the original ones. Each total \(J\) value has \((2J + 1)\) different \(M_J\) values. The number of different \(M_J\) values for all of the above levels must be 36.

**Problem 2.3**
Verify that there are 36 states by counting the number of different \(M_J\) values for each of the levels given above.

For more than two electrons the angular momenta are coupled in pairs starting with the innermost configuration. The first pair then gives rise to all terms allowed by the angular momentum coupling rules. The next electron’s angular momentum is then added to these terms, called parent terms, to obtain a new set of terms. Coupling angular momenta for four or more electrons from open subshells becomes more complicated and is treated in books on angular momentum theory.

The configuration \(2p3p3d\) can yield a lot of terms. For example,
\[ 2p3p(1S)3d \ 2D_{3/2,5/2} \]
\[ 2p3p(3P)3d \ 2^{4}P, \ 2^{4}D, \ 2^{4}F \ \Rightarrow \ 4F_{3/2,5/2,7/2,9/2} \]

This is only a selection of all possible terms that one could form. As a review of the terminology, consider where the second subscript is the \(M_J\) value.

an expression like \(2F\) is called a term
\(2F_{5/2}\) is called a level
\(2F_{7/2,5/2}\) is called a state
Do not confuse the notation $^2F_{5/2}^3/2$ with $^2F_{7/2}^5/2$. The first has $J = 5/2$ and $M_J = 3/2$ and is a state designation. The second is a shorthand for the two levels $^2F_{7/2}^5/2$ and $^2F_{5/2}^3/2$.

The configuration $2p3p3d$ has 360 different states, each of which has a Slater determinant in the basis $|n_\ell m_\ell m_s\rangle$. Coupling of the angular momentum represents a change of basis. In general, obtaining the transformation is complicated. Very often, only two or three electrons are outside closed subshells, which provides some simpler cases for consideration.

**Problem 2.4**

Write down all possible terms and levels from the configuration $2p3p3d$. Verify that in the coupled basis, there are 360 states. *Hint:* One must form all possible parent terms by coupling the inner two electrons before coupling the outer electron to each of these in turn.

The final coupling of $\vec{J} = \vec{L} + \vec{S}$ occurs only if the Hamiltonian has a term like $\vec{L} \cdot \vec{S}$ in it. This coupling is the weakest one and shall be ignored for the time being. Without such coupling, $L, S, M_L, M_S$ are good quantum numbers, and the state designations could be expressed as

$$(2S+1)L^M^L_M^S.$$

It will be made clear whenever such notation is used that the subscripts are $M_L$ and $M_S$ and not $J$ and $M_J$. Again, this simply represents a different basis, actually one a slightly easier one than $JM_J$. For a given term, the number of allowed $M_L$ and $M_S$ values is the same as the number of $JM_J$ values.

**Problem 2.5**

Verify the claim made in the previous sentence.

Finally, note that the parity of a given state is given by $(-1)^{\Sigma_\ell \ell_i}$, *not* by $(-i)^{L}$. Why so? Because any state is a linear combination of Slater determinants made up of the product of $q$ spin orbitals where $q$ is the number of electrons. Each spin orbital has a parity determined by $Y_{\ell}^{m}$ which is $(-1)^\ell$. The parity of a product of $q$ of them is then

$$(-1)^{\sum_{i=1}^{q}\ell_i}$$

_The parity of any state is determined by the electron configuration and not by the coupling scheme._

The notation introduced in this section is particularly important for everything that follows. In particular, the distinction between the total spin, $S$, and the multiplicity, $2S + 1$, is often missed by many students.
2.3 Equivalent Electrons

You have seen that a lot of terms result from the coupling of three angular momenta. But our example chose three orbitals that were all different. What if there were three electrons in the same orbital? The Pauli exclusion principle insists that every electron have a unique set of quantum numbers and the use of Slater determinants ensures that. Whenever more than one electron resides in the same orbital, the electrons are called equivalent. This is the situation now being considered.

As previously mentioned, whenever two electrons are in an $s^2$ configuration, only a single state is formed. This follows since there is only one Slater determinant which is nonzero, given by

$$
\frac{1}{\sqrt{2}} \begin{vmatrix}
| s^0 + \rangle_1 & | s^0 - \rangle_1 \\
| s^0 + \rangle_2 & | s^0 - \rangle_2 \\
\end{vmatrix}
$$

where the unspecified quantum number $n$ does not matter. The same argument holds for any filled subshell. But what happens to a partially filled subshell like $2p^2$? (Any $p$ will do; the $n$ value doesn’t matter.) There is a clever tabular method which enables one to work out not only the number of allowed states (fewer than 36, the number for two nonequivalent $p$ electrons) but also the allowed term values under $LS$ coupling:

<table>
<thead>
<tr>
<th>$M_L$</th>
<th>$M_S$</th>
<th>$m_{\ell_1}$</th>
<th>$m_{s_1}$</th>
<th>$m_{\ell_2}$</th>
<th>$m_{s_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>+1/2</td>
<td>1</td>
<td>+1/2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>+1/2</td>
<td>1</td>
<td>-1/2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>-1/2</td>
<td>1</td>
<td>+1/2</td>
<td></td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

One constructs a table in which each line represents one possible state available to the electrons in a given subshell. Each electron gets an entry designated by its $m_{\ell}$ and $m_s$ values. The sum of these values for all of the electrons in the table is written to the left under the column headings of $M_L$ and $M_S$. Now reflect for a moment that each electron has four possible quantum numbers, $n, \ell, m_{\ell}$ and $m_s$. By specifying only the $m_{\ell}$ and $m_s$ numbers, there is a tacit assumption that $n$ and $\ell$ are unimportant. The reason is that this table is only useful when all of the $n$ and $\ell$ values are the same for each electron. If either of these values were different for two different electrons, those would not be equivalent, and the coupling could be performed as done previously.

A table for two nonequivalent $p$ electrons would contain 36 entries since each electron can have six different $m_{\ell}, m_s$ combinations. Such a table is not particularly useful. However, when two of the $p$ electrons are equivalent, many of these 36
entries will be excluded by the Pauli principle. A table for only the allowed combinations of \( m_{\ell_1}, m_{s_1}, m_{\ell_2}, \) and \( m_{s_2} \) would look like the following:

<table>
<thead>
<tr>
<th>#</th>
<th>( M_L )</th>
<th>( M_S )</th>
<th>( m_{\ell_1} )</th>
<th>( m_{s_1} )</th>
<th>( m_{\ell_2} )</th>
<th>( m_{s_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>+1/2</td>
<td>1</td>
<td>-1/2</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>+1/2</td>
<td>0</td>
<td>+1/2</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>+1/2</td>
<td>0</td>
<td>-1/2</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-1/2</td>
<td>0</td>
<td>+1/2</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1/2</td>
<td>0</td>
<td>-1/2</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>+1/2</td>
<td>-1</td>
<td>+1/2</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>+1/2</td>
<td>-1</td>
<td>-1/2</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1/2</td>
<td>-1</td>
<td>+1/2</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>+1/2</td>
<td>0</td>
<td>-1/2</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1/2</td>
<td>-1</td>
<td>-1/2</td>
</tr>
<tr>
<td>11</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>+1/2</td>
<td>0</td>
<td>+1/2</td>
</tr>
<tr>
<td>12</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>+1/2</td>
<td>0</td>
<td>-1/2</td>
</tr>
<tr>
<td>13</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>-1/2</td>
<td>0</td>
<td>+1/2</td>
</tr>
<tr>
<td>14</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1/2</td>
<td>0</td>
<td>-1/2</td>
</tr>
<tr>
<td>15</td>
<td>-2</td>
<td>0</td>
<td>-1</td>
<td>+1/2</td>
<td>-1</td>
<td>-1/2</td>
</tr>
</tbody>
</table>

Any other combination you might think of is either zero upon forming a Slater determinant or is equivalent to one already written since the electrons are indistinguishable.

The terms of two inequivalent \( p \) electrons are

<table>
<thead>
<tr>
<th>Term:</th>
<th>1( S )</th>
<th>3( S )</th>
<th>1( P )</th>
<th>3( P )</th>
<th>1( D )</th>
<th>3( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degeneracy:</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>9</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

How many terms are possible for the case of \( 2p^2 \)? If any state belonging to a given term appears in the table, then all the states of that term must appear. It is best to start consideration from the largest value of \( M_L \). Here that value is 2, and the largest value of \( M_S \) associated with that is 0, so there must be a \( 1D \). By count, 5 of the 15 entries in the table above are associated with this term. The next largest value of \( M_L \) is 1, and there are four entries in the table. The \( 1D \) is responsible for one of these, one of the \( M_L = 1, M_S = 0 \). But there are three others, with \( M_S = 1, 0, \) and \( -1 \). A \( 3P \) gives rise to those entries and 6 others besides, so 14 of the 15 entries are accounted for. There are three entries with \( M_L = 0 \) and \( M_S = 0 \), and the two terms found so far account for 2 of them. The third must belong to a \( 1S \), which accounts for only this entry and in total all 15 entries have been accounted for.

Note that if there were more than two electrons, the final terms that can occur depend on parentage, that is, the terms that are formed coupling in pairs from the inside out. For example, for a configuration of \( 2p3p4p \), there are 21 possible terms. This raises a point worth pursuing. Angular momentum is coupled in pairs, and it is important to keep track of the intermediate quantum numbers. The coupling of \( 2p \) and \( 3p \) leads to six terms specified previously. The \( \ell \) and \( s \) values for the \( 4p \) electron need to be added to these six in turn. This procedure can be expressed as
2.4 Matrix Elements of the Hamiltonian

\[ 2p3p(1S)4p \, ^2P \]
\[ 2p3p(3S)4p \, ^2P \, ^4P \]
\[ 2p3p(1P)4p \, ^2S \, ^2P \, ^2D \]
\[ 2p3p(3P)4p \, ^2S \, ^2P \, ^4P \, ^2D \, ^4D \]
\[ 2p3p(1D)4p \, ^2P \, ^2D \, ^2F \]
\[ 2p3p(3D)4p \, ^2P \, ^4P \, ^2D \, ^4D \, ^2F \, ^4F \]

In total, there are 21 terms not 8. It is important to realize that \(^2P\) occurs six times. Each of those six has different energies and a recognizably different parentage. The same is true for many of the others. When being asked to give the terms that result from coupling three or more angular momenta, one must include the intermediate terms as part of the designation.

**Problem 2.6**

Show that the only allowed terms for a \(p^3\) configuration are \(^4S\), \(^2P\), and \(^2D\). How many states are there? If the configuration were \(2p3p4p\), how many states would there be?

2.4 Matrix Elements of the Hamiltonian

For elementary QM problems the “solution” will yield energy values (eigenvalues of the Hamiltonian) and wave functions simultaneously. One might think of such a solution as a “single-pass” solution. Problems that require iterative techniques for their solution need to evaluate the expectation value of the Hamiltonian as one step in a multi-pass algorithm. The variation technique, backbone for most approximate methods, is such an example. Besides this reason, there is the likelihood that the wave functions have been found for some approximate Hamiltonian (say, central potential) and that once these wave functions are known, you then desire to find the energy levels of the actual Hamiltonian. Either way one needs to know how to evaluate the matrix elements of the Hamiltonian between determinantal functions:

Let \( \mathbf{H} = \sum_i f_i + \sum_{i,j} g_{ij} \)

where \( f_i = -\frac{\nabla^2}{2} - \frac{Z}{r_i} \)

and \( g_{ij} = \frac{1}{r_{ij}} \)
Here, because $f_i$ is a function of the coordinates of a single electron, it is called a one-electron operator, and $g_{ij}$, having coordinates of two different electrons, is a two-electron operator.

The first step is to write the matrix element $\langle u | A | u' \rangle$ of any operator $A$ between determinantal functions:

$$\frac{1}{N!} \int \begin{vmatrix} u_1^+(1) & \cdots & u_1^+(N) \\ \vdots \\ u_N^+(1) & \cdots & u_N^+(N) \end{vmatrix} A \begin{vmatrix} u_1'(1) & \cdots & u_1'(N) \\ \vdots \\ u_N'(1) & \cdots & u_N'(N) \end{vmatrix} d\tau_1 \ldots d\tau_N \quad (2.11)$$

Here $u_1(1)$ is short for

$$u_1(a_1) = u_1(n_1, \ell_1, m_{\ell_1}, m_{s_1}) = R_{m_{\ell_1}}(r_1) Y_{\ell_1}^{m_{\ell_1}}(\theta_1, \phi_1) \chi_{m_{s_1}}(1)$$

$$u_2(a_1) = R_{n_1, \ell_1}(r_2) Y_{\ell_1}^{m_{\ell_1}}(\theta_2, \phi_2) \chi_{m_{s_1}}(2)$$

So the subscript on $u$ is the electron index which goes with the coordinates $(r, \theta, \phi)$ and thus with $d\tau_1$, $d\tau_2$, etc. ($d\tau_1 \equiv r_1^2 \sin \theta_1 \, dr_1 \, d\theta_1 \, d\phi_1$). This notation for $u_i(j)$ is backward from Slater’s $^1$ but consistent with what was introduced previously. Now consider the term arising from the principal diagonal on the left:

$$\frac{1}{N!} \int u_1^+(1) u_2^+(2) \ldots u_N^+(N) A \begin{vmatrix} u_1'(1) & \cdots & u_1'(N) \\ \vdots \\ u_N'(1) & \cdots & u_N'(N) \end{vmatrix} d\tau_1 \ldots d\tau_N \quad (2.12)$$

Another term from the determinant on the left might be

$$\frac{1}{N!} \int -u_1^+(2) u_2^+(1) u_3^+(3) \ldots u_N^+(N) A \begin{vmatrix} u_1'(1) & \cdots & u_1'(N) \\ \vdots \\ u_N'(1) & \cdots & u_N'(N) \end{vmatrix} d\tau_1 \ldots d\tau_N$$

Since the integration is performed over all electron coordinates, these are dummy indices. The above is the same as

$$\frac{1}{N!} \int -u_2^+(2) u_1^+(1) u_3^+(3) \ldots u_N^+(N) A \begin{vmatrix} u_2'(1) & \cdots & u_2'(N) \\ u_1'(1) & \cdots & u_1'(N) \\ \vdots \\ u_N'(1) & \cdots & u_N'(N) \end{vmatrix} d\tau_1 \ldots d\tau_N$$

---

Upon interchange of the first two rows of the determinant on the right, Eq. (2.12) is regained. In this way it can be shown that all \( N! \) terms from the determinant on the left are the same as (2.12) which leads to

\[
\langle u | A | u' \rangle = \int u_1^*(1) \ldots u_N^*(N) A \begin{pmatrix}
  u_1'(1) & \ldots & u_1'(N) \\
  \vdots & & \vdots \\
  u_N'(1) & \ldots & u_N'(N)
\end{pmatrix} d\tau_1 \ldots d\tau_N
\]

Further simplification depends on the form of the operator. It could be a constant, a one-electron operator, or a two-electron operator. Consider what happens if the operator is just a complex number. All \( u \)'s are orthonormal, so unless one permutation matches the term on the left, the result is zero. A match can occur only if \( u = u' \) for all \( N \). Thus, unity results from the principal diagonal and zero from all other terms so that

\[
\langle u | c | u' \rangle = c \langle u | u' \rangle = c \quad \text{for} \quad u = u' \\
= 0 \quad \text{for} \quad u \neq u'
\]

### 2.4.1 One-Electron Operators

Let \( A \) be any one-electron operator \( f_i \). There are three cases to consider. Either \( u' \) is identical to \( u \) (one case) or it is different. If different, it can differ in any number of spin orbitals. However, should two or more spin orbitals be different, the resultant matrix element must be zero. After presenting the generality, a specific example should make the following cases clearer:

**Case 1:** \( u = u' \) (diagonal matrix elements). Only the principal diagonal of the determinant on the right contributes yielding

\[
\langle u | \sum_i f_i | u \rangle = \int u_1^*(1) f_1 u_1(1) d\tau_1 + \int u_2^*(2) f_2 u_2(2) d\tau_2 + \ldots \\
+ \int u_N^*(N) f_N u_N(N) d\tau_N
\]

But \( f_i \) has the same functional form for each electron and the electron indices are dummy, so this expression may be written

\[
\langle u | \sum_i f_i | u \rangle = \sum_i \int u_i^*(i) f_i u_i(i) d\tau_i \\
\equiv \sum_i \langle i | f | i \rangle
\]
Don’t be confused by the index “1.” When we started this all of the electrons were numbered. Now that number is redundant (and will shortly be dropped), so the “1” could equally well have been any of the electron numbers:

**Case 2:** $u = u'$ except for one spin orbital. Only a single term survives:

$$\langle i | f | i' \rangle = \int u_1^*(i)f_1 u'_1(i') \, d\tau_1$$

**Case 3:** $u = u'$ except for more than one spin orbital.

Zero.

Before proceeding to two-electron operators, working through a specific example should clarify what has been presented. Consider the configuration $1s^2s^2p^t h r e e$ nonequivalent electrons. Choose the wave function (arbitrarily) to be

$$|u\rangle = A|1s^0 + \rangle_1 |2s^0 + \rangle_1 |2p^− \rangle_1$$

This is one of 24 possible determinants from the configuration $1s^2s^2p$. Written out explicitly, the wave function looks like

$$u = \frac{1}{\sqrt{6}} \begin{vmatrix} |1s^0 + \rangle_1 & |2s^0 + \rangle_1 & |2p^− \rangle_1 \\ |1s^0 + \rangle_2 & |2s^0 + \rangle_2 & |2p^− \rangle_2 \\ |1s^0 + \rangle_3 & |2s^0 + \rangle_3 & |2p^− \rangle_3 \end{vmatrix}$$

Let $f = 1/r_1$, for example. Then

$$\langle u | \sum_i f_i | u \rangle = \sum_i \langle (1s^0 +)_1 (2s^0 +)_2 (2p^−)_3 | \frac{1}{r_1} |$$

The first term in the sum over $i$ has six contributions from the determinant on the right. The one from the principal diagonal (the only nonzero one) is

$$\langle 1s^0 + | \frac{1}{r_1} | 1s^0 + \rangle_1 \langle 2s^0 + | 2s^0 + \rangle_2 \langle 2p^− | 2p^− \rangle_3$$

One of the five contributions not from the principal diagonal is

$$\langle 1s^0 + | \frac{1}{r_1} | 2s^0 + \rangle_1 \langle 2s^0 + | 1s^0 + \rangle_2 \langle 2p^− | 2p^− \rangle_3 = 0 \text{ by orthogonality}$$
In this way all contributions from terms not of the principal diagonal are zero because at least one overlap integral (an integral not containing the operator) is zero.

Performing the sum over $i$ would then yield

$$\langle u | \sum_i f_i | u \rangle = \langle 1 s 0^+ | \frac{1}{r_1} | 1 s 0^+ \rangle_1 + \langle 2 s 0^+ | \frac{1}{r_2} | 2 s 0^+ \rangle_2$$

$$+ \langle 2 p 1^- | \frac{1}{r_3} | 2 p 1^- \rangle_3$$

Next notice that $1/r_1$, $1/r_2$, and $1/r_3$ have the same functional form. Only the electron index is different. But this difference is now no longer relevant because the integrals are isolated in individual terms of the sum. Hence they may be written as

$$\langle u | \sum_i f_i | u \rangle = \langle 1 s 0^+ | \frac{1}{r_1} | 1 s 0^+ \rangle_1 + \langle 2 s 0^+ | \frac{1}{r_1} | 2 s 0^+ \rangle_1$$

$$+ \langle 2 p 1^- | \frac{1}{r_1} | 2 p 1^- \rangle_1$$

Now clearly the subscript 1 is irrelevant, and there is no possibility of confusion or ambiguity if the expression is written as

$$\langle u | \sum_i f_i | u \rangle = \langle 1 s 0^+ | \frac{1}{r} | 1 s 0^+ \rangle + \langle 2 s 0^+ | \frac{1}{r} | 2 s 0^+ \rangle + \langle 2 p 1^- | \frac{1}{r} | 2 p 1^- \rangle.$$  

**Problem 2.7**

Do you know what these integrals are for hydrogenic wave functions? Note that the sum over $i$ has become a sum over quantum numbers.

Off-diagonal matrix elements are nonzero only if $u'$ differs from $u$ by not more than one spin orbital. This is quite a simplification for something that started off looking so formidable. For the one-electron operator $1/r$, it happens that there are no nonzero off-diagonal elements at all between different states of the same configuration. This happens because these different states differ only in their angular or spin dependence and the operator $1/r$ is insensitive to such dependence. But for a general one-electron operator, $f(r, \theta, \phi)$, there can be nonzero elements.

Take another of our 24 possible determinants and write

$$| u' \rangle = \mathcal{A} | 1 s 0^+ \rangle | 2 s 0^+ \rangle | 2 p 0^- \rangle$$

Then $\langle u | \sum_i f_i | u' \rangle$ has only the single nonzero contribution
\[ \langle 1s0^+ | 1s0^+ \rangle_1 \langle 2s0^+ | 2s0^+ \rangle_2 \langle 2p1^- | f_3(r, \theta, \phi) | 2p0^- \rangle \]

or

\[ \langle u | \sum_i f_i | u' \rangle = \langle 2p1^- | f(r, \theta, \phi) | 2p0^- \rangle \]

Of course, even for a general one-electron operator, if it is not spin dependent, then the spins must be aligned, or the matrix element is zero, e.g.,

\[ \langle u | \sum_i f_i | u' \rangle = \langle 2p1^- | f(r, \theta, \phi) | 2p1^+ \rangle = 0 \]

because of spin orthogonality.

### 2.4.2 Two-Electron Operators

Let

\[ A = \sum_{\text{pairs } i,j} g_{ij} \equiv \sum_{i<j} g_{ij}. \]

For \( n \) electrons, there are \( n(n-1)/2 \) such terms:

**Case 1:** Diagonal matrix elements \((u = u')\).

\[ \langle u | A | u \rangle = \int u_1^*(1) \ldots u_N^*(N) \sum_{i<j} g_{ij} \begin{vmatrix} u_1(1) & \ldots & u_1(N) \\ \vdots \\ u_N(1) & \ldots & u_N(N) \end{vmatrix} d\tau_1 \ldots d\tau_N \]

Look at one of the terms in the sum over \( i \) and \( j \), say \( i = 1, j = 2 \). Then

\[ \langle u | g_{12} | u \rangle = \int u_1^*(1) \ldots u_N^*(N) g_{12} \begin{vmatrix} u_1(1) & \ldots & u_1(N) \\ \vdots \\ u_N(1) & \ldots & u_N(N) \end{vmatrix} d\tau_1 \ldots d\tau_N \]

Of all the terms from the determinant, two survive: the principal diagonal and the one which looks like

\[ -u_1(2)u_2(1)u_3(3) \ldots u_N(N). \]
The element becomes

\[ \langle u | g_{12} | u \rangle = \int u_1^*(1) u_2^*(2) g_{12} u_1(1) u_2(2) \, d\tau_1 \, d\tau_2 \]

\[ - \int u_1^*(1) u_2^*(2) g_{12} u_1(2) u_2(1) \, d\tau_1 \, d\tau_2 \]

Summing over \( i \) and \( j \), remembering that the electron indices are dummy, yields

\[ \langle u | \sum_{i<j} g_{ij} | u \rangle = \sum_{i<j} \left[ \int u_1^*(i) u_2^*(j) g_{12} u_1(i) u_2(j) \, d\tau_1 \, d\tau_2 \right. \]

\[ - \left. \int u_1^*(i) u_2^*(j) g_{12} u_1(j) u_2(i) \, d\tau_1 \, d\tau_2 \right] \]

Or

\[ \langle u | A | u \rangle = \sum_{i<j} \left[ (i\, j | g_{12} | i\, j) - (i\, j | g_{12} | j\, i) \right] \]

**Case 2:** \( u = u' \) except for one spin orbital.

\[ \langle u | \sum_{i<j} g_{ij} | u' \rangle = \sum_{i\neq j} \left[ (i\, j | g_{12} | i'\, j') - (i\, j | g_{12} | j'\, i') \right] \]

**Case 3:** \( u = u' \) except for two spin orbitals.

\[ \langle u | \sum_{i<j} g_{ij} | u' \rangle = (i\, j | g_{12} | i'\, j') - (i\, j | g_{12} | j'\, i') \]

where \( i' \) and \( j' \) indicate just those spin orbitals of \( u' \) which differ from \( u \). All others must be the same, and the spin of \( i' \) and \( j' \) must be aligned with those of \( i \) and \( j \) when \( g_{ij} \) is spin independent.

Example: Again choose a \( 1s2s2p \) configuration, and let

\[ | u \rangle = A| 1s \, 0^+ \rangle | 2s \, 0^+ \rangle | 2p \, 1^+ \rangle \]

Then

\[ \langle u | \sum_{i<j} g_{ij} | u \rangle = \langle (1s \, 0^+) | (2s \, 0^+) | g_{12} | (1s \, 0^+) | (2s \, 0^+) \rangle \]

\[ - \langle (1s \, 0^+) | (2s \, 0^+) | g_{12} | (1s \, 0^+) | (2s \, 0^+) \rangle \]

\[ + \langle (2s \, 0^+) | (2p \, 1^+) | g_{12} | (2s \, 0^+) | (2p \, 1^+) \rangle \]

\[ - \langle (2s \, 0^+) | (2p \, 1^+) | g_{12} | (2s \, 0^+) | (2p \, 1^+) \rangle \]

\[ + \langle (1s \, 0^+) | (2p \, 1^+) | g_{12} | (1s \, 0^+) | (2p \, 1^+) \rangle \]

\[ - \langle (1s \, 0^+) | (2p \, 1^+) | g_{12} | (1s \, 0^+) | (2p \, 1^+) \rangle \]
An expression like $\langle i j \mid g_{ij} \mid i j \rangle$ has not previously been encountered, and an expression for a general two-electron integral can be written as

$$\langle i j \mid g_{12} \mid r t \rangle = \int \int u_1^*(i) u_2^*(j) g_{12} u_1(r) u_2(t) \, dr_1 \, dr_2$$

The diagonal matrix elements of the two-electron operator have special names:

$$\langle i j \mid g_{12} \mid i j \rangle \Rightarrow \text{Coulomb integral}$$

$$\langle i j \mid g_{12} \mid ji \rangle \Rightarrow \text{exchange integral}$$

Antisymmetrization and indistinguishable particles gave us nothing for one-electron operators (or for c-numbers) that would not have resulted by letting $u = u_1(1) u_2(2) \ldots u_N(N)$ rather than $u = A u_1(1) u_2(2) \ldots u_N(N)$. The first new feature appears for two-electron operators and is the exchange integral.

Subsequently, explicit formulae for these matrix elements in terms of the $(R_n \ell Y^m_\ell \chi_{m_s})$ one-electron spin orbitals will be presented.

By the way, any problem you are asked to solve will only require the use of diagonal matrix elements. Take note of the fact that what has been derived is valid for both one- and two-electron operators of any functional form. Here our interest is in evaluating the energy, but in subsequent chapters other operators will be of interest.

The relevant energy operators are

$$H = \sum_i f_i + \sum_{i<j} g_{ij}$$

$$f_i \equiv -\frac{1}{2} \nabla^2_i - \frac{Z}{r_i}$$

$$g_{ij} \equiv \frac{1}{r_{ij}}$$

Consider now only diagonal matrix elements of the Hamiltonian

$$\langle u \mid \sum_i f_i \mid u \rangle = \sum_{n\ell} q_{n\ell} I(n, \ell)$$

$q(n, \ell)$ is the occupation number of a shell (given $n\ell$ value), e.g., for $1s^22s^22p^3$, $q_{1s} = 2$, $q_{2s} = 1$, and $q_{2p} = 3$.

$$I(n, \ell) \equiv \int u^*(n, \ell) \left( -\frac{\nabla^2}{2} - \frac{Z}{r} \right) u(n, \ell) \, dr$$

$$= \int_0^\infty \left[ \frac{1}{2} r^{2\ell+2} \frac{d}{dr} \left( \frac{R_{n\ell}^s}{r^\ell} \right) \frac{d}{dr} \left( \frac{R_{n\ell}}{r^\ell} \right) - Z r R_{n\ell}^s R_{n\ell} \right] dr$$
2.4 Matrix Elements of the Hamiltonian

Problem 2.8
Prove this.

So I(n, ℓ) is the same for all states of a given configuration. (The operator f_i has no off-diagonal elements between states of the same configuration.)

The two-electron operator is more cumbersome:

\[
\langle i j | \frac{1}{r_{ij}} | i j \rangle = \int \int R^{*}_{n_{i} \ell_{i}}(r_{1})R^{*}_{n_{j} \ell_{j}}(r_{2}) Y^{*m_{\ell_{i}}}_{\ell_{i}} Y^{*m_{\ell_{j}}}_{\ell_{j}} \left( \frac{1}{r_{12}} \right) R_{n_{i} \ell_{i}}(r_{1})R_{n_{j} \ell_{j}}(r_{2}) Y^{m_{i}}_{\ell_{i}}(\theta_{1}, \phi_{1}) Y^{m_{j}}_{\ell_{j}}(\theta_{2}, \phi_{2}) d\tau_{1} d\tau_{2}
\] (2.17)

The most reasonable way to handle an integral of this form is to invoke the spherical harmonic addition theorem:

\[
\frac{1}{r_{12}} = \sum_{k, m_{k}} \frac{4\pi}{2k + 1} \frac{r_{\leq k}}{r_{k+1}} Y^{*m_{k}}_{k}(\theta_{1}, \phi_{1}) Y^{m_{k}}_{k}(\theta_{2}, \phi_{2})
\]

where

\[
\frac{1}{r_{12}} \equiv \frac{1}{|\vec{r}_{1} - \vec{r}_{2}|}
\]

and r_> is the larger of |\vec{r}_{1}| and |\vec{r}_{2}| and r_< is the smaller of the two (see the appendix Polynomials and Spherical Harmonics for the derivation). This is an extremely useful expression but does demand that the user split any integral in which it is invoked into two regions, one in which |\vec{r}_{1}| is greater than |\vec{r}_{2}| and one in which the opposite is the case. Reflect on the fact that the angles which originally occurred in the denominator are now in the numerator and are in the form of the spherical harmonics. The price one pays is to have an infinite sum, which at first might seem high, but in fact, the sum is always constrained to the first few terms whenever the operator appears inside a matrix element in which one of the angular momenta is not ridiculously large. The index k cannot be larger than the sum of the angular momenta appearing in the bra and ket making up the matrix element. This is a consequence of what follows.

Our task is to perform the integration expressed in (2.17). There are six integrals in this expression over the variables r_1, r_2, \theta_1, \theta_2, \phi_1, and \phi_2. First look at the integrals just over \theta_1 and \phi_1 for a given value of k and reexpress them without complex conjugates:
\[
\left[ \frac{4\pi}{2k+1} \right]^{1/2} \sum_{m_k} Y_{k \ell_i}^{* m_k} Y_{\ell_i}^{m_k} (\theta_1, \phi_1) d\Omega_1
\]

\[
= \left[ \frac{4\pi}{2k+1} \right]^{1/2} \sum_{m_k} (-1)^{m_k+m_{\ell_i}} \int Y_{k \ell_i}^{-m_k} Y_{\ell_i}^{-m_{\ell_i}} Y_{\ell_i}^{m_{\ell_i}} (\theta_1, \phi_1) d\Omega_1 \quad (2.18)
\]

This integral over three spherical harmonics has a closed form in terms of Clebsch–Gordan coefficients or better still in terms of 3\(–j\) symbols. Its value will be tabulated in a convenient form, and its derivation would take us too far afield. The result is\(^2\)

\[
\int Y_p^m Y_q^n Y_s^m d\Omega = \left[ \frac{(2p+1)(2q+1)(2s+1)}{4\pi} \right]^{1/2} \begin{pmatrix} p & q & s \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} p & q & s \\ m_p & m_q & m_s \end{pmatrix} \quad (2.19)
\]

The last two expressions are 3\(–j\) symbols. Recall from the defining properties that \(p + q + s\) must be an even integer and that \(m_p + m_q + m_s = 0\). Applying these to the integral (2.18) results in

\[-m_k = m_p, \quad -m_{\ell_i} = m_q, \quad m_{\ell_i} = m_s.\]

So \(m_k = 0\). Now the integral can be rewritten as

\[
\left[ \frac{4\pi}{2k+1} \right]^{1/2} \int Y_k^0 Y_{\ell_i}^{* m_{\ell_i}} Y_{\ell_i}^{m_{\ell_i}} d\Omega
\]

The coefficient \(c^k\) can be defined as

\[
c^k(\ell_i m_{\ell_i}; \ell_j m_{\ell_j}) = \left[ \frac{4\pi}{2k+1} \right]^{1/2} \int Y_k^{m_{\ell_i} - m_{\ell_j}} Y_{\ell_i}^{* m_{\ell_i}} Y_{\ell_j}^{m_{\ell_j}} d\Omega \quad (2.20)
\]

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Shorthand notation for this same integral is \(c^k(i; j) \equiv c^k(\ell_i m_{\ell_i}; \ell_j m_{\ell_j})\). The integral above (2.18) is just \(c^k(i; i)\). The Coulomb integral that is being considered (2.17) may now be written as

\[
\langle ij | \frac{1}{r_{12}} | ij \rangle = \sum_{k=0}^{\infty} c^k(i; i)c^k(j; j)F^k(i, j)
\]

(2.21)

where \(c^k(i; i)\), the double integral that has just been completed, expresses the integral over \(\theta_1\) and \(\phi_1\). The double integral over \(\theta_2\) and \(\phi_2\) is \(c^k(j; j)\) done just as the previous case. What has not yet been done is the double integral over \(r_1\) and \(r_2\) which can be expressed as

\[
F^k(i, j) \equiv \int \int R^*_{n_i \ell_i}(r_1)R^*_{n_j \ell_j}(r_2) \frac{r_k^k}{r_{k+1}^k} R_{n_i \ell_i}(r_1)R_{n_j \ell_j}(r_2)r_1^2 r_2^2 \, dr_1 \, dr_2
\]

(2.22)

and \(F^k(i, j) = F^k(n_i \ell_i, n_j \ell_j)\). The evaluation of this integral for any specific problem is quite involved and obviously needs the radial wave functions which are specific to each different problem. It suffices for the present discussion to express this integral with notation that is commonly used.

It is customary to define

\[
a^k(i; j) \equiv a^k(\ell_i m_{\ell_i}; \ell_j m_{\ell_j}) \equiv c^k(i; i)c^k(j; j)
\]

So finally, the combined angular and radial integrals from Eq.(2.17) can be expressed as

\[
\langle ij | \frac{1}{r_{12}} | ij \rangle = \sum_{k=0}^{\infty} a^k(i; j)F^k(i, j)
\]

(2.23)

In practice, only very few terms are nonzero.

The exchange integral is done in the same manner, but the interchange of \(i\) and \(j\) on the right side of the ket means that the spin part of the wave functions do not automatically align and if they were not aligned, zero would result. In addition, the radial integral is more complicated than the Coulomb integral:

\[
\langle ij | \frac{1}{r_{12}} | ji \rangle = \delta_{m_i, m_j} \sum_{k=0}^{\infty} \left[c^k(i; j)\right]^2 G^k(i, j)
\]

(2.24)
where
\[
G^k(i, j) \equiv \int \int R_{n_i \ell_i}(r_1)R_{n_j \ell_j}(r_2) \frac{r_k^{r_k^*}}{r_{k+1}^{r_{k+1}}} R_{n_j \ell_j}(r_1)R_{n_i \ell_i}(r_2)r_1^2 r_2^2 \, dr_1 \, dr_2
\] (2.25)

Problem 2.9
Prove (2.24).

Putting it all together, the diagonal matrix elements of the Hamiltonian between determinantal spin orbitals is given by
\[
\langle u | H | u \rangle = \sum_{\text{shells}} q_{n\ell} I(n, \ell) + \sum_{i<j} \sum_{k=0}^{\infty} \left\{ a^k(i; j) F^k(i, j) - \delta_{m_{n_i} m_{n_j}} [c^k(i; j)]^2 G^k(i, j) \right\}. \tag{2.26}
\]

Some remarks are in order. \(I(n, \ell)\) will always be a very large negative number. The integrals \(F^k\) and \(G^k\) are always positive. The energy that results will be negative taken with respect to complete ionization of the atom.

Values for \(c^k\) and \(a^k\) have been tabulated. All that is needed to work out the energy for many excited states of any atom are the values of the Coulomb integrals \(F^k\) and the exchange integrals \(G^k\). However, the relative placement of different terms of a configuration can often be done without knowing the values of these integrals.

2.5 Energy Values for Some Simple Examples

Consider the configuration 1s2s of helium. There are four states; in the primitive basis of determinantal wave functions, they are
\[
\begin{align*}
|u_1\rangle &= |1s0^+\rangle|2s0^+\rangle \\
|u_2\rangle &= |1s0^+\rangle|2s0^-\rangle \\
|u_3\rangle &= |1s0^-\rangle|2s0^+\rangle \\
|u_4\rangle &= |1s0^-\rangle|2s0^-\rangle
\end{align*}
\]
In the basis $L$, $S$, $M_L$, and $M_S$, there are the states

\begin{align*}
3S_{01} & \quad (M_L = 0, M_S = 1) \\
3S_{00} \\
1S_{00} \\
3S_{0-1}
\end{align*}

Forming a table connecting these basis sets yields

<table>
<thead>
<tr>
<th>$M_L$</th>
<th>$M_S$</th>
<th>$m_{\ell_1}$</th>
<th>$m_{s_1}$</th>
<th>$m_{\ell_2}$</th>
<th>$m_{s_2}$</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>$1/2$</td>
<td>0</td>
<td>$1/2$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
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<td>$1/2$</td>
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<td>0</td>
<td>$-1/2$</td>
<td>0</td>
<td>$-1/2$</td>
</tr>
</tbody>
</table>

Clearly the state $3S_{01}$ is given by $u_1$ while $3S_{0-1}$ is $u_4$. But $1S_{00}$ is a linear combination of $u_2$ and $u_3$ while $3S_{00}$ is an orthogonal linear combination of $u_2$ and $u_3$.

For the Hamiltonian being considered, all the states of a given term are degenerate. The energy of the $3S$ term can then be found by

\[ E(3S) = \langle u_1 | H | u_1 \rangle \quad \text{or} \quad \langle u_4 | H | u_4 \rangle \]

To obtain the energy of the $1S$, one could proceed in two ways. Evaluate the matrix

\[ \langle u_2 | H | u_2 \rangle \langle u_2 | H | u_3 \rangle \]
\[ \langle u_3 | H | u_2 \rangle \langle u_3 | H | u_3 \rangle \]

and diagonalize it, thereby getting the $3S$ and $1S$ energies as eigenvalues. There is, however, a much easier way which avoids evaluating off-diagonal matrix elements. Called the Slater sum rule, it reminds you that the trace of a matrix is invariant to a unitary transformation. So the sum of the diagonal matrix elements above must be the sum of the $3S$ and $1S$ energies. The $3S$ energy is known from before, so subtract that from the sum to find the $1S$ energy.

Use (2.26) to obtain

\[ E(3S) = \langle u_1 | H | u_1 \rangle = I(1s) + I(2s) + F^0(1s, 2s) - G^0(1s, 2s) \]

Then

\[ \langle u_2 | H | u_2 \rangle = I(1s) + I(2s) + F^0(1s, 2s) \]
\[ \langle u_3 | H | u_3 \rangle = I(1s) + I(2s) + F^0(1s, 2s) \]
Adding these and subtracting the above gives

\[ E(1S) = I(1s) + I(2s) + F^0(1s, 2s) + G^0(1s, 2s) \]

So the triplet lies below the singlet. If determinantal wave functions had not been used, one would have obtained \( I(1s) + I(2s) + F^0(1s, 2s) \) for both of these. The exchange interaction, an electrostatic effect that has nothing to do with any magnetic moment associated with spin, has split the energy between singlet and triplet.

If the configuration had been \( 1s^22s3s \), the analysis would go through as before, but there would be many more terms to the energy expression:

\[ E(1s^22s3s\ 3S) = 2I(1s) + I(2s) + I(3s) \]
\[ + F^0(1s, 1s) \]
\[ + 2F^0(1s, 2s) - G^0(1s, 2s) \]
\[ + 2F^0(1s, 3s) - G^0(1s, 3s) \]
\[ + F^0(2s, 3s) - G^0(2s, 3s) \]

\[ E(1s^22s3s\ 1S) = 2I(1s) + I(2s) + I(3s) \]
\[ + F^0(1s, 1s) \]
\[ + 2F^0(1s, 2s) - G^0(1s, 2s) \]
\[ + 2F^0(1s, 3s) - G^0(1s, 3s) \]
\[ + F^0(2s, 3s) + G^0(2s, 3s) \]

Warning: The formulae above are applicable whenever the configuration is \( 1s^22s3s \), but the actual values of the integrals depend on the value of \( Z \). This configuration exists for \( \text{Be} \) but also for \( \text{B}^+ \), \( \text{C}^{++} \), \( \text{N}^{+++} \), etc., and is called the \( \text{Be} \) isoelectronic sequence. Spectroscopic notation for these ions is 

\( \text{Be I, B II, C III, N IV, etc.} \)

Consider \( 2p^2 \). Our previous work concluded that there are only three terms: \( ^3P \), \( ^1S \), and \( ^1D \). Refer to the table on page 50. The numbers in the left column label the states in the basis \( |n_i\ell_im_{\ell_i}m_{s_i}\rangle \). Use of the Slater sum rule allows us to restrict our attention to just five of these. Using the same numbers as on page 50, there are

<table>
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<tr>
<th>#</th>
<th>( M_L )</th>
<th>( M_S )</th>
<th>( m_{\ell_1} )</th>
<th>( m_{s_1} )</th>
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<td>(-1 )</td>
<td>(-\frac{1}{2} )</td>
</tr>
<tr>
<td>8</td>
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<td>(-1 )</td>
<td>( \frac{1}{2} )</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>(-\frac{1}{2} )</td>
</tr>
</tbody>
</table>
Now #1 labels the state $u_1 = \langle 2p^1 1^+ \rangle | 2p 1^- \rangle$. In the coupled basis, there is the state $1D_{20}$ which must equal $u_1$. The energy of the $1D$ can be found by evaluating $\langle u_1 | H | u_1 \rangle$. Similarly the energy of the $3P$ can be found by $\langle u_2 | H | u_2 \rangle$. Now $1S$ has only one state: the $1S_{00}$. But this must be a linear combination of $u_7$, $u_8$, and $u_9$. The $1D_{00}$ and $3P_{00}$ are also orthogonal linear combinations of $u_7$, $u_8$, and $u_9$. So by adding together $\langle u_7 | H | u_7 \rangle$, $\langle u_8 | H | u_8 \rangle$, and $\langle u_9 | H | u_9 \rangle$, one obtains the sum of the $1D$, $3P$, and $1S$ energies. The first two are known, and by subtraction the energy of the $1S$ can be obtained:

$$E(2p^2 1D) = \langle u_1 | H | u_1 \rangle$$

(One could just as well use $\langle u_{15} | H | u_{15} \rangle$.)

$$E(1D) = 2I(2p) + F^0(2p, 2p) + \frac{1}{25} F^2(2p, 2p)$$

In like fashion,

$$E(2p^2 3P) = \langle u_2 | H | u_2 \rangle$$

(One could just as well use $\langle u_5 | H | u_5 \rangle$ or $\langle u_6 | H | u_6 \rangle$ or $\langle u_{10} | H | u_{10} \rangle$ or $\langle u_{11} | H | u_{11} \rangle$ or $\langle u_{14} | H | u_{14} \rangle$.)

$$E(3P) = 2I(2p) + F^0(2p, 2p) - \frac{2}{25} F^2(2p, 2p) - \frac{3}{25} G^2(2p, 2p)$$

$$= 2I(2p) + F^0(2p, 2p) - \frac{1}{5} F^2(2p, 2p)$$

because $G^k(n\ell, n\ell) = F^k(n\ell, n\ell)$.

The desired sum is $\langle u_7 | H | u_7 \rangle + \langle u_8 | H | u_8 \rangle + \langle u_9 | H | u_9 \rangle$.

$$\langle u_7 | H | u_7 \rangle = 2I(2p) + F^0(2p, 2p) + \frac{1}{25} F^2(2p, 2p)$$

$$\langle u_8 | H | u_8 \rangle = 2I(2p) + F^0(2p, 2p) + \frac{1}{25} F^2(2p, 2p)$$

$$\langle u_9 | H | u_9 \rangle = 2I(2p) + F^0(2p, 2p) + \frac{4}{25} F^2(2p, 2p)$$

$$E(1S) = 2I(2p) + F^0(2p, 2p) + \frac{2}{5} F^2(2p, 2p)$$

Because the $F^k$ integrals are positive, this analysis tells us that the $3P$ lies lowest in energy, the $1D$ is next, and the $1S$ lies highest. That the $3P$ lies lowest is a verification of Hund’s rules.

Hund’s rules:

1. Of the terms given by equivalent electrons, those with the greatest multiplicity (largest $S$ value) lie deepest, and of these, the lowest is that with the greatest $L$. 

2. Multiplets formed from equivalent electrons are regular when less than half the shell is occupied but inverted when more than half the shell is occupied.

The second rule requires some clarification. When one considers all the levels (nondegenerate for real systems) associated with a given term, that grouping is called a multiplet, e.g., \( ^3P_{0,1,2} \). Regular spacing means that the level of lowest \( j \) lies deepest, while inverted means that the level of highest \( j \) lies deepest. The first example in the periodic table of this rule is that the ground state of carbon, \( 1s^22s^22p^2 \), is \( ^3P_0 \) while the ground state of oxygen, \( 1s^22s^22p^4 \), is \( ^3P_2 \).

For the configuration \( 1s^22s^22p^2 \), the energy for the \( ^1D \) term is

\[
E(1s^22s^22p^2 \, ^1D) = 2I(1s) + 2I(2s) + 2I(2p) \\
+ F^0(1s, 1s) \\
+ 4F^0(1s, 2s) - 2G^0(1s, 2s) \\
+ 4F^0(1s, 2p) - 2/3G^1(1s, 2p) \\
+ F^0(2s, 2s) \\
+ 4F^0(2s, 2p) - 2/3G^1(2s, 2p) \\
+ F^0(2p, 2p) + 1/25F^2(2p, 2p)
\]

Every line but the last is the same for each of the three terms \( ^1D, ^1S, \) and \( ^3P \). All one needs to obtain the relative placement of the three terms is the value of \( F^2(2p, 2p) \) for CI:

\[
\text{CI: } F^2(2p, 2p) = 0.2433 \text{ Hartrees}
\]

**Problem 2.10**

Place the three terms for the lowest configuration of carbon on an energy level diagram with the lowest term at 0 and the top of the diagram at the ionization limit of carbon. Use any consistent set of units.

The energy of CIII is a subset of the contributions considered above. Specifically, it has only a single-state \( ^1S_{00} \) in the ground level whose energy is given by

\[
E(\text{CIII} \, 1s^22s^2 \, ^1S) = 2I(1s) + 2I(2s) \\
+ F^0(1s, 1s) \\
+ 4F^0(1s, 2s) - 2G^0(1s, 2s)
\]

The energy of CI \( 1s^22s^22p^2 \, ^1D \) could then be written as
2.6 Average Energy of a Configuration

\[ E(\text{CI } 1s^22s^22p^2^1D) = E(\text{CIII ground state }) + 2I(2p) \]

\[ + 4F^0(1s, 2p) - \frac{2}{3}G^1(1s, 2p) \]

\[ + 4F^0(2s, 2p) - \frac{2}{3}G^1(2s, 2p) \]

\[ + F^0(2p, 2p) + \frac{1}{25}F^2(2p, 2p) \]

If someone were to tell you the energy of C III in the ground state and ask for the energy of some term of CI, your labor has been cut, in this instance, almost in half. For a heavier atom, the saving in effort would be greater still!

2.6 Average Energy of a Configuration

The energy of the three terms \( ^1D, \ ^1S, \) and \( ^3P \) differs only in the coefficients of the \( F^2(2p, 2p) \) integral. The energies can be written as

\[
\begin{align*}
E(^1D) &= E_0 + \frac{1}{25}F^2(2p, 2p) \\
E(^1S) &= E_0 + \frac{2}{3}F^2(2p, 2p) \\
E(^3P) &= E_0 - \frac{1}{3}F^2(2p, 2p)
\end{align*}
\]

(2.27)

Here \( E_0 \) represents all of the energy terms common to the above expressions.

The average energy of the configuration \( 1s^22s^22p^2 \) is obtained by multiplying each term energy by its statistical weight (the number of states which share that energy), adding them, and dividing by the total number of states, which for this case is 15. The \( ^1D \) has five states, the \( ^3P \) nine, and the \( ^1S \) one. The average energy is then

\[ E(\text{av } 1s^22s^22p^2) = E_0 - \frac{2}{25}F^2(2p, 2p) \]

Each of the term energies could now be written with respect to this average:

\[
\begin{align*}
E(^1D) &= E(\text{av}) + \frac{3}{25}F^2(2p, 2p) \\
E(^1S) &= E(\text{av}) + \frac{12}{25}F^2(2p, 2p) \\
E(^3P) &= E(\text{av}) - \frac{3}{25}F^2(2p, 2p)
\end{align*}
\]

(2.28)

Expressions for evaluating the average energy of the configuration have been derived in Condon and Odabasi.\(^3\) Such expressions might save a significant amount of time for performing calculations, by hand, for atoms heavier than neon. Practically

speaking, one rarely wishes to do that, and the expressions given here enable one to understand what the computer is doing when such evaluations are performed numerically.

2.7 Hartree–Fock Equations

This section will offer a very brief look at the Hartree–Fock equations written with a notation different from what has been used previously in this book. The reason for doing this is that one sees many different sets of notations and it is useful to learn their equivalence. Let $H = H_1 + H_2$:

$$H_1 \equiv \sum_{i=1}^{N} f_i = \sum f_i \left[ -\frac{\nabla^2 i}{2} - \frac{Z}{r_i} \right]$$

$$H_2 = \sum_{i<j=1}^{N} \frac{1}{r_{ij}}; \quad r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$$

An antisymmetrized product of one-electron spin orbitals will form the basis and be written as

$$\Phi \equiv Au_1(q_1)u_2(q_2) \ldots u_N(q_N)$$

The total energy can be written as (compare to (2.26))

$$E[\Phi] = \sum_{\lambda} I_{\lambda} + \frac{1}{2} \sum_{\lambda} \sum_{\mu} \left[ J_{\lambda\mu} - \delta_{m_{s\lambda}m_{s\mu}} K_{\lambda\mu} \right]$$

$$I_{\lambda} \equiv \langle u_{\lambda}(q_i) | f_i | u_{\lambda}(q_i) \rangle$$

$$J_{\lambda\mu} \equiv \langle u_{\lambda}(q_i)u_{\mu}(q_j) | \frac{1}{r_{ij}} | u_{\lambda}(q_i)u_{\mu}(q_j) \rangle$$

$$K_{\lambda\mu} \equiv \langle u_{\lambda}(q_i)u_{\mu}(q_j) | \frac{1}{r_{ij}} | u_{\mu}(q_i)u_{\lambda}(q_j) \rangle$$

and $\lambda, \mu$ stand for a set of quantum numbers

$$\lambda \leftrightarrow n_{\lambda}\lambda m_{\ell_{\lambda}} m_{s_{\lambda}}$$

---

and $i$ and $j$ serve to distinguish two different sets of electron coordinates, but any of the two—there is no sum over $i$ and $j$. To try to relate this notation to what was done previously, note that $J_{\lambda\mu}$ is given by (2.23) while $K_{\lambda\mu}$ is given by (2.24).

Using the method of Lagrange multipliers a variational equation can be written as

$$\delta E - \sum_{\lambda,\mu} \epsilon_{\lambda\mu} \delta \langle u_\mu | u_\lambda \rangle = 0$$

By performing a unitary transformation the above equation can be written in diagonal form as

$$\delta E - \sum_\lambda \epsilon_\lambda \delta \langle u_\lambda | u_\lambda \rangle = 0$$

Performing the variation on the expression for the total energy yields the Hartree–Fock equations for closed shells:

$$\left[ -\nabla_i^2 - \frac{Z}{r_i} \right] u_\lambda(q_i) + \left[ \sum_\mu \int u_\mu^*(q_j) \frac{1}{r_{ij}} u_\mu(q_j) \, dq_j \right] u_\lambda(q_i)$$

$$- \sum_\mu \left[ \delta_{m_\lambda m_\mu} \int u_\mu^*(q_j) \frac{1}{r_{ij}} u_\lambda(q_j) \, dq_j \right] u_\mu(q_i) = \epsilon_\lambda u_\lambda(q_i)$$

These are a set of coupled integrodifferential equations which have replaced the Schrödinger equation for a multi-electron atom. Indistinguishability of particles, antisymmetrization (Pauli principle), and the form of one-electron spin orbitals (appropriate for a central potential) have all been built in.

$\epsilon_\lambda$ is approximately the energy needed to remove the electron with quantum numbers $\lambda$. This is Koopman’s theorem.

The equations are solved iteratively for the functions $u_\lambda(q_i)$. Note that the noncentral potential, $H_2$, has been integrated over, forming an effective central potential. This is the potential alluded to early in this chapter when describing the self-consistent field approximation.
2.8 Tables

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*aThe number of terms of the given type is given under the term designation*
The Fundamentals of Atomic and Molecular Physics
Brooks, R.L.
2013, X, 179 p. 24 illus., Softcover