

Multi-Electron Atoms I

This set of notes is a simplified version of parts of Chapters VI and VII of *The Theory of Atomic Spectra* by Condon and Shortley. The next few sections describe description of how to construct multi-electron wave functions which satisfy the Pauli Principle, and calculate matrix elements in them. In the next set of notes, $L-S$ coupling is discussed and an application to low-lying energy levels of elements in the IVA column of the periodic table (C, Si, Ge, Sn, Pb) is treated in some detail. Finally, methods of determining the ground state configuration of other atoms are discussed.

States with N electrons For a treatment of electrons in atoms, a_j represents a set of quantum numbers n, l, m_l, m_s for electron j in a central field. The same notation could be used for other situations involving fermions. For states, we use a generalized Dirac notation. The *coordinate* ket of electron “1”, or $|x_1, y_1, z_1, m_{s1} \rangle$ is simply denoted as $|1 \rangle$. On the other hand its *quantum number* ket is denoted as $|a_1 \rangle$. We are only interested in *totally antisymmetric* states of N electrons, i.e. ones satisfying the Pauli Principle. These are denoted by capital letters, e.g. $|A \rangle$, where the number N of electrons is specified by context. Consider the case of $N = 2$. For this case, we have

$$|A \rangle = \frac{1}{\sqrt{2!}} (|a_1, a_2 \rangle - |a_2, a_1 \rangle),$$

where $a_1 \neq a_2$. This state has one electron with quantum numbers a_1 , and a second electron with quantum numbers a_2 . A statement like “electron 1 has quantum numbers a_1 and electron 2 has quantum numbers a_2 ” is meaningless for the state $|A \rangle$.

Going on to $N = 3$, we have

$$|A \rangle = \frac{1}{\sqrt{3!}} (|a_1, a_2, a_3 \rangle - |a_1, a_3, a_2 \rangle - |a_2, a_1, a_3 \rangle + |a_2, a_3, a_1 \rangle + |a_3, a_1, a_2 \rangle - |a_3, a_2, a_1 \rangle)$$

Permutations For an arbitrary value of N , we need to consider permutations on symbols and permutation operators on states. We will use the letter P for both. For a permutation P on $1, 2, \dots, N$, we write

$$P(1, 2, \dots, N) \equiv (1^P, 2^P, \dots, N^P), \quad (1)$$

or on the symbols a_1, a_2, \dots, a_N ,

$$P(a_1, a_2, \dots, a_N) = a_1^P, a_2^P, \dots, a_N^P \quad (2)$$

Then the permutation operator which acts on states is defined by

$$P|a_1, a_2, \dots, a_N \rangle = |P(a_1, a_2, \dots, a_N) \rangle = |a_1^P, a_2^P, \dots, a_N^P \rangle \quad (3)$$

The scalar product of $|a_1, a_2, \dots, a_N \rangle$, with another state of the same type is defined by

$$\langle a_1, a_2, \dots, a_N | b_1, b_2, \dots, b_N \rangle \equiv \prod_{i=1}^N \langle a_i | b_i \rangle \quad (4)$$

Using Eq.(4), we can show that the P operator defined in Eq.(3) is unitary. Using our definitions, we have

$$\begin{aligned} \langle a_1, a_2, \dots, a_N | P^\dagger P | b_1, b_2, \dots, b_N \rangle &= \langle P(a_1, a_2, \dots, a_N) | P(b_1, b_2, \dots, b_N) \rangle \\ &= \langle a_1^P, a_2^P, \dots, a_N^P | b_1^P, b_2^P, \dots, b_N^P \rangle = \prod_{i=1}^N \langle a_i^P | b_i^P \rangle . \end{aligned}$$

The product $\prod_{i=1}^N \langle a_i^P | b_i^P \rangle$ is just a re-arrangement of $\prod_{i=1}^N \langle a_i | b_i \rangle$, so we have

$$\prod_{i=1}^N \langle a_i^P | b_i^P \rangle = \prod_{i=1}^N \langle a_i | b_i \rangle = \langle a_1, a_2, \dots, a_N | b_1, b_2, \dots, b_N \rangle ,$$

which establishes the unitarity of P .

Each permutation P has a parity (even or odd). For the permutation P , we set $p = 1$ if P is odd, and $p = 0$ if P is even. The product of two permutations is again a permutation, so

$$PP' = P'' ,$$

and the parities will satisfy

$$(-1)^p (-1)^{p'} = (-1)^{p''} .$$

Antisymmetric States After these preliminaries, we are ready to define $|A\rangle$ for arbitrary N . We set

$$|A\rangle = \frac{1}{\sqrt{N!}} \sum_P (-1)^p P |a_1, a_2, \dots, a_N\rangle , \quad (5)$$

where we sum on all permutations P of N objects, and $(-1)^p$ is the parity of P . To make the state $|A\rangle$ of Eq.(5) completely well-defined, we impose an order on the quantum numbers. For $|a_1, a_2, \dots, a_N\rangle$, we require $a_1 < a_2 < \dots < a_N$, where $a_i < a_j$ must be given a meaning. We do this by saying $a_1 = (n, l, m_l, m_s)_1 < a_2 = (n, l, m_l, m_s)_2$ if $n_1 < n_2$, or if $n_1 = n_2$, then $a_1 < a_2$ if $l_1 < l_2$, etc.

Given a set of different quantum numbers a_1, a_2, \dots, a_N , and corresponding vectors $|a_1, a_2, \dots, a_N\rangle$, only the particular linear combination defined in Eq.(5) is an actual physical state. For a vector like $|a_1, a_2, \dots, a_N\rangle$, it does make mathematical sense to say that electron 1 has quantum numbers a_1 , electron 2 has quantum numbers a_2 , and so on, but when we form the combination of Eq.(5), identification of particular electrons with particular quantum numbers is no longer possible.

Exercise 1 Suppose an arbitrary permutation P_0 is applied to $|A\rangle$. Use the definition of $|A\rangle$ and the results of previous sections to show that

$$P_0 |A\rangle = (-1)^{p_0} |A\rangle$$

Wave Functions For the moderate values of N that occur in atoms, an explicit electron wave function is often desirable. For a single electron, the wave function is the overlap of a coordinate ket with a state vector, e.g. $\Psi(x) = \langle x | \Psi \rangle$. Generalizing this, for an N electron state satisfying the Pauli principle, we define the wave function by

$$\Psi_A(1, 2, \dots, N) \equiv \langle 1, 2, \dots, N | A \rangle$$

It is important to realize that this is a wave function in a generalized sense, a function of continuous coordinates x, y, z and the discrete coordinate m_s for each electron.

The wave function $\Psi_A(1, 2, \dots, N)$ may be written as a so-called ‘‘Slater determinant.’’ For the $N = 2$ case, we have

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}} (\langle 1 | a_1 \rangle \langle 2 | a_2 \rangle - \langle 1 | a_2 \rangle \langle 2 | a_1 \rangle).$$

This can be expressed as a determinant,

$$\Psi_A(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \langle 1 | a_1 \rangle & \langle 2 | a_1 \rangle \\ \langle 1 | a_2 \rangle & \langle 2 | a_2 \rangle \end{vmatrix}$$

Similarly, for $N = 3$, we have

$$\Psi_A(1, 2, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \langle 1 | a_1 \rangle & \langle 2 | a_1 \rangle & \langle 3 | a_1 \rangle \\ \langle 1 | a_2 \rangle & \langle 2 | a_2 \rangle & \langle 3 | a_2 \rangle \\ \langle 1 | a_3 \rangle & \langle 2 | a_3 \rangle & \langle 3 | a_3 \rangle \end{vmatrix}$$

These formulae generalize easily to an arbitrary value of N .

Exercise 2 Show that the wave function is anti-symmetric. Explicitly, show that

$$\Psi_A(P(1, 2, \dots, N)) = (-1)^p \Psi_A(1, 2, \dots, N)$$

One, Two, Three,... Body Operators In an N electron system, there are various physical quantities which are (i) additive over individual electrons, (ii) additive over distinct pairs of electrons, or (iii) additive over distinct triplets of electrons, etc. The first are one body operators, the second two body, etc. Three body operators are not needed in atomic physics.

Examples of one body operators

- The total kinetic energy of the electrons
- The total orbital angular momentum of the electrons

- The total spin angular momentum of the electrons
- The total potential energy between the electrons and the nucleus

We will use the letter F for a generic one body operator, and write

$$F = \sum_{i=1}^N F_i, \quad (6)$$

where F_i acts on the coordinates of the i th electron.

The only important two body operator

- The total potential energy between the electrons.

We will use the letter G for a generic two body operator, and write

$$G = \frac{1}{2} \sum_{i \neq j=1}^N G_{ij} = \sum_{i < j=1}^N G_{ij}, \quad (7)$$

where G_{ij} acts on electrons i and j . Both F and G are symmetric functions of the electron coordinates. From this it is easy to establish that

$$P^\dagger F P = F, \quad P^\dagger G P = G. \quad (8)$$

Matrix Elements of One and Two Body Operators This section is concerned with the diagonal matrix elements $\langle A|F|A \rangle$ and $\langle A|G|A \rangle$.

The one body matrix element Writing out $\langle A|F|A \rangle$, we have

$$\langle A|F|A \rangle = \frac{1}{N!} \sum_{P, P'} (-1)^{(p+p')} \langle a_1, a_2, \dots, a_N | P^\dagger F P' | a_1, a_2, \dots, a_N \rangle \quad (9)$$

Inserting a factor of $P P^\dagger = I$, we have

$$\langle A|F|A \rangle = \frac{1}{N!} \sum_{P, P'} (-1)^{(p+p')} \langle a_1, a_2, \dots, a_N | P^\dagger F P P^\dagger P' | a_1, a_2, \dots, a_N \rangle. \quad (10)$$

Now $P^\dagger P'$ is again a permutation. Call it P'' . Then, using Eq.(8), we have

$$\langle A|F|A \rangle = \frac{1}{N!} \sum_{P, P''} (-1)^{p''} \langle a_1, a_2, \dots, a_N | F P'' | a_1, a_2, \dots, a_N \rangle, \quad (11)$$

where we replaced the sum on P' by the sum on P'' , and used $(-1)^{p+p'} = (-1)^{p''}$. Next, we note that the summand of Eq.(11) is independent of the permutation P . The sum

over P then generates $N!$ identical terms, and the factor $1/N!$ is cancelled. We have, dropping the now unnecessary superscript,

$$\langle A|F|A \rangle = \sum_P (-1)^p \langle a_1, a_2, \dots, a_N | \left(\sum_{i=1}^N F_i \right) P | a_1, a_2, \dots, a_N \rangle . \quad (12)$$

Let us write out the term involving F_1 in Eq.(12). This is

$$\langle A|F_1|A \rangle = \sum_P (-1)^p \langle a_1, a_2, \dots, a_N | F_1 P | a_1, a_2, \dots, a_N \rangle . \quad (13)$$

Evaluating the matrix element in this equation, we have

$$\langle a_1, a_2, \dots, a_N | F_1 P | a_1, a_2, \dots, a_N \rangle = \langle a_1 | F_1 | a_1^P \rangle \langle a_2 | a_2^P \rangle \langle a_3 | a_3^P \rangle \dots \langle a_N | a_N^P \rangle . \quad (14)$$

Since it requires $a_2 = a_2^P, a_3 = a_3^P, \dots, a_N = a_N^P$, the matrix element in Eq.(14) vanishes unless the permutation P is the identity. An entirely similar result holds for the matrix element of F_i for arbitrary i . As a result, the sum on P collapses; only $P = I$ gives a non-vanishing result. We finally have

$$\langle A|F|A \rangle = \sum_{i=1}^N \langle a_i | F_i | a_i \rangle . \quad (15)$$

This result is simple and intuitive. We have an N electron state, where the electrons have quantum numbers a_1, \dots, a_N . Then the value of, say the kinetic energy is the sum of the expected values of the kinetic energy in each of these states.

The two body matrix element Writing out $\langle A|G|A \rangle$, we have

$$\langle A|G|A \rangle = \frac{1}{N!} \sum_{P, P'} (-1)^{(p+p')} \langle a_1, a_2, \dots, a_N | P^\dagger G P' | a_1, a_2, \dots, a_N \rangle \quad (16)$$

Using the same steps as in the one body matrix element, we can transform $\langle A|G|A \rangle$ into

$$\langle A|G|A \rangle = \sum_P (-1)^p \langle a_1, a_2, \dots, a_N | \left(\sum_{i < j=1}^N G_{ij} \right) P | a_1, a_2, \dots, a_N \rangle . \quad (17)$$

Let us write out the term involving G_{12} in Eq.(17). This is

$$\langle A|G_{12}|A \rangle = \sum_P (-1)^p \langle a_1, a_2, \dots, a_N | G_{12} P | a_1, a_2, \dots, a_N \rangle . \quad (18)$$

Evaluating the matrix element in this equation, we have

$$\langle a_1, a_2, \dots, a_N | G_{12} P | a_1, a_2, \dots, a_N \rangle = \langle a_1, a_2 | G_{12} | a_1^P, a_2^P \rangle \langle a_3 | a_3^P \rangle \dots \langle a_N | a_N^P \rangle . \quad (19)$$

The matrix element of Eq.(19) vanishes unless $a_3 = a_3^P, \dots, a_N = a_N^P$, so P acts like the identity on the indices $3, 4, \dots, N$. However, $\langle a_1, a_2 | G_{12} | a_1^P, a_2^P \rangle$ is non-vanishing for P either the identity or the simple interchange of the quantum numbers a_1, a_2 . As a result, we have

$$\langle A | G_{12} | A \rangle = \langle a_1, a_2 | G_{12} | a_1, a_2 \rangle - \langle a_1, a_2 | G_{12} | a_2, a_1 \rangle \quad (20)$$

The result for other terms in $\langle A | G | A \rangle$ is completely analogous. We finally have

$$\langle A | G | A \rangle = \sum_{i < j=1}^N (\langle a_i, a_j | G_{ij} | a_i, a_j \rangle - \langle a_i, a_j | G_{ij} | a_j, a_i \rangle) \quad (21)$$

Unlike the case of a one body operator, the matrix element of a two body operator directly shows the effect of the Pauli Principle. The second term in Eq.(21) is a direct consequence of the facts that (i) electrons are identical particles, (ii) states with several electrons are anti-symmetric under interchange of any two electrons.