18 Multi-electron Atom

So far we have dealt with the properties of one particle moving in several different potentials. This has allowed us to solve everything exactly and obtain analytic expressions for the wavefunction and energy of the system. However, there are very few problems for which the Schrödinger equation can be solved exactly. In fact, as soon as the potential is more complicated than what we already have seen or that we have more that two interacting particles we cannot solve the equations exactly. Before we start discussing how we can obtain approximate solution let start by considering the Hamiltonian of a system with many electrons with a fixed nucleus.

18.1 The many electron Hamiltonian

Remember the form for the Hamiltonian for the hydrogen-like atom

\[
\hat{H} = \hat{T} + \hat{V} = -\frac{1}{2} \nabla^2 - \frac{Z}{R}
\]

in atomic units \((m_e = \hbar = 1, e = -1)\), where \(R\) is the distance between the nucleus and the electron, and \(Z\) is the atomic number of the nucleus. Similar for a system of \(n\) electrons the Hamiltonian is

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{n} \nabla_i^2 - \sum_{i=1}^{n} \frac{Z}{R_i} + \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{r_{ij}}
\]

where the first term is the kinetic energy operator for each electron, the second term is due to the attraction between the electron and the nucleus, and the last term accounts for the repulsion due to electron-electron interactions. The factor \(\frac{1}{2}\) in front of the double sum prevents counting the electron-electron interactions twice, and the prime excludes the \(i = j\) terms. If we compare with the Hamiltonian for the hydrogen-like atom we realize that we can express the many-electron Hamiltonian as

\[
\hat{H} = \sum_{i=1}^{n} \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z}{R_i} \right] + \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{r_{ij}}
\]

\[
= \sum_{i=1}^{n} \hat{h}(i) + \frac{1}{2} \sum_{i,j=1}^{n} \frac{1}{r_{ij}}
\]
where $\hat{h}(i)$ is the hydrogen-like Hamiltonian for the $i$’th electron. Let’s consider the simplest system having more than one electron which is the helium atom.

For He the Hamiltonian reads (see figure for definitions of distances),

$$\hat{H} = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{R_1} - \frac{2}{R_2} + \frac{1}{r_{12}}$$

(797)

$$= \hat{h}(1) + \hat{h}(2) + \frac{1}{r_{12}}$$

(798)

We already know how to solve for $\hat{h}(1)$ and $\hat{h}(2)$, but what about the last term? Since the term depends on both the position of electron 1 and 2 we cannot separate their motion. This means that we cannot use the trick of separating variables which we have used so far and we cannot obtain an analytic solution to the Schrödinger equation.

### 18.2 The independent electron approximation

The simplest approximation is simply to ignore the electron-electron repulsion. Obviously this is a very bad approximation but it allows us to separate variables and thereby illustrate some important physics of a many-electron system. Since we neglect the interactions between the electrons we treat the electrons as independent of each other, hence the name ”independent electron approximation”. The approximate Hamiltonian is then

$$\hat{H}_{\text{approx.}} = \hat{h}(1) + \hat{h}(2)$$

(799)

where each of the individual hydrogen-like Hamiltonians obey a one-electron Schrödinger equation

$$\hat{h}(1)\phi_i(1) = \epsilon_i \phi_i(1)$$

(800)
where $\phi_i$ is the atomic orbital and $\epsilon_i$ is the orbital energy. This means that an orbital is simply a one-electron wavefunction. We already know the solution to these one-electron Schrödinger equation from our treatment of the hydrogen atom, i.e.

$$ \phi_i \in \{1s, 2s, 2p, \cdots \}, \epsilon_i = -\frac{1}{2} \frac{Z^2}{n^2} \quad (801) $$

Previously, we have shown that if we can separate the Hamiltonian into independent terms we can write the total wavefunction as product of eigenfunctions of the individual terms. Therefore, the wavefunction for He in the independent electron approximation becomes

$$ \psi(He) = \phi_i(1)\phi_j(2) \quad (802) $$

Now, let's show that this is wavefunction is an eigenfunction of the approximate Hamiltonian,

$$ \hat{H}_{approx}\psi(He) = (\hat{h}(1) + \hat{h}(2))\phi_i(1)\phi_j(2) \quad (803) $$

$$ = \hat{h}(1)\phi_i(1)\phi_j(2) + \hat{h}(2)\phi_i(1)\phi_j(2) \quad (804) $$

where $\hat{h}(1)$ and $\hat{h}(2)$ only works on variables of electron 1 and electron 2, respectively. This gives us

$$ \hat{H}_{approx}\psi(He) = \hat{h}(1)\phi_i(1)\phi_j(2) + \phi_i(1)\hat{h}(2)\phi_j(2) \quad (805) $$

$$ = \epsilon_i\phi_i(1)\phi_j(2) + \phi_i(1)\epsilon_j\phi_j(2) \quad (806) $$

$$ = (\epsilon_i + \epsilon_j)\phi_i(1)\phi_j(2) \quad (807) $$

$$ = (\epsilon_i + \epsilon_j)\psi(He) \quad (808) $$

and we see that the total energy is the sum of the individual orbital energies.

### 18.3 Electron exchange symmetry

We can now write the ground state of the He atom in the independent electron approximation as 1s(1)1s(2), for which the electron configuration is 1s$^2$. Now let's instead consider the first excited state of He. What would we expect? There are only two different ways of arranging the electrons in a simple product

$$ \psi(1, 2) = 1s(1)2s(2), \text{ or } \psi(2, 1) = 2s(1)1s(2) \quad (809) $$

98
which both have the same energy but describes different physics, e.g. electron distribution. This can be illustrated by considering the electron distribution

\[ |\psi(1, 2)|^2 = \frac{8}{\pi} e^{\frac{1}{4} (1 - 2r_2 + r_2^2)} e^{\frac{1}{4} (1 - 2r_1 + r_1^2)} \]  

and

\[ |\psi(2, 1)|^2 = \frac{8}{\pi} e^{\frac{1}{4} (1 - 2r_1 + r_1^2)} e^{\frac{1}{4} (1 - 2r_2 + r_2^2)} \]  

Therefore, we see that

\[ |\psi(1, 2)|^2 \neq |\psi(2, 1)|^2 \]  

The two wavefunctions therefore differ by exchange of electron indices, something that is wrong. While in classical mechanics it is always possible to distinguish between identical particles, however, this is not the case in quantum mechanics due to the uncertainty principle. Therefore, in quantum mechanics identical particles are indistinguishable and the probability has to be invariant under exchange of indices. This implies that the wavefunction itself must be either symmetric or antisymmetric under the exchange. Let \( \hat{P}_{ij} \) be an operator that when acting on a function interchange the indices \( i \) and \( j \) such that

\[ \hat{P}_{ij} \psi(ij) = \pm \psi(ij) \]  

For He we can construct the following symmetric and antisymmetric wavefunction from linear combinations of the original functions

\[ \psi_s = \frac{1}{\sqrt{2}} [1s(1)2s(2) + 2s(1)1s(2)] \]  

and

\[ \psi_a = \frac{1}{\sqrt{2}} [1s(1)2s(2) - 2s(1)1s(2)] \]  

If we now operate on these wave functions with \( \hat{P}_{12} \) we see that

\[ \hat{P}_{12} \psi_s = \frac{1}{\sqrt{2}} [1s(2)2s(1) + 2s(2)1s(1)] = +\psi_s \]  

\[ \hat{P}_{12} \psi_a = \frac{1}{\sqrt{2}} [1s(2)2s(1) - 2s(2)1s(1)] = -\psi_a \]  

If we now plot (see figure) the probability density of these new functions we will see that the antisymmetric function has a depletion of density as the
distance goes to zero, which is called a Fermi hole. Similar the symmetry function has an increase in density near the region called a Fermi heap. Does this look like something familiar?

![Fermi Hole and Fermi Heap](image)

18.4 Stern-Gerlach experiment

Up to this point, we have treated the particles as structureless with a mass and a charge which can be described by a wavefunction specified by the spatial coordinates, $x, y, z$, as variables. However, our empirical evidence points to the need for attributing an intrinsic angular momentum to the particles as well. The most direct evidence comes from the work of Stern and Gerlach in their now famous experiment from 1922, although it was not realized at that time. In the experiment they pass an unexcited beam of silver atoms through an inhomogeneous magnetic field, see figure.

![Stern-Gerlach Experiment](image)

If a particle have a magnetic moment $\mu$ (we have seen that the angular momentum of a charged species gives rise to a magnetic moment $\mu = -\beta eL$) they will be deflected due to a force, $F \sim \mu B \nabla B$. Thus, particles with different moments will be deflected differing amounts by the magnetic field. If the particles are classical, "spinning" particles, then the distribution of their spin angular momentum vectors is taken to be truly random and each particle would be deflected up or down by a different amount, producing an even distribution on the screen of a detector. Consider the electronic configuration of silver, $\text{Ag} = [\text{Kr}]4d105s1$, what would you expect classical for the moment and what would you expect to see in the experiment?
Thus, the magnitude magnetic moment of the electron is fixed, and the
direction it points is quantized and can take on one of two values. Since any
component of \( \mathbf{L} \) has \( 2l + 1 \) eigenvalues we would expect that the magnetic
moment to have \( 2l + 1 \) eigenvalues. However, experimentally only two dis-
tinct traces where seen (although, nothing was seen due to very thin layer
deposited until Stern’s breath full of sulfur from cheap cigars developed AgS
which is ”jet” black ). The solution to this comes from the postulate by
Goudsmit and Uhlenbeck in 1925 that the electron have an intrinsic angular
moment now called spin with an angular magnitude of \( \frac{1}{2} \hbar \). They postu-
lated the existents of the spin in order to explain the fine structure of atomic
spectra. However, it was not until 1928 when Dirac combined Einstein’s rel-
ativity with quantum mechanics that the treatment of electron spin arised
naturally. This is well beyond the scope of this class.

18.5 Spin and the Pauli exclusion principle

The spin angular momentum is denoted by \( \hat{S} \) and similar to the orbital
angular momentum they obey the following eigenvalue equations

\[
\hat{S}^2 \left| sm_s \right\rangle = \hbar^2 s(s + 1) \left| sm_s \right\rangle, \quad \hat{S}_z \left| sm_s \right\rangle = \hbar m_s \left| sm_s \right\rangle
\]

where the allowed values of \( m_s = -s, -s + 1, \ldots, s - 1, s \). Electrons have
a spin of \( s = \frac{1}{2} \) which gives two values for \( m_s = \pm \frac{1}{2} \hbar \). The eigenstate
corresponding to \( \left| \frac{1}{2}, \frac{1}{2} \right\rangle \) is traditional called \( \alpha \) or spin-up and \( \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \) is called
\( \beta \) or spin-down. We will not express then spin function in explicit form but
rather keep the symbolic representation \( \alpha \) and \( \beta \). Therefore, the wavefunction
\( \psi = \phi(1)\alpha(1) \) refer to an electron in space orbital \( \phi(1) \) with spin \( \alpha \), and is
called a spin-orbital. Since the electrons are indistinguishable we require
that the wavefunction is either symmetric or antisymmetric with respect to
interchange of electron space and spin indices. Lets consider the possible
combination of space and spin wavefunctions for the ground state of He

\[
\left\{ \begin{array}{c}
\alpha(1)\alpha(2) \quad \text{symmetric} \\
\alpha(1)\beta(2) \quad \text{unsymmetric} \\
\beta(1)\alpha(2) \quad \text{unsymmetric} \\
\beta(1)\beta(2) \quad \text{symmetric}
\end{array} \right.
\]

101
Similar to what we did for the unsymmetric space wavefunctions we need to make linear combinations in to form correct wavefunctions

\[
1s(1)1s(2) \begin{cases} 
\alpha(1)\alpha(2) & \text{symmetric} \\
\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] & \text{symmetric} \\
\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] & \text{antisymmetric} \\
\beta(1)\beta(2) & \text{symmetric}
\end{cases}
\]  

Instead of one wavefunction we now have four different wavefunctions that all obey the correct exchange properties, where three of these are symmetric and only one that is antisymmetric. Experimentally we know that the ground state of He is a singlet. This indicates that the wavefunction should be antisymmetric under electron exchange. In general experimental evidence showed that for electrons only the antisymmetric wavefunction occur. This lead Pauli to postulate his now famous principle, here given in its most general form.

The total wavefunction must by \textbf{antisymmetric} under the interchange of any pair of identical \textbf{fermions} and \textbf{symmetrical} under the interchanges of any two pair of identical \textbf{bosons},

where fermions are spin half-integer particles (electrons, protons) and bosons are spin integer particles (photons, \(\alpha\)-particles). Lets consider the consequences of the Pauli principle by considering the ground state of Li and for a minute forget what we already know. Similar to He we assume that we can write the wavefunction as a product of hydrogen-like functions as \(1s^3\)

\[
\psi(Li) = \begin{cases} 
\alpha(1)\alpha(2)\alpha(3) & \text{symmetric} \\
\alpha(1)\alpha(2)\beta(3) & \text{unsymmetric} \\
\alpha(1)\beta(2)\alpha(3) & \text{unsymmetric} \\
\beta(1)\alpha(2)\alpha(3) & \text{symmetric} \\
\alpha(1)\beta(2)\beta(3) & \text{symmetric} \\
\beta(1)\alpha(2)\beta(3) & \text{unsymmetric} \\
\beta(2)\beta(2)\alpha(3) & \text{unsymmetric} \\
\beta(1)\beta(2)\beta(3) & \text{symmetric}
\end{cases}
\]

Is is possible to find any linear combinations that are totally antisymmetric? No, which is in good agreement with our experimental observation that no states have \(1s^3\) electronic configuration. If this was possible we would not have a periodic table! Therefore, from the Pauli exclusion principle we see that no two electrons and occupy the same spin-orbital. For Li the lowest function most therefore have a space wavefunction of the form \(1s(1)1s(2)2s(3)\)
18.6 Slater-determinants

This procedure for generate wavefunctions that exhibit the correct symmetry easily becomes very tedious. Slater realized that writing the wavefunction as a determinant was an easy way of generating wavefunctions that are antisymmetric. A 2 x 2 determinant is given by

\[
\begin{vmatrix}
  a_{11} & a_{12} \\
  a_{21} & a_{22}
\end{vmatrix} = a_{11}a_{22} - a_{12}a_{21}
\]  

(822)

For a general \( A(n \times n) \) determinant we need to use the cofactor (or Laplace expansion of the determinant as

\[
det(A) = \sum_{k=1}^{n} (-1)^{i+k}a_{ik}det(A_{ik})
\]  

(823)

where \( A_{jk} \) is the determinant that remain after removing the \( i \)th row and the \( k \)th column of \( A \). These determinant are now known as Slater determinants.

The properties of determinant ensures the Pauli principle since 1) change sign when interchange two rows (or columns), 2) if two rows are identical the determinant is zero, i.e. no two electrons can be in the same spin-orbital and 3) if a row is zero then the determinant is zero. The general form for a \( N \) electron wavefunction is

\[
\psi_{\alpha} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_{1}(x_1) & \phi_{2}(x_1) & \cdots & \phi_{N}(x_1) \\
\phi_{1}(x_2) & \phi_{2}(x_2) & \cdots & \phi_{N}(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\phi_{1}(x_N) & \phi_{2}(x_N) & \cdots & \phi_{N}(x_N)
\end{vmatrix}
\]  

(824)

where \( \phi_{i} \) is a general spin-orbital. Therefore, for Li the Slater determinant would be

\[
\psi(Li) = \frac{1}{\sqrt{6}} \begin{vmatrix}
1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) \\
1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) \\
1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3)
\end{vmatrix}
\]  

(825)

\[
= \frac{1}{\sqrt{6}} \begin{vmatrix}
1s(1) & \overline{1s}(1) & 2s(1) \\
1s(2) & \overline{1s}(2) & 2s(2) \\
1s(3) & \overline{1s}(3) & 2s(3)
\end{vmatrix}
\]  

(826)

Since we can always construct the full Slater determinant if we know a list of all the spin-orbitals a simplified notation is

\[
\psi = |\phi_{1}\phi_{2}\phi_{3}\cdots\phi_{n}|
\]  

(827)

103
Example: Write the normalized Slater determinant for the beryllium in the $1s^22s^2$ configurations. Explain how you would expand it.

$$
\psi(Be) = \frac{1}{\sqrt{4!}} \left| \begin{array}{cccc}
1s(1) & \overline{1s}(1) & 2s(1) & \overline{2s}(1) \\
1s(2) & \overline{1s}(2) & 2s(2) & \overline{2s}(2) \\
1s(3) & \overline{1s}(3) & 2s(3) & \overline{2s}(3) \\
1s(4) & \overline{1s}(4) & 2s(4) & \overline{2s}(4)
\end{array} \right| \tag{828}
$$

18.7 The Hamiltonian and spin

Since the Hamiltonian is independent of spin, at the non-relativistic level of theory, we know that it commutes with the spin operators

$$
[\hat{H}, \hat{S}_z] = [\hat{H}, \hat{S}^2] = [\hat{S}^2, \hat{S}_z] = 0 \tag{829}
$$

thus, we can specify simultaneous eigenfunctions of these operators. What about the energies:

$$
\hat{H}\Psi(x, y, z, \sigma) = [\hat{H}\psi(x, y, z)]g(\sigma) = [E\psi(x, y, z)]g(\sigma) = E\Psi(x, y, z, \sigma) \tag{830}
$$

and our energies are the same as we previously found.

18.8 Singlet and Triplet excited states of Helium

For the $1s2s$ state of He we saw that there is two different space functions that have the correct symmetry, one symmetric and one symmetric. We have also learned that for electron it is the total wavefunction that needs to be antisymmetric with respect the interchange of both space and spin labels. Therefore, we need to combined the symmetric space part with an antisymmetric spin part and a symmetric spin part with the antisymmetric space functions. The give us for the $1s2s$

$$
\psi_{s,a}(He) = \frac{1}{\sqrt{2}} \left[ 1s2s + 2s1s \right] \frac{1}{\sqrt{2}} \left[ \alpha \beta - \beta \alpha \right] \tag{831}
$$
called a singlet state, and,

$$
\psi_{a,s}(He) = \frac{1}{\sqrt{2}} \left[ 1s2s - 2s1s \right] \left\{ \frac{1}{\sqrt{2}} \left[ \alpha \alpha \right] - \frac{1}{\sqrt{2}} \left[ \beta \beta \right] \right\} \tag{832}
$$
call a triplet state. Since all four state satisfy the correct symmetry and are linear independent it indicates that there are 4 distinct physical states. Is it possible to write a single Slater determinant for each of these states? The answer is no and is very important to realize. It is not always possible with only one Slater determinant to write a wave function that has the correct symmetry of the full wavefunctions,

\[
\psi_{s,a}(He) = \frac{1}{\sqrt{2}} \left\{ \begin{array}{c|cc}
1 & 1s & 2s \\
1s & 2s & \end{array} \right\} - \frac{1}{\sqrt{2}} \left\{ \begin{array}{c|cc}
1 & 1s & 2s \\
1s & 2s & \end{array} \right\}
\]  

(833)

but instead we need to make linear combinations of Slater determinants. All four state are degenerate with the independent electron model, would we expect this to be the case for the full Hamiltonian?

Let evaluate the energy of these state using the full Hamiltonian. What is the expression for the full Hamiltonian? and how do we evalua
t the energy?

\[
\langle E \rangle = \int \psi^* \hat{H} \psi d\tau 
\]  

(834)

\[
+ \int \psi^* \left[ \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] \psi d\tau 
\]  

(835)

\[
= \int \psi^* \left[ -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{2}{R_1} - \frac{2}{R_2} + \frac{1}{r_{12}} \right] \psi d\tau 
\]  

(836)

Since the Hamiltonian do not dependent on spin we can integrate the spin out first. This means that the energy is completely determined by the space functions. We can now substitute the space function for the triplet and singlet case in the energy expression

\[
\langle E_{1,3} \rangle = \int \int [1s^*2s^* \pm 2s^*1s^*] \left[ \hat{h}_1 + \hat{h}_2 + \frac{1}{r_{12}} \right] [1s2s \pm 2s1s] \ d1d2 
\]  

(837)

using that the orbitals are ortho-normal we can simplify the integrals

\[
\langle E_{1,3} \rangle = \int 1s^* \hat{h}_1 1sd1 + \int 2s^* \hat{h}_1 2sd1 
\]  

(838)

\[
+ \int \int 1s^*2s^* \frac{1}{r_{12}} 1s2sd1d2 
\]  

(839)

\[
\pm \int \int 1s^*2s^* \frac{1}{r_{12}} 2s1sd1d2 
\]  

(840)

\[
= E_{1s} + E_{2s} + J \pm K 
\]  

(841)
where $J$ is the Coulomb integral and $K$ is the exchange integral. $J$ represents the Coulomb repulsion between two electrons where $K$ is similar but with one indices exchanged. Therefore, the triples state is lower in energy than the singlet since $K$ (and $J$) is positive. This is in agreement with our experimental observation of the the 1s2s configurations for which two states are found and the lowest split into 3 state in a magnetic field.

18.9 Angular momentum in many-electron atoms

When dealing with many-electron systems we need to account for the spin and orbital angular momentum of the electrons. We therefore need to understand the rules for adding angular momentum. For many electron atom the individual angular momentum operators do not commute with the Hamiltonian, however, their sum does. The total orbital angular momentum is defined as the vector sum of the orbital angular momenta of the individual electrons

$$L = \sum_i L_i$$

with eigenvalues

$$\hat{L}^2 |LM_L\rangle = \hbar^2 L(L+1) |LM_L\rangle$$

and for the projection

$$\hat{L}_z |LM_L\rangle = \hbar M_L |LM_L\rangle$$

In general the addition of two angular momenta with quantum number $l_1$ and $l_2$ will result in a total quantum number whose number $J$ has the following possible values

$$L = |l_1 + l_2|, |l_1 + l_2 - 1|, \ldots, |l_1 - l_2|$$

and

$$M = m_1 + m_2$$

The total orbital angular momentum quantum number $L$ of an atom is denoted by $S$ for $L=0$, $P$ for $L=1$, $D$ for $L=2$, $F$ for $L=3$, and so forth.
18.10 Ladder operators

Similar for $S$ we have

$$\hat{S}^2 |SM_S\rangle = \hbar^2 S(S + 1) |SM_S\rangle \quad (847)$$

and for the projection

$$\hat{S}_z |SM_S\rangle = \hbar M_S |SM_S\rangle \quad (848)$$

So far we have seen how to work with $\hat{S}^2$ and $\hat{S}_z$ operators. Similar to what we did for the orbital angular momentum we can define ladder operators as

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \quad (849)$$

for the raising operator and

$$\hat{S}_- = \hat{S}_x - i\hat{S}_y \quad (850)$$

for the lowering operator. Operating with these operators on our spin functions gives

$$\hat{S}_+ \beta = \hbar \alpha \quad (851)$$

$$\hat{S}_+ \alpha = 0 \quad (852)$$

$$\hat{S}_- \beta = 0 \quad (853)$$

$$\hat{S}_- \alpha = \hbar \beta \quad (854)$$

Using these we can now operate with the other two components on the functions and get

$$\hat{S}_x \beta = 1/2(\hat{S}_+ + \hat{S}_-) \beta = 1/2 \hbar \alpha \quad (856)$$

$$\hat{S}_y \beta = 1/(i2)(\hat{S}_+ - \hat{S}_-) \beta = -i/2 \hbar \alpha \quad (857)$$

$$\hat{S}_x \alpha = 1/2 \hbar \beta \quad (858)$$

$$\hat{S}_y \alpha = i/2 \hbar \beta \quad (859)$$

(860)
18.11 Eigenvalues of a two-electron spin function

The excited state configuration of He (1s2s) have the following possible spin eigenfunctions

\[ \alpha(1)\alpha(2) \] (861)

\[ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \] (862)

\[ \beta(1)\beta(2) \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \] (863)

Where the possible total spin is \( S = (1/2 + 1/2), (1/2 - 1/2) = (1, 0) \) with degeneracy \( d = (2L + 1)(2S + 1) \) which gives 3 and 1, respectively. Thus, the term symbols are \( ^3S_1 \) and \( ^1S_0 \), respectively. Now lets use the spin operators and verify this. First lets start with the projection

\[ \hat{S}_z \alpha(1)\alpha(2) = \hat{S}_{1z}\alpha(1)\alpha(2) + \hat{S}_{2z}\alpha(1)\alpha(2) \] (865)

\[ = \frac{1}{2} \hbar \alpha(1)\alpha(2) + \frac{1}{2} \hbar \alpha(1)\alpha(2) \] (866)

\[ = \hbar \alpha(1)\alpha(2) \] (867)

Similar for the other functions we find

\[ \hat{S}_z \beta(1)\beta(2) = -\hbar \beta(1)\beta(2) \] (868)

\[ \hat{S}_z[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)] = 0 \] (869)

For \( \hat{S}^2 \) we get:

\[ \hat{S}^2 = (\hat{S}_1 + \hat{S}_2) \cdot (\hat{S}_1 + \hat{S}_2) = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z}) \] (870)

Operating with this on the eigenfunctions give

\[ \hat{S}^2\alpha(1)\alpha(2) = \alpha(2)\hat{S}_1^2\alpha(1) + \alpha(1)\hat{S}_2^2\alpha(2) + 2\hat{S}_{1x}\alpha(1)\hat{S}_{2x}\alpha(2) \] (871)

\[ + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z} \] (872)

\[ = (3/4\hbar^2 + 3/4\hbar^2 + 1/2\hbar^2)\alpha(1)\alpha(2) = 2\hbar^2\alpha(1)\alpha(2) \] (873)

Similarly for the other eigenfunctions we get

\[ \hat{S}^2\beta(1)\beta(2) = 2\hbar^2\beta(1)\beta(2) \] (874)

\[ \hat{S}^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2\hbar[\alpha(1)\beta(2) + \beta(1)\alpha(2)]\hat{S}^2[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \] (875)

Therefore, we see that for the singlet we indeed get \( S = 0, m_s = 0 \) and for all of the triplet states we \( S = 1, m_s = -1, 0, 1 \) as expected.
18.12 Term symbols

Example: Find the possible quantum number $L$ for states of the Carbon atom with the following electron configuration $1s^22s^22p^3$? Since the $s$ electrons have zero angular momentum they do not contribute. The $2p$ has $l = 1$ and the $3p l = 1$ gives $L$ from $1+1 = 2$ to $|1-1| = 0$, therefore $L = 0, 1, 2$

Example: Find the possible values for $S$ for the states arising from $1s^22s^22p^3$. $s$ electrons will contribute nothing due to Pauli principle, i.e. $1/2 - 1/2 = 0$. For the last two electrons we can get $S = 0$ and $S = 1$.

For a given $S$ we have $2S + 1$ values for $M_s$ where $2S + 1$ is called the multiplicity. For $2S + 1 = 1, 2, 3, 4$ is called singlet, doublet, triplet, quartet. The total angular momentum is then

$$J = L + S \quad (876)$$

The allow us to characterize the different electronic states in a multi-electron atoms using what is know as a term symbol

$$^2S^J$$

where

- $S$ is the total spin quantum number. $2S + 1$ is the spin multiplicity: the maximum number of different possible states of $J$ for a given $(L, S)$ combination.

- $L$ is the total orbital quantum number in spectroscopic notation. The symbols for $L = 0, 1, 2, 3, 4, 5$ are $S, P, D, F, G, H$ respectively.

- $J$ is the total angular momentum quantum number.

for which a total number of states are given by $(2S + 1)(2L + 1)$. An alternative statement of Hund’s rule is that the term with the highest multiplicity is lowest in energy. Remember that Hund’s rule works well for the ground state, however, can fail for excited states.

Example: Write down the possible term symbols for Carbon atom in the $1s^22s^22p^3$ configuration.
$L = 2, S = 1$ gives $^3D_3, ^3D_2, ^3D_1$, 
$L = 2, S = 0$ gives $^1D_2$, 
$L = 1, S = 1$ gives $^3P_2, ^3P_1, ^3P_0$, 
$L = 1, S = 0$ gives $^1P_1$, 
$L = 0, S = 1$ gives $^3S_1$, and 
$L = 0, S = 0$ gives $^1S_0$.

### 18.13 The atomic hamiltonian

Although our non-relativistic hamiltonian do not include spin, there is a small term in the true Hamiltonian which comes from the interactions between the spin and orbital angular momentum and is referred to as spin-orbit interactions. The atomic hamiltonian is then given by a sum of three terms

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{rep}} + \hat{H}_{\text{S.O}}$$  \hspace{1cm} (878)

where the first term is a sum of hydrogen-like Hamiltonians

$$\hat{H}_0 = \sum_{i=1}^{n} \left( -\frac{1}{2}\nabla^2 - \frac{Z}{r_i} \right)$$  \hspace{1cm} (879)

the second term is the electron-electron repulsion term

$$\hat{H}_{\text{rep}} = \frac{1}{2} \sum_{i,j}^{n'} \frac{1}{r_{ij}}$$  \hspace{1cm} (880)

and the third term is the spin-orbit interactions

$$\hat{H}_{\text{S.O}} = \sum_{i=1}^{n} \xi \hat{L}_i \cdot \hat{S}_i$$  \hspace{1cm} (881)

The repulsion operator splits antisymmetric and symmetric space wavefunctions into terms and the spin-orbitat interactions splits the terms into the individual levels, resulting in the fine-structure of electronic spectra. Finally we can use a magnetic field perturbation to split the individual levels in states. The magnetic field perturbation is given

$$\hat{H}_{\text{mag}} = \beta_e (\hat{J} + \hat{S}) \cdot B = \beta_e B (\hat{J}_z + \hat{S}_z)$$  \hspace{1cm} (882)

and is known as the Zeeman effect.
Splitting of the He 1s2p states:

<table>
<thead>
<tr>
<th>Configurations</th>
<th>Terms</th>
<th>Levels</th>
<th>States</th>
<th>$M_J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_0$</td>
<td>$H_0 + H_{coup}$</td>
<td>$H_0 + H_{coup} + H_{LDA}$</td>
<td>$H_0 + H_{coup} + H_{LDA} + H_{Zee}$</td>
<td></td>
</tr>
<tr>
<td>1s2p</td>
<td>1P</td>
<td>1P₁</td>
<td>1P₂</td>
<td>1 0 -1</td>
</tr>
<tr>
<td></td>
<td>3P</td>
<td>3P₀</td>
<td>3P₁</td>
<td>0 1 -1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3P₂</td>
<td>2 1 0 -2</td>
</tr>
</tbody>
</table>

Exchange  Fine structure  Zeeman