

Many-Electron Atomic States, Terms, and Levels

29th April 2008

I. Hartree-Fock with Antisymmetrized Wavefunctions

Recall the earlier discussion of the Hartree-Fock self-consistent method. For the purposes of that introduction, we used trial wavefunctions that were simple products of single-electron orbitals. We did not account for antisymmetry and Pauli exclusion. Here, we will briefly formulate the Hartree-Fock method with anti-symmetric wavefunctions. The results of this analysis will give rise to the already determined orbital energies and electron-electron repulsion terms (Coulomb integral), as well as a new term arising from the antisymmetric nature of the wavefunction—exchange integral. Keep in mind that the following does still not consider explicitly effects of electron correlation (though, depending on the source, the exchange term is thought to contribute some amount to correlation).

The N-electron Slater determinantal wavefunction form, recall, is:

$$\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(\mathbf{r}_1, \sigma_1) & u_2(\mathbf{r}_1, \sigma_1) & \dots & u_N(\mathbf{r}_1, \sigma_1) \\ u_1(\mathbf{r}_2, \sigma_2) & u_2(\mathbf{r}_2, \sigma_2) & \dots & u_N(\mathbf{r}_2, \sigma_2) \\ \vdots & \vdots & & \vdots \\ u_1(\mathbf{r}_N, \sigma_N) & u_2(\mathbf{r}_N, \sigma_N) & \dots & u_N(\mathbf{r}_N, \sigma_N) \end{vmatrix}$$

For **closed shell** systems each spatial orbital is occupied by 2 electrons (of opposite spin). Thus we require a single Slater determinant:

$$\frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \phi_1(\mathbf{r}_1)\alpha(\sigma_1) & \phi_2(\mathbf{r}_1)\beta(\sigma_1) & \dots & \phi_N(\mathbf{r}_1)\alpha(\sigma_1) & \phi_N(\mathbf{r}_1)\beta(\sigma_1) \\ \phi_1(\mathbf{r}_2)\alpha(\sigma_2) & \phi_2(\mathbf{r}_2)\beta(\sigma_2) & \dots & \phi_N(\mathbf{r}_2)\alpha(\sigma_2) & \phi_N(\mathbf{r}_2)\beta(\sigma_2) \\ \vdots & \vdots & & \vdots & \vdots \\ \phi_1(\mathbf{r}_{2N})\alpha(\sigma_{2N}) & \phi_2(\mathbf{r}_{2N})\beta(\sigma_{2N}) & \dots & \phi_N(\mathbf{r}_{2N})\alpha(\sigma_{2N}) & \phi_N(\mathbf{r}_{2N})\beta(\sigma_{2N}) \end{vmatrix} = \Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \dots, \mathbf{r}_{2N}, \sigma_{2N})$$

The Hamiltonian **operating only on spatial coordinates** in atomic units is:

$$\hat{H} = -\frac{1}{2} \sum_{j=1}^{2N} \nabla_j^2 - \sum_{j=1}^{2N} \frac{Z}{r_j} + \sum_{i=1}^{2N} \sum_{j>i}^{2N} \frac{1}{r_{ij}}$$

The Hartree-Fock total energies, **for this closed-shell configuration** much like we have seen earlier are:

$$E = 2 \sum_{j=1}^N I_j + \sum_{i=1}^N \sum_{j=1}^N (2J_{ij} - K_{ij})$$

The various terms in the energy expression are:

$$\begin{aligned} I_j &= \int \phi_j^*(\mathbf{r}_j) \left[-\frac{\nabla_j^2}{2} - \frac{Z}{r_j} \right] \phi_j(\mathbf{r}_j) d\mathbf{r}_j \\ J_{ij} &= \int \int \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_1) \phi_j(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad \text{Coulomb Integral} \\ K_{ij} &= \int \int \phi_i^*(\mathbf{r}_1) \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) \phi_j(\mathbf{r}_1) d\mathbf{r}_1 d\mathbf{r}_2 \quad \text{Exchange Integral } i \neq j \end{aligned}$$

NOTE:

In the definitions of the various one- and two-electron integrals listed immediately above, the summations are effectively over *orbitals*. These can be written in terms of summations over electrons with minor modifications in the leading multiplicative factors (see Szabo and Ostlund for further details).

Let's consider the meaning of the Coulomb and Exchange terms we have discussed just now. The coulomb integral can be rearranged as:

$$\int \int \phi_i^2(\mathbf{r}_1) \frac{1}{r_{12}} \phi_j^2(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

The square of the wavefunction is the probability of finding an electron at a given point in space. So this term is the energy of the Coulombic interaction between an electron in orbital *i* with an electron in orbital *j*. For this

reason, this integral is called the Coulomb Integral. Because the Coulomb potential is always positive for like charges, and the square of the wavefunction is always positive, this term contributes a *positive* energy to the total energy. This is a destabilizing energy contribution (arising from unfavorable repulsion).

The Exchange integral has no immediate classical interpretation. The name arises from the fact that the 2 electrons exchange their positions from the left to the right of the integrand, and in this sense the integral is connected to the Pauli principle.

The probability density for two electrons is significantly different in the case of an antisymmetrized Slater Determinant than in the simple Hartree product. The total density is not a simple product of each orbital density. The Coulomb integral expression suggests that the total probability is of a product-like nature. But since we have incorporated the antisymmetric nature of electronic wavefunctions via the Slater Determinantal form, the effect is apparent in the form of the exchange integrals which arise naturally. The total density is not a simple product of each orbital density. The Coulomb integral expression suggests that the total probability is of a product-like nature. But since we have incorporated the antisymmetric nature of electronic wavefunctions via the Slater Determinantal form, the effect is apparent in the form of the exchange integrals which arise naturally. The exchange integrals "correct" the Coulomb integrals to take into account the antisymmetry of the wavefunction. It is easy to show that electrons of the same spin are more "correlated" in the Slater Determinantal form than in the Hartree Product form, so the Coulomb integrals should exaggerate the Coulomb repulsion of the electrons since the purely Coulomb integrals represent a probability that is of the form of a Hartree product wavefunction. Keep in mind that the "correlation" we introduce here is still not the total correlation between electrons, as the effect fundamentally arises from the indistinguishability of electrons (as embodied in the antisymmetrized wavefunctions) and has nothing to do with electron correlation. This is a subtle matter of semantics one should bear in mind.

The Hartree-Fock Method with Antisymmetric Wavefunctions

The variational principle yields the Hartree-Fock equation for each orbital:

$$\begin{aligned}\hat{F}_i \phi_i &= \epsilon_i \phi_i \\ \hat{F}_i &= \hat{f}_i + \sum_{j=1}^N (2\hat{J}_j - \hat{K}_j) \quad \text{Fock Operator}\end{aligned}$$

The various secondary operators embedded in the Fock operator are defined as:

$$\begin{aligned}\hat{f}_i &= -\frac{\nabla_i^2}{2} - \frac{Z}{r_i} \\ \hat{J}_j(\mathbf{r}_1)\phi_i(\mathbf{r}_1) &= \phi_i(\mathbf{r}_1) \int \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_j(\mathbf{r}_2) d\mathbf{r}_2 \\ \hat{K}_j(\mathbf{r}_1)\phi_i(\mathbf{r}_1) &= \phi_j(\mathbf{r}_1) \int \phi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \phi_i(\mathbf{r}_2) d\mathbf{r}_2\end{aligned}$$

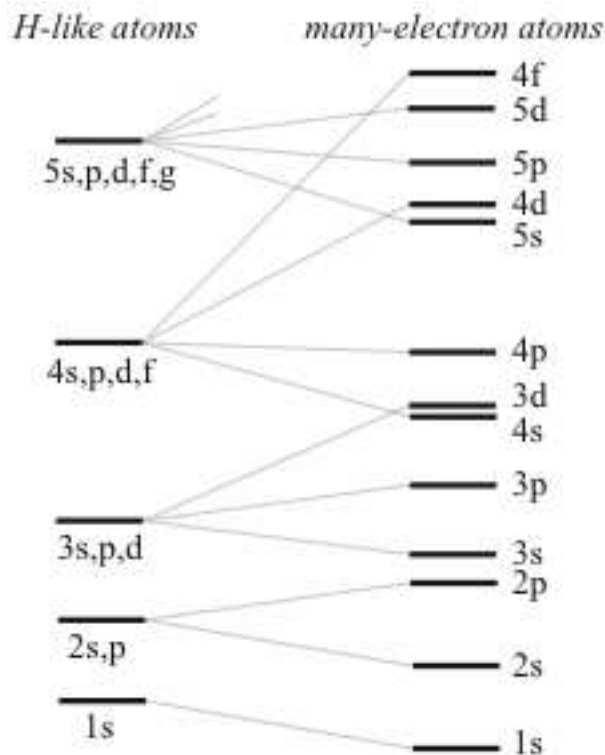
With these operators defined, one follows the protocol introduced earlier to solve the individual orbital Fock equations to obtain self-consistently the orbitals and orbital energies.

To summarize:

- Coulomb integrals describe repulsions between pairs of electrons. Always positive: integrands are positive everywhere (repulsion!)
- Exchange integrals arise through exchange of indistinguishable electrons. Positive, but have positive and negative integrand contributions.
- Orbital energies are generally associated with ionization potentials (Koopman's Theorem).

Splitting of Hydrogen atom orbital energies due to many-electron shielding effects.

Splitting of Hydrogen Atom energy levels in Many-Electron Atoms



- Orbital energies are non-degenerate
- Relative orbital energetics for many-electron atoms are determined through interplay of one-electron kinetic and nuclear-electron interactions, electron-electron repulsions, and exchange effects. Thus, relative stabilities of many-electron atom orbitals are defined in a non-intuitive manner
- Aufbau principle guides filling of orbitals

Angular Momentum of Many-Electron Atoms

Energies for various orbitals of many-electron atoms are dependent on **spin** and **orbital** angular momentum.

For lighter atoms ($Z < 30 - 40$), spin-orbit coupling is minimal. A scheme named the Russell-Saunders coupling scheme can be applied to combine electron orbital and spin angular momenta in order to arrive at a description of atomic states.

In the R-S scheme, spin and orbital angular momenta **add as vectors**. Thus, their components add up in parallel. Consider:

$$\begin{aligned}
\mathbf{L} &= \sum_i \mathbf{l}_i \\
L_z &= \sum_i l_{z_i} = \sum_i m_{l_i} \equiv M_L \\
M_L &= -L, -L+1, \dots, L-1, L \quad (2L+1 \text{ possible values}) \\
L &= 0, 1, 2, \dots \quad S, P, D, \dots \text{ states}
\end{aligned}$$

For spins:

$$\begin{aligned}
\mathbf{S} &= \sum_i \mathbf{s}_i \\
S_z &= \sum_i s_{z_i} = \sum_i m_{s_i} \equiv M_S \quad (2S+1 \text{ possible values}) \\
2S+1 &= \text{Spin Multiplicity}
\end{aligned}$$

The total angular momentum is :

$$\begin{aligned}
\mathbf{J} &= \mathbf{L} + \mathbf{S} \\
J_z &= L_z + S_z = (M_L + M_S) \equiv M_J \\
J &= L + S, L + S - 1, \dots, |L - S|
\end{aligned}$$

Atomic states for many-electron atoms are characterized by the term symbol:

$${}^{2S+1}L_J$$

Table 1. Names for the leading superscripts of atomic term symbols.

Multiplicity, $2S+1$	Name
1	Singlet
2	Doublet
3	Triplet

Table 2. Letter conversions for atomic term symbols.

L	Letter
0	S
1	P
2	D
3	F
4	G
5	H

In the R-S scheme, then, the good quantum numbers are the L and S (the Hamiltonian commutes with these operators). In the spin-orbit coupling scheme, the J operator commutes with the Hamiltonian.

Determining Atomic Terms

A. Russel-Saunders Coupling.

Let's consider what terms arise for a particular electronic configuration of an atom. We will also see what microstates are associated with each term. In the R-S scheme, each term will have degenerate microstates. In the spin-orbit coupling scheme, these states will split (j-j coupling scheme).

A1. Helium $1s^2$ Configuration

Ground state of Helium. 2 electrons in 1s orbital; Pauli exclusion dictates opposite spin.

Addition of l_z as sum of m_l values gives: $M_L = m_l(\text{electron1}) + m_l(\text{electron2}) = 0 + 0 = 0$.

Thus, L = 0.

Addition of s_z as sum of m_s values gives: $M_S = m_s(\text{electron1}) + m_s(\text{electron2}) = \frac{1}{2} + \frac{-1}{2} = 0$

Thus, S=0.

Spin Multiplicity = 1 Total angular momentum, $J = L + S = 0$.

So, the term is: 1S_0 , a **singlet S**.

A2. Helium Excited State $1s^1 2s^1$ Configuration

This case is slightly different. The configuration includes two orbitals, the

1s and 2s.

1. First compute M_L : $M_L = m_{l_{e_1^-}} + m_{l_{e_2^-}} = 0 + 0 = 0$. Thus, $L=0$ and we will have "S" terms.

2. Second compute M_S : $M_S = m_{s_{e_1^-}} + m_{s_{e_2^-}} = 1/2 + 1/2 = 1$ or

$$M_S = m_{s_{e_1^-}} + m_{s_{e_2^-}} = 1/2 - 1/2 = 0$$

2a. The number of microstates is then $(2S + 1)(2L + 1) = 3$ or 1 depending on the spin pairing. Thus, in tabular format:

Table 3. Microstates for Helium $1s^1 2s^1$.

M_L	M_S		
	1	0	-1
0	$(0^+, 0^+)$	$(0^+, 0^+), (0^+, 0^+)$	$(0^+, 0^+)$

The **terms** are then both "S" terms since $L=0$. For "S" $=1$, the term is: 3S_1 (multiplicity of 3 and 3 degenerate states in R-S scheme).

For "S" $=0$, the term is: 1S_0 .

A3. Carbon Atom Ground State: $1s^2 2s^2 2p^2$

In this case, we have two electrons in the valence shell that contribute to coupling. The table for constructing the terms goes as follows:

Table 4. Microstates for Ground State Carbon $1s^1 2s^2 2p^2$.

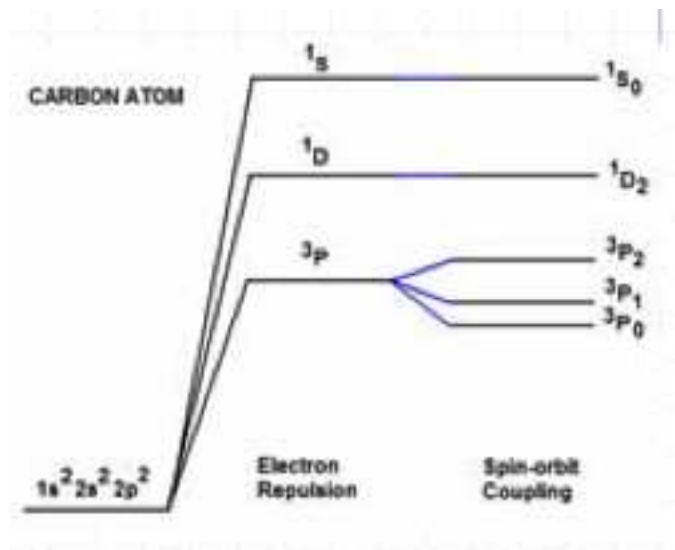
M_L	M_S		
	1	0	-1
2		$(1^+, 1^-)$	
1	$(0^+, 1^+)$	$(1^+, 0^-), (0^+, 1^-)$	$(0^-, 1^-)$
0	$(1^+, -1^+)$	$(1^+, -1^-), (-1^+, 1^-), (0^+, 0^-)$	$(1^-, -1^-)$
-1	$(0^+, -1^+)$	$(-1^+, 0^-), (0^+, -1^-)$	$(0^-, -1^-)$
-2		$(-1^+, -1^-)$	

Now let's analyze the table. First, the values of L can be 2, 1, or 0. The values of S can be 1 or 0.

- L=2; only S=0 is allowed. $J=L+S=2$ (J=2 only). Thus, $(2L+1)(2S+1) = \mathbf{5}$ **microstates**. These are along the center column of the table. The term symbol is thus 1D_2 . The degeneracy is $2J+1 = 5$.
- L=1; S=1. $J=2,1,0$. Thus, $(2L+1)(2S+1) = \mathbf{9}$ **microstates**. Term symbols. ${}^3P_2, {}^3P_1, {}^3P_0$.
- L=0; S=0. $J=0$. Term symbol: 1S_0 .

Splitting of Carbon atom Ground State orbital energies due to many-electron effects.

Splitting of Carbon Atom energy levels in Many-Electron Atoms



Atomic States Have Different Energies: Consequence of Coulomb Repulsion and Exchange!

In this short discussion, we will see how the interplay between Coulomb repulsion and particle exchange (recall the associated integrals in the Hartree-Fock protocol) leads to splitting of atomic states into different (degenerate) energy levels. This is an interesting consequence.