

Many-Electron Atoms

For pure two-body systems, like the hydrogen atom, it is possible to solve the Schroedinger equation analytically. For systems with few electrons, such as helium, the "many-electron" problem can be solved more or less exactly. More general many-electron systems cannot be treated with such precision, however. A majority of the elements in the periodic table are many-electron systems where the motion of every electron is coupled to the motion of all the other electrons as well as to the nucleus. To study such systems we have to rely on some approximation method.

1. One-electron Method

One widely used approximation method is the Hartree-Fock method. It is based on the rather natural approximation that every electron moves in the potential created by the nucleus plus the *average* potential of all the other electrons. This assumption leads to the *independent-particle model*, which essentially reduces the many-electron problem to the problem of solving a number of coupled single-electron equations.

1.1 The Hartree Approximation

The single-electron equations are solved in an iterative manner until a chosen level of self-consistent accuracy is achieved. Hartree made the first calculation based on these ideas by hand in 1928, but calculations of this type are, of course, best suited for computers.

The Hartree method applied to the ground state of Helium

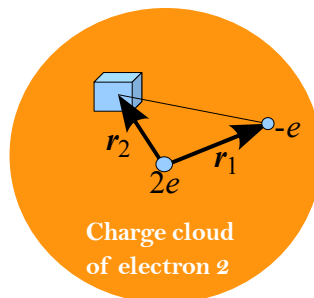
We write the total wavefunction approximately

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \quad (1)$$

where the one-electron function ψ_1 satisfies the equation

$$\left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{r_1} + V_1(r_1) \right] \psi_1 = \epsilon_1 \psi_1 \quad (2)$$

and there is a similar equation for ψ_2 . Hartree chose the potential function $V_1(r_1)$ to be the potential energy of the first electron in the field of the *average* charge distribution, or *charge cloud* of electron 2, whose density at any point r_2 is $-e|\psi_2(r_2)|^2$.



The potential energy of electron 1 due to the whole cloud charge is

$$V_1(r_1) = e^2 \int \frac{|\psi_2(r)|^2}{r} d\mathbf{r} \quad (3)$$

The integration being throughout all space.

The Hartree equation for ψ_1 is thus

$$\left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{r_1} + e^2 \int \frac{|\psi_2(r)|^2}{r} d\mathbf{r} \right] \psi_1 = \epsilon_1 \psi_1 \quad (4)$$

This equation can be further simplified because of the fact that ψ_1 and ψ_2 are the same, and the equation for $\psi(r)$ is then

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{2e^2}{r} + e^2 \int \frac{|\psi(r')|^2}{|r-r'|} d\mathbf{r}' \right] \psi = \epsilon \psi \quad (5)$$

The problem becomes: Find the eigenfunction of equation (5) which has the lowest eigenvalue.

Equation 5 is called an integro-differential equation (the integration can not be done directly, because the integrand depends on ψ). A method of successive approximation is employed.

1. Choose an approximation to ψ (for example, the function $e^{-\frac{27r}{16a_0}}$ after normalization).
2. Evaluate the integral in equation (5).
3. The equation becomes an ordinary Schrödinger equation, which can be solved using numerical methods, and the solution should be a better approximation.

This process is repeated again and again until two successive repetitions yield results which do not differ significantly. The solution is then said to be *self-consistent*, and the associated field is called the **self-consistent field** (SCF).

For the approximate energy of the ground state

$$\begin{aligned} E &= \int \Psi^* H \Psi d\tau \\ &= \int \int \psi^*(r_1) \psi^*(r_2) \left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - 2\frac{e^2}{r_1} - 2\frac{e^2}{r_2} + \frac{e^2}{r_{12}} \right] \psi_1(r_1) \psi_2(r_2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= 2\epsilon - \int \int \frac{e^2}{r_{12}} |\psi(r_1)|^2 |\psi(r_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2 \end{aligned} \quad (6)$$

The error is only two thirds of that obtained by the variational method. From the point view of the variational principle, the Hartree wavefunction is the best wavefunction of the simple product from (1). The error is due essentially to the fact the electrons do not move independently, which is neglected in the Hartree method. Owing to their mutual repulsion, the electrons tend to avoid each

other, and their motion is said to be *correlated*. *Electron correlation is not considered in the Hartree method.*

The Hartree Method in General

In the case of N-electrons, each electron is supposed to move in the field of the nucleus and that due to the charge cloud of all the other electrons:

$$V_i(\mathbf{r}_i) = e^2 \sum_{j \neq i}^N \int \frac{|\psi_j(\mathbf{r}_j)|^2}{|\mathbf{r}_i - \mathbf{r}_j|} d\mathbf{r}_j \quad (7)$$

The Hartree equations for the system now become

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + e^2 \sum_{j \neq i}^N \int \frac{|\psi_j(\mathbf{r}_j)|^2}{r_{ij}} d\mathbf{r}_j \right] \psi_i(\mathbf{r}_i) = \epsilon_i \psi_i(\mathbf{r}_i) \quad i=1, 2, \dots, N. \quad (8)$$

These equations are called the Hartree equations. We choose a set of approximate ψ_i (1s, 2s, 2p and so on) and with them calculate the N potential functions.

The approximate total wavefunction is now taken to be

$$\Psi = \psi_1(\mathbf{r}_1) \psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N) \quad (9)$$

The total energy is

$$\begin{aligned} E &= \int \Psi^* H \Psi \\ &= \int \dots \int \psi_1^*(\mathbf{r}_1) \dots \psi_N^*(\mathbf{r}_N) \left[-\sum_{i=1}^N \left(\frac{\hbar^2}{2m} \nabla_i^2 + \frac{Ze^2}{r_i} \right) + \frac{1}{2} \sum_{i \neq j}^N \sum_{r_{ij}} \frac{e^2}{r_{ij}} \right] \psi_1(\mathbf{r}_1) \dots \psi_N(\mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= -\sum_{i=1}^N \int \psi_i^* \left(\frac{\hbar^2}{2m} \nabla_i^2 + \frac{Ze^2}{r_i} \right) \psi_i(\mathbf{r}_i) d\mathbf{r}_i + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \int \int \psi_i^*(\mathbf{r}_i) \psi_j^*(\mathbf{r}_j) \frac{e^2}{r_{ij}} \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j \\ &= \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \int \int \frac{e^2}{r_{ij}} |\psi_i(\mathbf{r}_i)|^2 |\psi_j(\mathbf{r}_j)|^2 d\mathbf{r}_i d\mathbf{r}_j \\ &= \sum_{i=1}^N \epsilon_i - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N J_{ij} \end{aligned} \quad (10)$$

The total energy is the sum of the one-electron eigenvalues minus the average interaction of electrons.

1.2 The Hartree-Fock Method

The Hartree-Fock approximation is an extension of the above Hartree approximation to include the permutation symmetry of the wavefunction which leads to the exchange interaction.

The many electron wavefunction Ψ is a Slater determinant (an antisymmetric linear combination of products of spin orbitals).

$$\Psi = \begin{vmatrix} \phi_1(\mathbf{x}_1) & \phi_1(\mathbf{x}_2) & \cdots & \phi_1(\mathbf{x}_N) \\ \phi_2(\mathbf{x}_1) & \phi_2(\mathbf{x}_2) & \cdots & \phi_2(\mathbf{x}_N) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_N(\mathbf{x}_1) & \phi_N(\mathbf{x}_2) & \cdots & \phi_N(\mathbf{x}_N) \end{vmatrix} \quad (11)$$

$$= |\phi_1 \ \phi_2 \ \cdots \ \phi_N|$$

Why is it an approximation?

By approximating the many electron wavefunction with a single determinant, we neglect Coulomb correlations, i.e., the Hartree-Fock Method does not take account of electron correlation effects. (but we will see it includes correlations of another sort. These correlations among the positions of electrons with parallel spins only, and are due, not to the Coulomb force, but to the Pauli exclusion principle).

The solution of the Hartree-Fock method is the Slater determinant that results in the lowest Hartree-Fock energy, i.e. This is the best 1-determinantal wavefunction that exists.

$$E = \int \Psi^* \hat{H} \Psi d\tau = \sqrt{N!} \int \Psi^* \Psi_0 d\tau \quad (12)$$

$$E = \sum_i^N \int \phi_i^*(\mathbf{x}_i) \left[\frac{-\hbar^2}{2m} \nabla_i^2 + V(\mathbf{x}_i) \right] \phi_i d\mathbf{x}_i \quad (13)$$

$$+ \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \iint [\phi_i^*(\mathbf{x}_i) \phi_j^*(\mathbf{x}_j) - \phi_j^*(\mathbf{x}_j) \phi_i^*(\mathbf{x}_i)] \frac{e^2}{r_{ij}} \phi_i(\mathbf{x}_i) \phi_j(\mathbf{x}_j) d\mathbf{x}_i d\mathbf{x}_j$$

$$E = \sum_i^N \int \phi_i^*(\mathbf{x}_i) \left[\frac{-\hbar^2}{2m} \nabla_i^2 + V(\mathbf{x}_i) \right] \phi_i d\mathbf{x}_i \quad (14)$$

$$+ \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \iint \frac{e^2}{r_{ij}} |\phi_i(\mathbf{x}_i)|^2 |\phi_j(\mathbf{x}_j)|^2 d\mathbf{x}_i d\mathbf{x}_j$$

$$- \frac{1}{2} \sum_i^N \sum_{j \neq i}^N \iint \frac{e^2}{r_{ij}} \phi_i^*(\mathbf{x}_j) \phi_j^*(\mathbf{x}_i) \phi_i(\mathbf{x}_i) \phi_j(\mathbf{x}_j) d\mathbf{x}_i d\mathbf{x}_j$$

If ϕ_i and ϕ_j have the same spin

$$\sum_{\zeta_i, \zeta_j = \pm 1} \iint \frac{e^2}{r_{ij}} \psi_i^*(\mathbf{r}_j) \psi_j^*(\mathbf{r}_i) \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j |\alpha(\zeta_i)|^2 |\alpha(\zeta_j)|^2 \quad (15)$$

$$= \iint \frac{e^2}{r_{ij}} \psi_i^*(\mathbf{r}_j) \psi_j^*(\mathbf{r}_i) \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j$$

If ϕ_i and ϕ_j have the opposite spins

$$\sum_{\zeta_i, \zeta_j = \pm 1} \iint \frac{e^2}{r_{ij}} \psi_i^*(\mathbf{r}_j) \psi_j^*(\mathbf{r}_i) \psi_i(\mathbf{r}_i) \psi_j(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j \alpha(\zeta_i) \beta(\zeta_i) \alpha(\zeta_j) \beta(\zeta_j) = 0 \quad (16)$$

Following exactly the same method of minimizing the expectation value of H with respect to the one-electron wavefunctions as was used in the derivation of the Hartree equations, results in the following set of one-electron equations, the **Hartree-Fock equations**:

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{2e^2}{r_i} + e^2 \sum_{j \neq i}^N \int \frac{|\psi_j(r')|^2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - e^2 \sum_{j \neq i}^N \delta_{s_i s_j} \int \frac{\psi_j^*(r') \psi_i(r')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \psi_i(\mathbf{r}_i) = \epsilon_i \psi_i(\mathbf{r}_i) \quad (17)$$

where s_i labels the spin of particle i . The Hartree-Fock equations are often written

$$\hat{F}_i \psi_i = \epsilon_i \psi_i \quad (18)$$

where \hat{F}_i is called the Fock operator, $i=1, \dots, N$.

The extra term in these equations, when compared to equation (8), is known as the exchange term and is only non-zero when considering electrons of the same spin. The effect of exchange on the many-body system is that electrons of like spin tend to avoid each other. As a result of this, each electron has a "hole" associated with it which is known as the *exchange hole* (or the *Fermi hole*). This is a small volume around the electron which like-spin electrons avoid. The charge contained in the exchange hole is positive and exactly equivalent to the absence of one-electron.

Exchange charge distribution (fictitious), whose density at \mathbf{r}_2 is:

$$e \sum_{j(\text{spin } j = \text{spin } i)}^N \frac{\psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_1)}{\psi_i(\mathbf{r}_1)}$$

the total exchange charge is $e \sum_{j(\text{spin } j = \text{spin } i)}^N \int \frac{\psi_j^*(\mathbf{r}_2) \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_1)}{\psi_i(\mathbf{r}_1)} d\mathbf{r}_2 = e$ (why?)

Furthermore, the exchange charge density at \mathbf{r}_1 obtained by putting $\mathbf{r}_1 = \mathbf{r}_2$ is

$$e \sum_{j(\text{spin } j = \text{spin } i)}^N |\psi_j(\mathbf{r}_1)|^2 \quad (19)$$

Which is equal in magnitude, but opposite in sign, to the average charge density of electrons with spins parallel to that of electron at \mathbf{r}_1 .

Correlation energy

$$E_{corr} = E_{norel} - E_{HF} \quad (20)$$

Koopman's theorem

We may assume that the functions ψ_i are essentially unchanged after the removal of a single electron. Now we have seen that a given ψ_i only appears in the expression for E through the terms shown in equation (14). If an electron in the state ψ_i is removed, then the total energy must be reduced by the energy of ϵ_i . The result is generally known as Koopman's theorem: *The orbital energy ϵ_i can be shown to be a good approximation to the negative of the energy needed to ionize a close-shell atom by removing an electron from spin-orbital i .*

1.3 Slater Type Orbitals

For atoms, the Hartree-Fock equations can be solved numerically if it is assumed that the electron distribution is spherically symmetrical. For hydrogenic atoms, the analytical form of the wavefunctions can be written

$$\psi = R_{nl}(r) Y_{lm}(\theta, \phi) \quad (21)$$

The radial functions obtained from the hydrogen atom can not be used directly for many-electron atoms due to

1. The screening of the nuclear charge by the inner-shell electrons. (an orbital exponent can be used as a remedy).
2. The hydrogen atom functions are not particularly convenient in large system orbital calculations due to their complicated form.

Slater (1930) suggested a simpler analytical form for the radial functions

$$R_{nl}(r) = N r^n e^{-\zeta r} \quad (22)$$

where N is the normalization factor $N = \sqrt{\frac{(2\zeta)^{n+1}}{(2n!)}}$, n is the principle quantum number, ζ the orbital exponent. These functions are universally known as *Slater type orbitals* (STOs). A Slater orbital replaces the polynomial in r in a hydrogenic orbital with a single power of r . Hence, a single Slater orbital *does not* have the proper number of radial nodes and *does not* represent well the inner part of an orbital.

Slater provided a series empirical rules for choosing the orbital exponents, which are given by

$$\zeta = \frac{Z - \sigma}{n^*} \quad (23)$$

Z is the atomic number and σ is a shielding constant. n^* is an effective principle quantum number, which takes the same as the true quantum number for $n=1, 2, 3$ but for $n=4, 5, 6$ has the values of 3.7, 4.0, 4.2 respectively.

1.4 The Roothaan-Hall Equation

We shall consider initially a closed-shell system with N electrons in $N/2$ orbitals. The derivation of the Hartree-Fock equations for such a system was first proposed by Roothaan and (independently) Hall (1951). Unlike the integro-differential equations, Roothaan and Hall recast equation (12) in matrix form.

The Hartree-Fock orbitals are represented as linear combinations of a complete set of known functions, called *basis functions*. A commonly used set of basis functions for atomic HF calculations is the set of Slater-Type orbitals. Accurate representation of a many-electron atomic orbital (AO) requires a linear combination of several STOs.

$$\psi_i = \sum_{\nu}^K c_{\nu i} \phi_{\nu} \quad (24)$$

Substituting for the corresponding spin orbital χ_i into equation (13),

$$\hat{F}_i(1) \sum_{\nu=1}^K c_{\nu i} \phi_{\nu}(1) = \epsilon_i \sum_{\nu=1}^K c_{\nu i} \phi_{\nu}(1) \quad (25)$$

Pre-multiplying each side by $\phi_{\mu}(1)$ (where ϕ_{μ} is one of the basis functions), and integrating gives the following matrix equation:

$$\sum_{\nu=1}^K c_{\nu i} \int \phi_{\mu}(1) \hat{F}_i(1) \phi_{\nu}(1) d\mathbf{r}_1 = \epsilon_i \sum_{\nu=1}^K c_{\nu i} \int \phi_{\mu}(1) \phi_{\nu}(1) d\mathbf{r}_1 \quad (26)$$

$\int \phi_{\mu}(1) \phi_{\nu}(1) d\mathbf{r}_1$ is the overlap integral between the basis functions μ and ν , written $S_{\mu\nu}$. (they are not necessarily orthogonal). The elements of the *Fock matrix* are given by

$$F_{\mu\nu} = \int \phi_{\mu}(1) \hat{F}_i(1) \phi_{\nu}(1) d\mathbf{r}_1 \quad (\text{more will be given here.. introducing the charge density matrix}).$$

Equation (19) can be conveniently written

$$\mathbf{FC} = \mathbf{SCE} \quad (27)$$

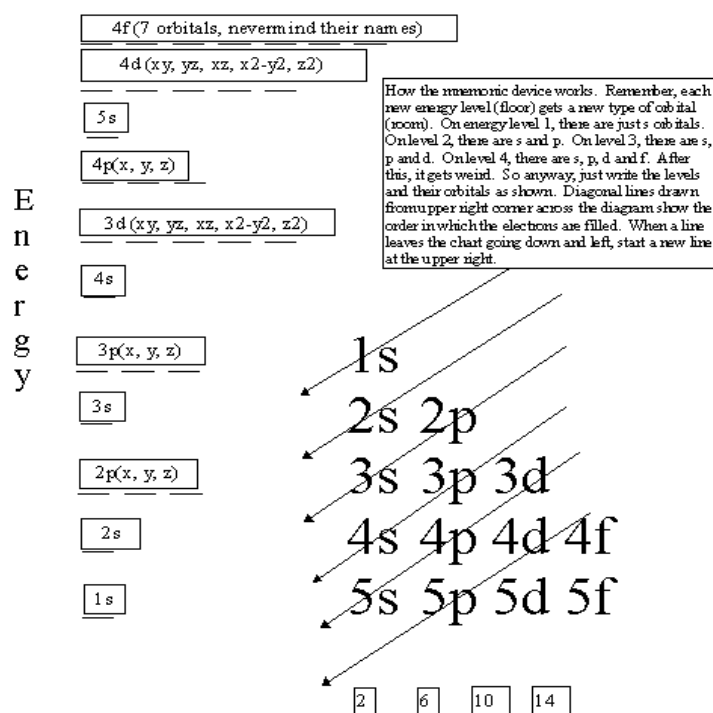
The Fock matrix is a $K \times K$ square matrix that is symmetric if real basis functions are used. The elements of the Fock matrix, which appear on the left side of the equation, depends on the coefficient matrix $c_{\mu\nu}$, which also appear on the right-hand side of the equation. Thus an iterative method will be used.

A common computation scheme for solving the Roothaan-Hall equations is:

1. Calculate the integrals to form the Fock matrix \mathbf{F}
2. Calculate the overlap matrix \mathbf{S}
3. Diagonalize \mathbf{S}
4. Form $\mathbf{S}_{1/2}$
5. Guess, or otherwise calculate, an initial density matrix
6. Form the Fock matrix using the integrals and the density matrix

7. Form F'
8. Solve the secular equation to give the eigenvalues E and the eigenvectors C' by diagonalizing F'
9. Calculate the orbital coefficients, C form $C = S_{-1/2} C'$
10. Calculate a new density matrix P from the matrix C .
11. Check for convergence. If the calculation has converged, stop. Otherwise, repeat from (6).

The result of a Hartree-Fock calculation is a set of K orbitals, which K is the number of basis functions in the calculation. The N electrons are then fed into these orbitals in accordance with the *Aufbau* principle, two electrons per orbital. The remaining orbitals do not contain any electrons, these are known as the virtual orbitals. (more advanced calculations will be discussed later).



2. Post Hartree-Fock methods

In computational quantum mechanics, **Post-Hartree-Fock** methods are the set of methods developed to improve on the Hartree-Fock (HF), or self-consistent field (SCF) method. They add electron correlation which is a more accurate way of including the repulsions between electrons than in the Hartree-Fock method where repulsions are only averaged.

In general, the SCF procedure makes several assumptions about the nature of the multi-body Schrödinger equation and its set of solutions:

- The Born Oppenheimer is inherently assumed. The true wavefunction should also be a function of the coordinates of each of the nuclei. (more will be touched in the next lecture).
- Typically, relativistic effects are completely neglected. The momentum operator is assumed to be completely classical.
- The basis set is composed of a finite number of orthogonal functions. The true wavefunction is a linear combination of functions from a complete (infinite) basis set.
- The energy eigenfunctions are assumed to be products of one-electron wavefunctions. The effects of electron correlation, beyond that of exchange energy resulting from the anti-symmetry are totally ignored.

For the great majority of systems under study, in particular for excited states and processes such as molecular dissociation reactions, the fourth item is by far the most important. As a result, the term *post-Hartree-Fock method* is typically used for methods of approximating the electron correlation of a system.

Usually, post-Hartree-Fock methods give more accurate results than Hartree-Fock calculations, although the added accuracy comes with the price of added computational cost, of course.

Configuration Interaction

One way to provide consider the instantaneous electron correlation is “configuration interaction”. The corrections to the wavefunction will mix in contributions from excited configurations producing **Configuration Interaction**.

Two meanings are connected to the term *configuration interaction* in this context:

- Mathematically, *configuration* simply describes the linear combination of Slater determinants used for the wavefunction Ψ .
- *Interaction* means the mixing (interaction) of different electronic configurations (states). Due to the long CPU time and immense hardware required for CI calculations, the method is limited to relatively small systems.

How to do a Configuration Calculation?

The definition of configuration state function (CSFs) Φ_i

We express the the true wavefunction to the Schroedinger equation as a linear combination of the CSFs

$$\Psi = \sum_i c_i \Phi_i \quad (28)$$

Variation of the coefficients c_i leads to the equation

$$\det(H_{ij} - E S_{ij}) = 0 \quad (29)$$

where $H_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle$ and $S_{ij} = \langle \Phi_i | \Phi_j \rangle$.

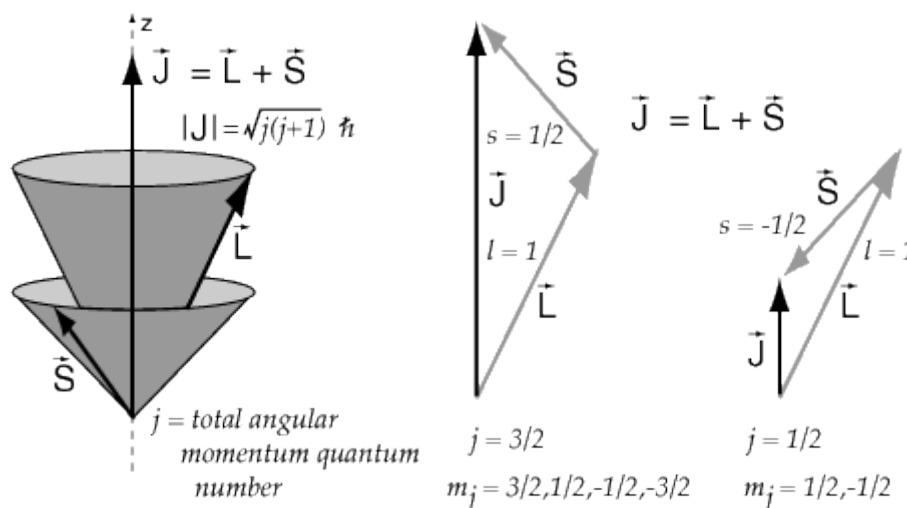
Other Post-Hartree-Fock methods will be discussed in the future.

3. L-S coupling (or Russell-Saunders coupling)

For multi-electron atoms where the spin-orbit coupling is weak, it can be presumed that the orbital angular momenta of the individual electrons add to form a resultant orbital angular momentum L . Likewise, the individual spin angular momenta are presumed to couple to produce a resultant spin angular momentum S . Then L and S combine to form the total angular momentum

$$J = L + S \quad (30)$$

This kind of combination is visualized in terms of a vector of angular momentum.



This kind of coupling gives good agreement with the observed spectral details for many light atoms. (For heavier atoms, another coupling scheme called “j-j coupling” provides better agreement with experiment).

The vector model illustrated above was applied to a single electron, but a similar model can be applied when multiple electrons contribute to the net angular momentum. If identical electrons are involved, then proper care must be taken to make sure the combinations produce an antisymmetric wavefunction upon exchange of identical electrons. For example, consider the electron configuration of titanium, $(Ar)3d^24s^2$. The $4s$ electrons contribute to a closed shell and the $3d^2$ electrons contribute the net angular momentum. Under the L-S coupling conditions this gives the following.

$$\vec{L}_1 + \vec{L}_2 = \vec{L}$$

$$\vec{2} + \vec{2} = 0, 1, 2, 3, 4$$

$$\vec{S}_1 + \vec{S}_2 = \vec{S}$$

$$\vec{1/2} + \vec{1/2} = 0, 1$$

$$\vec{J} = \vec{L} + \vec{S} = 0, 1, 2, 3, 4$$

These identical electrons must produce an antisymmetric wavefunction.

$$\Psi = \Psi_{spin} \Psi_{orbital}$$

Since $S=1$ represents a symmetric spin state, it must couple with antisymmetric orbital states $L=1$ and $L=3$

The possibility of $J=5$ is excluded by symmetry considerations for the identical electrons, but the other states can be visualized by the vector model.

Spin-orbit interaction is not covered in this class.

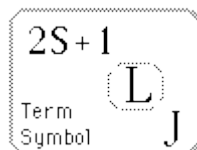
4. Term Symbols

The hierarchy of labels for the electrons of multi-electron atoms is configuration, term, level, and state.

Electron multiplicity $2S+1$: all the spins combine to produce S .

Total orbital momentum L : all the orbital angular momenta couple to produce L

Total angular momentum J : the spin and orbital terms combine to produce J .

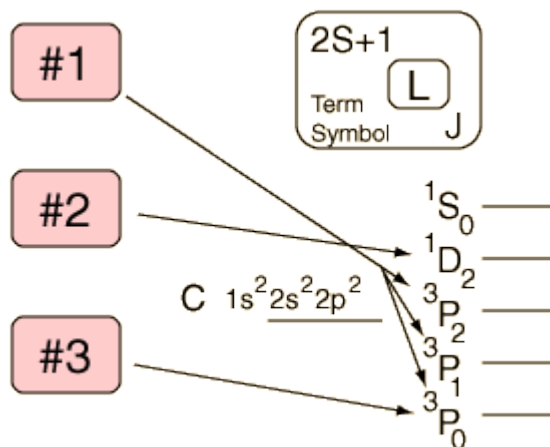


Term (S, L) ; Level (S, L, J) ; State (S, L, J, m_J)

Different terms will in general have different energies, and the order of those energies is usually that given by Hund's rules, although there are exceptions.

Hund's rules:

1. The term with maximum multiplicity lies lowest in energy
2. For a given multiplicity, the term with the largest value of L lies lowest in energy.
3. For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.



Influences on Electronic Energy levels

