Chapter 8: Multielectron Atoms

**Lecture 26: Sections 3,7**
Hartree-Fock Self-Consistent Field (HF-SCF) Method

**Lecture 27: Sections 4-6**
Electron spin,
Writing antisymmetric wave functions as Slater determinants
MathChapter E (pp. 231-235): Determinants

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**Hartree-Fock Self-Consistent Field Calculations (HF-SCF)**

Approximate method to solve Schrödinger equation

This is a variational method (total energy is too high).

Recall problem:

\[
\hat{H} = -\frac{\hbar^2}{2m} \left( \nabla_x^2 + \nabla_y^2 \right) - 2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_1 r_2}
\]

Electron-electron repulsion term:

instantaneous motions (probabilities) of the electrons are correlated; try to avoid each other

But, then can’t solve exact S. equation: \( \hat{H} \Psi_n = E_n \Psi_n \)

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**Hartree-Fock Self-Consistent Field Calculations (HF-SCF)**

Use approximate electron-electron repulsion term: \( V_{\text{eff}} \)

Fundamental assumption:
electrons move independently;
each electron (here #1) “feels” the other (here, #2) as a static, spatially averaged charge distribution

Neglected: instantaneous correlation of electrons’ motions

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**Hartree-Fock Self-Consistent Field Calculations (HF-SCF)**

Converts the exact S. equation for \( n \) electrons (here, 2) with...

\[ \hat{H} = -\frac{\hbar^2}{2m} \left( \nabla_x^2 + \nabla_y^2 \right) - 2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{1}{r_1 r_2} \]

... into \( n \) 1-electron approximate S. equations with:

\[ \hat{\mathcal{H}}_{1}^{\text{eff}} = -\frac{\hbar^2}{2m} \left( \nabla_x^2 + \nabla_y^2 \right) - 2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + V_1^{\text{eff}} \]

Hartree-Fock equation:

\[ \hat{\mathcal{H}}_{1}^{\text{eff}} \phi_j(r_1) = \varepsilon_j \phi_j(r_1) \]

position of e- “#1” (r, θ, φ)

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Engel p. 180
Hartree-Fock Self-Consistent Field Calculations (HF-SCF)

Hartree-Fock equation:

\[ \hat{H}_i \phi \left( r_i \right) = \epsilon_i \phi \left( r_i \right) \]

How to evaluate \( V_{\text{eff}} \)?

\[ V_{\text{eff}} \left( r_i \right) = - \frac{1}{2} \left( \nabla_i^2 \right) + V_{\text{eff}} \]

\[ \nabla_i = \left( \frac{r_i^2 + r_i^2}{2} - 2 \frac{r_i \cdot r_i \cdot \cos \alpha}{r_i^2} \right) \nabla_i \]

\[ V_{\text{eff}} \left( r_2 \right) = \int \phi^* \left( r_2 \right) \frac{1}{r_{1k}} \phi \left( r_1 \right) d^2 \]

Repulsion felt by \( e^- \) due to \( e^- \)

Self-consistent Field Method for He (1s)²

(assuming 2 electrons have same spatial orbital, \( \Phi \))

Guess a trial function, \( \Phi \), with variational parameters

Use this \( \Phi \) to evaluate \( V_{\text{eff}} \)

Plug this \( V_{\text{eff}} \) into \( \hat{H}_{\text{eff}} \)

Use the variational method to optimize parameters in \( \Phi \)

Iterate until self-consistent (no significant change)

Koopmans’ Approximation:

The HF orbital energies, \( \epsilon \), provide approximate ionization energies (IE) of the atoms:

\[ \epsilon_i = - \text{IE} = E_{\text{neutral atom}} - E_{\text{positive ion}} \]

IE: \( X_{\text{gas}} \rightarrow X^+_{\text{gas}} + e^- \)

Approximation: same orbitals are used to calculate the energy of the neutral atom and the energy of the cation.

Fig. 8.1 p. 292 Experimental (solid line) atomic ionization energies vs. calculated values (x) from Koopmans’ approximation

\[ \epsilon_i = - \text{IE} \]
Hartree-Fock Self-Consistent Field Calculations (HF-SCF)

Koopmans’ Theorem

\[ \hat{H}^\sigma \phi \left( \vec{r} \right) = \varepsilon \phi \left( \vec{r} \right) \]

The orbital energies, \( \varepsilon \), provide approximate IE’s of the atoms:

\[ \varepsilon_i = -IE = E_{\text{atom}} - E_{\text{cation}} \]

The Koopmans’ approximation is not limited to the valence orbitals.

1 megajoule/mol \( \approx 10 \) eV

Recall: Hydrogenic (1-electron) atomic wave functions depend on nuclear charge \( Z \), with \( \sigma = Z r / a_0 \)

where \( a_0 \) is the Bohr radius (4\( \pi \varepsilon_0 \hbar^2 / (m_e e^2) = 0.5292 \) Å)

Another important result (variational parameter) obtained from HF calculations is an “effective nuclear charge.”

The difference between the full and the effective nuclear charges is a direct measure of the “shielding” effect.
How to calculate the total energy of the atom in a particular electronic state?

E.g., for He, the HF orbital energy ($\varepsilon$) for the 1s orbital is -25.0 eV (close to measured IE = 24.6 eV).

What is the total energy of the He atom in its ground state, according to the HF-SCF method?

-77.9 eV

To obtain the total energy of the atom, we do not simply add up the orbital energies ($\varepsilon$) of the occupied orbitals.

\[
\mathcal{E} = \int \phi^*(r_i) \phi(r_j) \hat{H} \phi(r_i) \phi(r_j) \, d^2r_i \, d^2r_j
\]

\[
\hat{H} = -\frac{1}{2} \left( \nabla_i^2 + \nabla_j^2 \right) - 2 \left( \frac{1}{r_i} + \frac{1}{r_j} \right)
\]

The total energy of the He ground state turns out to be (Problem 8-10):

\[E_{\text{He}} = I_1 + I_2 + J_{12}\]

where (Z=2) and

\[I_1 = \int \phi^*(r_i) \left[ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} \right] \phi(r_i) \, d^2r_i\]

\[I_2 = \int \phi^*(r_j) \left[ -\frac{1}{2} \nabla_j^2 - \frac{Z}{r_j} \right] \phi(r_j) \, d^2r_j\]

\[J_{12} = \int \phi^*(r_i) \phi(r_j) \frac{1}{r_{ij}} \phi(r_i) \phi(r_j) \, d^2r_i \, d^2r_j\]

"Coulomb Integral" e$^-$-e$^-$ repulsion (positive)

The orbital energy for electron "#1" (same for e- "#2") is:

\[\int \phi^*(r_i) \hat{H} \phi(r_i) \, d^2r_i = \varepsilon_1 = I_1 + J_{12}\]

Therefore, the total energy of the He atom is not just the sum of the orbital energies of the 2 electrons:

\[\varepsilon_1 + \varepsilon_2 = (I_1 + J_{12}) + (I_2 + J_{12}) = I_1 + I_2 + 2J_{12}\]

\[E_{\text{He}} = I_1 + I_2 + J_{12}\]
(HF-SCF) \[ H_i \phi_i(r_i) = \varepsilon_i \phi_i(r_i) \]

\[ E = \iint \phi^*(r_1) \phi^*(r_2) \hat{H} \phi(r_1) \phi(r_2) \, dr_1^2 \, dr_2^2 \]

\[ E_{\text{TOT}} = I_1 + I_2 + J_{12} \quad \varepsilon_1 + \varepsilon_2 = I_1 + I_2 + 2J_{12} \]

When we add up the orbital energies, the e-e repulsion terms \((J_{12})\) are each counted twice – should be once.

**Problem:** What is the calculated (HF-SCF) electron-electron repulsion energy in the He ground state? Given HF results:

\[ E_{\text{TOT}} = -77.9 \text{ eV} \quad \varepsilon_1 = \varepsilon_2 = -25.0 \text{ eV} \]

\[ J_{12} = \langle V_{\text{ee}} \rangle = \sum_i \varepsilon_i - E_{\text{Tot}} = \varepsilon_1 + \varepsilon_2 - E_{\text{TOT}} \]

\[ = 2(-25.0 \text{ eV}) - (-77.9 \text{ eV}) = +27.9 \text{ eV} \]

Problem:

According to extensive HF calculations, the total energy of the ground state carbon atom is \(-1025 \text{ eV}\).

The calculated HF orbital energies for the ground state of the carbon atom are:

- \(\varepsilon_{2p} = 11.07 \text{ eV}\)
- \(\varepsilon_{2s} = 19.39 \text{ eV}\)
- \(\varepsilon_{1s} = 308.7 \text{ eV}\)

(a) What is the meaning of the “total energy”?

(b) Predict the ionization potential (i.e., first IE) of C.

(c) What is the calculated total electron-electron repulsion energy in the C ground state?

\[ \langle V_{\text{ee}} \rangle = \sum_i \varepsilon_i - E_{\text{Tot}} \]

For a very large basis set, the HF-SCF total energy of the ground state He atom is:

\[ E_{\text{He}} = -77.9 \text{ eV} \]

But the true (measured) energy is:

\[ -79.0 \text{ eV} \]

The HF-SCF energy is too high.

The HF-SCF method is variational, and gives the lowest (best) energy assuming 1-electron wave functions.
The difference between the true energy and the best calculated HF-SCF energy is the "correlation energy".

\[ E_{\text{true}} - E_{\text{HF}} = \text{electron correlation energy} = 1.1 \text{ eV for He} \]

This HF-SCF error is due to neglecting the instantaneous correlations between the electrons' motions.

Much effort in current computational chemistry is directed to reducing this "electron correlation" problem.

HF wave functions can predict e− density as a function of r.

Good agreement with experimental results.

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**Figure 10-1**
Comparison between experimental and theoretical electron densities in the argon atom. Both the Hartree-Fock and the experimental values were determined by L. S. Bartell and L. O. Brockway, Phys. Rev., 90:833 (1953).

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**Caption:** Order for filling energy sublevels with electrons

Determine electron configurations of the ground electronic states of the atoms by placing 2 electrons (with opposite spin) in each orbital in this order.

- **s:** 1 orbital 2 electrons
- **p:** 3 \( \rightarrow \) 6
- **d:** 5 \( \rightarrow \) 10

Hund’s Rules
Pauli Exclusion Principle

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*Silberberg “Chemistry” 3rd Ed.*

**REVIEW**

Chap. 8

“Electron Configuration and Chemical Periodicity”

Figure 8.7 p. 295
Example: For the oxygen and sulfur atoms, the nuclear charges, Z, are 8 and 16. What are their ground state electron configurations?

Answer:

What are the ground state electron configurations of the potassium, calcium and scandium atoms (Z=19-21)?

Answer:

HF calculations obtain the correct ground state electron configurations for all of these atoms.

What is the ordering of orbital energies, ε, according to HF calculations?

According to HF calculations, the energy of the 3d orbital is lower (more negative) than that of the 4s.

\[ \varepsilon_{3d} < \varepsilon_{4s} \]

E.g., for Sc:

\[ \varepsilon_{4s} = -5.8 \text{ eV} \]
\[ \varepsilon_{3d} = -9.1 \text{ eV} \]

Then, why is the 4s filled before the 3d?

The ground state is the state with the lowest total energy, not necessarily the state with the lowest sum of orbital energies.

Although \( \varepsilon_{3d} < \varepsilon_{4s} \), a lower total energy is obtained if 1 or 2 electrons occupy the 4s rather than the 3d orbital in period 4 atoms K, Ca, Sc, ... Ni.

Hint: When we add up the orbital energies, the e\(-\)e\(-\) repulsion terms are each counted twice – should be once.
Since a 4s electron has a greater probability of being close to the nucleus (penetrates [Ar] core more) than a 3d electron, the e\textsuperscript{-}e\textsuperscript{-} repulsion is greater when the 4s is occupied.

The e\textsuperscript{-}e\textsuperscript{-} repulsions are doubly counted when the energies of the occupied orbitals are simply summed, so:

\[ <V_{ee}> = \sum \epsilon_i - E_{tot} \]

\( E_{TOT} \) turns out to be lower (although \( \sum \epsilon_i \) is higher) when an e\textsuperscript{-} occupies 4s rather than 3d. (Exceptions: Cr, Cu)

HF orbital energies for the Sc atom (Z=21) ground state:
\[ \epsilon_{4s} = -5.8 \text{ eV} \]
\[ \epsilon_{3d} = -9.1 \text{ eV} \]
\[ E_{TOTAL} = -20,766 \text{ eV} \]

So need only 0.016\% difference in \( V_{ee} \) to offset the 3.3 eV difference in orbital energies. In this case, can’t predict the total energy of the atom from the orbital energies alone.

This discrepancy highlights the limitations of the orbital approximation central to the HF method:

The Hamiltonian operator is not really separable into terms that each depend only on the coordinates of a single electron,

\[ \hat{H} = -\frac{1}{2} \left( \nabla_1^2 + \nabla_2^2 \right) - r_1 \hat{r}_2 \]

and therefore the total energy \( (E_{TOT}) \) is not really the sum of the energies \( (\epsilon) \) of the 1-electron wave functions (orbitals).

Multielectron Atoms (Chapter 8)

Lecture 27: Sections 4-6
Electron spin
Writing antisymmetric wave functions as Slater determinants
MathChapter E (pp. 231-235): Determinants

Lecture 28: Sections 8-9
Addition of spin & orbital angular momentum vectors
Russell Saunders coupling
Term Symbols for a given electron configuration
Example: Carbon atom (1s\textsuperscript{2} 2s\textsuperscript{2} 2p\textsuperscript{2}) gives 3P, 1D, 1S terms
Electron Spin

- an intrinsic (built-in) angular momentum of electrons - doesn’t matter what orbital they’re in
- a nonclassical effect - derived using a relativistic treatment of quantum mechanics
- (but classically, one often thinks of an electron spinning about its axis)

Electron Spin

Electron spin angular momentum has properties analogous to orbital angular momentum:

<table>
<thead>
<tr>
<th>Orbital</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angular momentum vector</td>
<td>$\vec{L}$</td>
</tr>
<tr>
<td>Quantum # (determines magnitude)</td>
<td>$\ell$</td>
</tr>
<tr>
<td>...its possible values</td>
<td>$\ell = 0, 1, 2, \ldots n-1$ (for e$^-$ in atom)</td>
</tr>
<tr>
<td>Magnitude (length of vector)</td>
<td>$</td>
</tr>
</tbody>
</table>

So, in the H atom, each electron has 4 quantum numbers:

$n, \ell, m_\ell, m_s$

The complete wave function must also contain information about spin.

For the H atom, the “spin orbital” can be written:

$\Psi (r, \theta, \phi, \sigma) = \Psi (r, \theta, \phi) \alpha (\sigma)$

or

$\Psi (r, \theta, \phi) \beta (\sigma)$

2 possible spin eigenfunctions

3 spatial variables

spin variable

“sigma”
Electron Spin

\[ \Psi(r, \theta, \phi, \sigma) = \Psi(r, \theta, \phi, \sigma) \alpha(\sigma) \]

or

\[ \Psi(r, \theta, \phi, \sigma) = \Psi(r, \theta, \phi, \sigma) \beta(\sigma) \]

2 possible spin eigenfunctions

3 spatial variables

spin variable “sigma”

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The spin functions are orthonormal (orthogonal to each other, and normalized)

\[ \int \alpha^* \alpha \, d\sigma = 1 \]

\[ \int \beta^* \beta \, d\sigma = 1 \]

\[ \int \alpha^* \beta \, d\sigma = 0 \]

The spin functions are orthonormal (orthogonal and normalized)

\[ \int \alpha^* \alpha \, d\sigma = 1 \]

\[ \int \beta^* \beta \, d\sigma = 1 \]

\[ \int \alpha^* \beta \, d\sigma = 0 \]

\[ \alpha \text{ and } \beta \text{ are eigenfunctions of the spin operators } \hat{S}_z \text{ and } \hat{S}^2: \]

\[ \hat{S}_z \alpha = \frac{s_z}{2} \alpha = \pm \frac{1}{2} \alpha \]

\[ \hat{S}^2 \alpha = \frac{s(s+1)}{2} \alpha = \frac{1}{2} \alpha \]

\[ \hat{S}_z \beta = \frac{s_z}{2} \beta = -\frac{1}{2} \beta \]

\[ \hat{S}^2 \beta = \frac{s(s+1)}{2} \beta = \frac{1}{2} \beta \]

\[ |\hat{S}| = \sqrt{s} \]

How to write the wave function for the He atom ground state?

Let “(1)” refer to the 4 coordinates \((r, \theta, \phi, \sigma)\) of e\(^-\) “#1”

“(2)”

e\(^-\) “#2”

Represent 2 electrons with opposite spins in the 1s orbital:

or

\[ \Psi_1(r_2) \Psi_2(r_2) \]

\[ 1s \alpha(1) 1s \beta(2) \]

\[ \Psi_1(r_2) \Psi_2(r_2) \]

\[ 1s \alpha(2) 1s \beta(1) \]

Problem:

Can’t distinguish between the electrons.

Can’t say e\(^-\) #1 has \(m_s = +\frac{1}{2}\) and e\(^-\) #2 has \(m_s = -\frac{1}{2}\).

This is a quantum mechanical result:

can’t follow e\(^-\)’s “trajectories” to label them individually.

So, a good wave function must not specify which e\(^-\) is in which spin orbital. They are indistinguishable.

So, can we use instead (not normalized):

\[ \Psi_A = 1s\alpha(1) 1s\beta(2) + 1s\alpha(2) 1s\beta(1) \]

\[ \Psi_B = 1s\alpha(1) 1s\beta(2) - 1s\alpha(2) 1s\beta(1) \]

\[ \Psi_A \text{ is “symmetric” under the interchange of the two e\(^-\)’s.} \]

That is, if reverse (1) and (2), get back exactly the same \(\Psi_A\).
Wavefunctions for Multi-electron Atoms

\[ \Psi_A = 1s \alpha(1) \ | s \beta(2) + 1s \alpha(2) \ | s \beta(1) \]
\[ \Psi_B = 1s \alpha(1) \ | s \beta(2) - 1s \alpha(2) \ | s \beta(1) \]

\(\Psi_A\) is “symmetric” under the interchange of the two e⁻’s. That is, if reverse (1) and (2), get back exactly the same \(\Psi_A\).

\(\Psi_B\) is “antisymmetric” under the interchange of the two e⁻’s. That is, if reverse (1) and (2), get back - \(\Psi_B\).

\(\Psi_B\) is “antisymmetric” under the interchange of the two e⁻’s.

That is, if reverse (1) and (2), get back - \(\Psi_B\).

Experimentally, for all electronic wave functions (not just He), only antisymmetric wave functions are observed.

Derived in 1940 by Pauli from relativistic quantum field theory.

Pauli Exclusion Principle (“Postulate 6”, p. 287)
All electronic wave functions must be antisymmetric under the interchange of any two electrons.

In general, can write antisymmetric wave functions as “Slater Determinants”.

E.g., for the lithium atom: \((1s)^2 \ (2s)^1\)

\[ \Psi_{(1,2,3)} = \begin{vmatrix} 1s \alpha(1) & 1s \beta(1) & \delta s \alpha(1) \\ 1s \alpha(2) & 1s \beta(2) & 2s \alpha(2) \\ 1s \alpha(3) & 1s \beta(3) & 2s \alpha(3) \end{vmatrix} \]

Recall:
\[ \begin{vmatrix} a & b \\ c & d \end{vmatrix} = ad - bc \]

determinant

In general, can write antisymmetric wave functions as “Slater Determinants”.

In general, can write antisymmetric wave functions as “Slater Determinants”.

label each row with a different electron’s coordinates

label each column with a different spin orbital or \(\beta\) (doubly degenerate)
Wavefunctions for Multi-electron Atoms

Why does writing a wave function as a determinant automatically make it antisymmetric?

\[ \Psi_{(\uparrow,\downarrow)} = \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1) \]

Interchanging any two rows (or two columns) multiplies a determinant by -1. (p. 235)

Interchanging 2 rows corresponds to interchanging 2 e^-.

\[ \begin{vmatrix} 1s\alpha(2) & 1s\beta(2) \\ 1s\alpha(1) & 1s\beta(1) \end{vmatrix} = 1s\alpha(2)1s\beta(1) - 1s\alpha(1)1s\beta(2) = -\Psi_{(\uparrow,\downarrow)} \]

Wavefunctions for Multi-electron Atoms

Interchanging any two rows (or two columns) multiplies a determinant by -1. (p. 235)

Interchanging 2 rows corresponds to interchanging 2 e^-.

\[ \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix} = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1) = 0 \]

Determinantal wave functions automatically ensure that only two electrons can occupy an orbital, and they must have opposite spin (usual statement of the Pauli Principle).

Multielectron Atoms (Chapter 8)

Lecture 28: Sections 8-9
Addition of spin & orbital angular momentum vectors
Russell Saunders coupling
Term Symbols for a given electron configuration
Example: Carbon atom (1s^2 2s^2 2p^2) gives 3P, 1D, 1S terms

Lecture 29: Sections 10-11
Hund’s Rules: energy ordering terms for a given e^- configuration
Short-cut for predicting the lowest energy term
Spin-orbit coupling (e.g., for C atom 3P_0, 3P_1, 3P_2)
Selection rules for atomic spectroscopy
Atomic excited states in atmospheric chemistry

What is the energy of the ground state of the carbon atom?

There is not just one energy!

The different “terms” differ in their spin and/or orbital angular momentum properties.

Note:
In this energy level diagram, the zero of energy is that of the lowest term (3P_0).
Russell Saunders (or “L-S”) coupling: works for light (small Z) atoms

$L =$ quantum number for the magnitude of the total orbital angular mom. of all $(i)$ electrons

$| \vec{L} | = \sqrt{L(L+1)} \hbar$

$M_L =$ quantum number for the total projection on the z axis of the orbital angular momenta of all the electrons

$M_L = \sum_i m_\ell,i$

$L_z = M_L \hbar$

Fig. 8.2 p. 294
Addition of ang. momentum vectors

(Note: this diagram is not for carbon)

Analogous relations hold for spin:

$S =$ quantum number for the magnitude of the total spin angular momenta of all of the electrons

$| \vec{S} | = \sqrt{S(S+1)} \hbar$

$M_S =$ quantum number for the total projection on the z axis of the spin angular momenta of all of the electrons

$M_S = \sum_i m_s,i$

$S_z = M_S \hbar$

Fig. 8.2 p. 294
Addition of ang. momentum vectors

Angular momentum vectors of individual electrons do not add as scalars.

(The length of vector $L$ is not the sum of the lengths of the three individual $\ell$ vectors shown.)

Projections on the z axis of the ang. mom. of the individual electrons do add as scalars.

Here, for 3 electrons:

$L_z = \sum_{i=1}^{3} \ell_z,i = \hbar \sum_{i=1}^{3} m_\ell,i = M_L \hbar$

Fig. 8.2 p. 294
Addition of ang. momentum vectors

Similarly, for spin (for $i$ electrons):

$S_z = \sum_i s_z,i = \hbar \sum_i m_s,i = M_S \hbar$

Possible values of $M_L$ and $M_S$:

$M_L = -L, -L+1, -L+2, \ldots +L$

$M_S = -S, -S+1, -S+2, \ldots +S$

So, if we know the maximum values of $M_L$ and $M_S$, we can deduce the values of $L$ and $S$. 

Vector diagram for $S=1$

Vector diagram for $L=1$
Method to Obtain Term Symbols Associated with a Given Electron Configuration

1. Write out all possible microstates consistent with Pauli Principle.
   (A “microstate” specifies the ms and ml values for each electron)

2. Look for the maximum Ms and, for this, the maximum Ml.
   Set S = Ms and L = Ml
   Check off (2L+1) x (2S+1) microstates corresponding to this set of S and L values.

3. Repeat until all of the microstates are accounted for.

4. Use Hund’s Rules to order the resulting terms in energy.

List all of the microstates associated with the (1s)^2(2s)^2(2p)^2 ground state electron configuration (of the carbon atom)

Can consider just the two 2p electrons (since closed subshells have zero total Ml and zero total Ms).

What is the total number of microstates associated with the (2p)^2 configuration?

-- -- 2p

6 possibilities for “1st” electron (3 orbitals, ↑ or ↓ spin)
5 “2nd”
Order doesn’t matter, so have 6 x 5 / 2 = 15 microstates

15 microstates associated with the (2p)^2 configuration

What terms are associated with these microstates?

Max Ms = 1
for this, Max Ml = 1
So, must have S=1, L=1.

This set of S, L values corresponds to 9 microstates:

M_s, M_l = 1,-1  1,0  1,1
0,-1  0,0  0,1
-1,-1 -1,0 -1,1
Check off 9 microstates.

Of the 6 microstates remaining,

Max Ms = 0
for this, Max Ml = 2

So, must have S=0, L=2.

This set of S, L values corresponds to 5 microstates:

M_s, M_l = 0,-2  0,-1  0,0  0,1  0,2
Check off 5 microstates.
For the 1 microstate remaining, 
\[ M_s = 0 \]
\[ M_L = 0 \]

So, must have \( S=0, L=0 \).

So, the 15 microstates associated with the \((2p)^2\) configuration arise from 3 sets of \( S, L \) values:
- \( S=1 \) and \( L=1 \)
- \( S=0 \) and \( L=2 \)
- \( S=0 \) and \( L=0 \)

Next: Use "Term Symbols" to name these 3 states and Hund’s Rules to order them in energy.

Multielectron Atoms

Lecture 29: Sections 10-11

Hund’s Rules: energy ordering terms for a given \( e^- \) configuration
- Short-cut for predicting the lowest energy term
- Spin-orbit coupling (e.g., for C atom, \( ^3P_0, ^3P_1, ^3P_2 \))
- Selection rules for atomic spectroscopy
- Atomic excited states in atmospheric chemistry

Lecture 30: Diatomic Molecules (Chap. 9)

Recall - Observed energies of terms arising from the carbon \((1s)^2(2s)^2(2p)^2\) electron configuration:

To predict the energy ordering, use Hund’s Rules.

Hund’s Rules (3)

Empirical rules for predicting the energy ordering of the terms arising from the same electronic configuration:

1. The term with the highest total spin quantum number (\( S \)) is most stable (that is, is lowest in energy).

The stabilities of the terms decrease with decreasing \( S \).

Reasons: the higher spin state has...
- reduced \( e^-e^- \) repulsion, since more electrons have the same spin and must therefore be in different orbitals
- increased electron-nuclear attraction due to orbital contraction

For the \((1s)^2(2s)^2(2p)^2\) electron configuration, we obtained 3 terms:
- \( S=1 \) and \( L=1 \)
- \( S=0 \) and \( L=2 \)
- \( S=0 \) and \( L=0 \)

Most stable \((S=1)\)
**Hund’s Rules**

2. For the same S, the term with the largest orbital angular momentum quantum number (L) is most stable.

**Reason:** this also reduces e⁻e⁻ repulsions

For the \((1s)^2 (2s)^2 (2p)^2\) electron configuration, we obtained 3 terms:

- S=1 and L=1  → Most stable (S=1)
- S=0 and L=2  → Next most stable
- S=0 and L=0  → Highest in energy

Recall - Observed energies of terms arising from the carbon \((1s)^2(2s)^2(2p)^2\) electron configuration:

- S=0 and L=0
- S=0 and L=2
- S=1 and L=1

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**Atomic Term Symbols**

- **Spin multiplicity**  
  \(2S+1\)
  - 2S+1 is the # of \(M_S\) values for a given S
  - How to say it:
    - “Singlet” if \(S=0\), so 2S+1=1
    - “Doublet” \(\frac{1}{2}\) 2
    - “Triplet” 1 3
    - “Quartet” \(\frac{3}{2}\) 4
    - “Quintet” 2 5
  - etc.

**Term Symbols**

- **Spin multiplicity**  
  \(2S+1\)
  - Write here:
    - S if L = 0
    - P 1
    - D 2
    - F 3
  - etc.

**Predicted energy ordering:**  
\(3P < 1D < 1S\)
Predicted energy ordering: \[ ^3P < ^1D < ^1S \]

Correct!

Atomic Term Symbols

What is the term symbol for the ground state of the neon atom (Z=10)?

First, write the electron configuration: \((1s)^2 (2s)^2 (2p)^6\)

Next, write the microstate(s) consistent with the Pauli Principle:

Total \(S = 0\) since \(M_S = \text{sum of } m_s\) values for 10 electrons \(= 0\)

Total \(L = 0\) since \(M_L = \sum m_\ell = 0\)

(So, we can ignore filled subshells when determining term symbols.)

Term symbol: \( ^1S \)

Here \(S\) means \(L = 0\), not \(S\) for spin

Short-Cut to Determining the Lowest Energy Term Symbol

Example: what is the ground state term symbol for the Cr (chromium) atom (Z=24)?

- Write electron configuration: \([\text{Ar}] (3d)^5 (4s)^1\)
- Find the microstate with the highest value of \(M_S\), and set \(S = M_S\)
  - \(4s\)
  - \(3d\)
  - \(m_\ell\) -2 -1 0 1 2
  - \(M_S = 6 \left( \frac{1}{2} \right) = 3\), so \(S = 3\)
  - But: remember this isn’t the only microstate associated with this term
- For this \(M_S\), find the microstate with the highest value of \(M_L\): \(L = M_L\)
  - No choice for Cr: \(M_L = 0\) so \(L = 0\)
- So for Cr, the lowest energy term is: \( ^7S \) “septet S”

Predicted energy ordering: \[ ^3P < ^1D < ^1S \]
Spin-Orbit Coupling

The spin and orbital angular momenta of a given electron also interact.

Classical Description:

- The apparent orbital motion of the nucleus (of charge $+Ze$) around the $e^-$ (if considered at rest) creates a magnetic field
- ...which interacts with the $e^-$'s spin magnetic moment and shifts the $e^-$'s energy
- ...by an amount that depends on the relative orientations of the spin and orbital angular momentum vectors for that electron, and on the nuclear charge, $Z$.
- Note: spin-orbit coupling is not due to interactions between different electrons, and it occurs even in the absence of an external field.

Russell-Saunders Coupling

$J$ total (spin + orbital) angular momentum quantum number
(this is not the same as quantum number $J$ for the rigid rotor or the “$J$” Coulomb integral !)

Possible values of $J$: $L+S$, $L+S-1$, $L+S-2$, ...
$J$ is never negative

$L$ and $S$ vectors point in same direction
$L$ and $S$ vectors point in opposite directions

What are the possible $J$ values for the $^3P$ ground state of the C atom?
Answer: $S=1$ and $L=1$ so $J = 2$, $1$, $0$

The complete Hamiltonian operator also contains a spin-orbit coupling term ($\hat{H} = \hat{H}_0 + \hat{H}_{\text{spin-orbit}}$).

(Complete) Atomic Term Symbols

Write here: $2S+1 L_J$

E.g., $^3P_0$
pronounce “triplet P zero”

total (spin + orbital) angular momentum quantum number

Hund’s Rule #3:

3. For the same values of $S$ and $L$: if the unfilled subshell is...
less than half-filled, then the smallest $J$ term is lowest in energy
more largest

Which term is most stable for $(1s)^2 (2s)^2 (2p)^2$? $^3P_2$ $^3P_1$ $^3P_0$

Observed energies of terms arising from the ground state electron configuration of the carbon atom

Predicted energy ordering:
$^3P_0 < ^3P_1 < ^3P_2 << ^1D_2 << ^1S_0$

In light (small $Z$) atoms, the energy splittings due to differences in $S$ and $L$ are much larger than the “spin-orbit splittings” due to differences in $J$.

However, in heavy (high $Z$) atoms, spin-orbit splittings can be larger than energy differences due to different $S$ and/or $L$ values, or even different $e^-$ configurations.
Example: What is the complete term symbol for the ground state of the Zr atom (zirconium, Z=40)?

The electron configuration is: \([\text{Kr}] (4d)^2 (5s)^2\)

Answer:

Using the short-cut, can determine that the lowest energy term has \(S=1\) and \(L=3\)

Since the 4d orbital has 2 electrons so is less than half filled, the lowest value of \(J\) is lowest in energy:

\(3F^2\)

Selection Rules for Atomic Spectroscopy

... specify between what types of states an atom can make transitions accompanied by the absorption or emission of light.

Assuming \(L\) and \(S\) are “good” quantum numbers, requirements are:

\(\Delta L = \pm 1\) due to conservation of angular momentum

\(\Delta S = 0\) no change in spin

\(\Delta J = 0, +1 \text{ or } -1\) total ang. mom. quantum number

(but no transitions between \(J=0\) levels)

\(\Delta L = \pm 1\) Selection Rules for Atomic Spectroscopy

\(\Delta S = 0\)

\(\Delta J = 0, +1 \text{ or } -1\)

Which transitions are observed in the H atom emission spectrum to the ground state (Lyman series)?

Term symbol for ground state: \(2S_{1/2}\)

\((1s)^1\) is the electron configuration

- \(2s \rightarrow 1s\) ? \(2S_{1/2} \rightarrow 2S_{1/2}\)
- \(3d \rightarrow 1s\) ? \(2D \rightarrow 2S_{1/2}\)
- \(2p \rightarrow 1s\) ? \(2P_{1/2} \rightarrow 2S_{1/2}\)
  \(\rightarrow 2P_{3/2} \rightarrow 2S_{1/2}\)
In spectra of low Z atoms, the $\Delta S=0$ selection rule produces separate manifolds of transitions among states with the same value of S.

Fig. 8.5 p. 308
Helium atom energy level diagram showing singlet states (left) and triplet states (right)

Atomic Excited States in Atmospheric Chemistry

For atoms (as well as molecules), excited electronic states can show very different chemical behaviors than the ground state.

**Example:** O atom Ground state: $^3\text{P}$

The lowest energy singlet excited state, the $^1\text{D}$, can be produced by photodissociation of diatomic oxygen ($\lambda < 315$ nm):

$$
\text{O}_2 + h\nu \rightarrow \text{O} (^3\text{P}) + \text{O} (^1\text{D}) \quad \text{Long-lived due to } \Delta S=0 \text{ selection rule for emission}
$$

The excited O ($^1\text{D}$) atom has an excess energy of 190 kJ/mol relative to O ($^3\text{P}$).

This energy can be used to overcome a reaction activation barrier:

$$
\text{O} (^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \quad 120 \text{ kcal/mol exothermic}
$$

Important source of atmospheric hydroxyl radicals.

Ref: Engel p. 228