Complex Atoms

Tennyson Chapter 4

Schrödinger Equation

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Electron-Electron repulsion

Even for the simplest case (N=2), the equation is not analytically soluble.

Central Field Model

The best hope for a solution to the complex atom Schrödinger equation is to make approximations such that it becomes similar to the analogous to the hydrogen atom. This is done by assuming each electron can be treated independently.

$$[-\frac{\hbar^2}{2m_e}\nabla_i^2 + V_i(\mathbf{r}_i)]\phi_i(\mathbf{r}_i) = E_i\phi_i(\mathbf{r}_i)$$

Under this assumption, the potential seen by each electron is given by the average potential from all other electrons.

$$V_i(\mathbf{r}_i) = \frac{-Ze^2}{4\pi\epsilon_o r_i} + \sum_{i\neq j} < \frac{e^2}{4\pi\epsilon_o |\mathbf{r}_i - \mathbf{r}_j|} >$$

This approximation has solutions for the orbitals, $\Phi(\mathbf{r})$, that are similar in form to the solution to the hydrogen atom. The total energy of the system is given by the summation of the energy of each electron.

Indistinguishable Particles

What we observed is not the wave function but the probability distribution, $|\Psi|^2$. If two electrons are truly indistinguishable, then the probability function of two particles should be the same if the particles are interchanged.

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

This has a symmetric and antisymmetric solutions:

$$\psi(1,2) = +\psi(2,1) \qquad \psi(1,2) = -\psi(1,2)$$

Electrons are fermions which follow the antisymmetric solution, and hence, the wavefunction can be written as the combination of orbitals of the two electrons

$$\psi(1,2) = \frac{1}{\sqrt{2}}[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] = -\psi(2,1)$$

However, if $\Phi(\textbf{r}) = \Phi(\textbf{r})$, then $\Psi = 0$. This led to the Pauli Exclusion Principle:

No two electrons can occupy the same spin-orbital

Electron Configuration

So no two electrons can have the same quantum numbers (*nlms*). So as we configure the distribution of electrons in a complex atom, the electrons fill in different shells at the lowest energies.

For each *l* value, there are 2*l*+1 different *m* values with each value able to hold a spin up and spin down electron.

Orbits will lower *l* values will spend time closer to the center and hence generally experience a higher Columb attractive force. For this reason orbits with lower *l* will be at lower energy-- unlike in the Hydrogen atom.
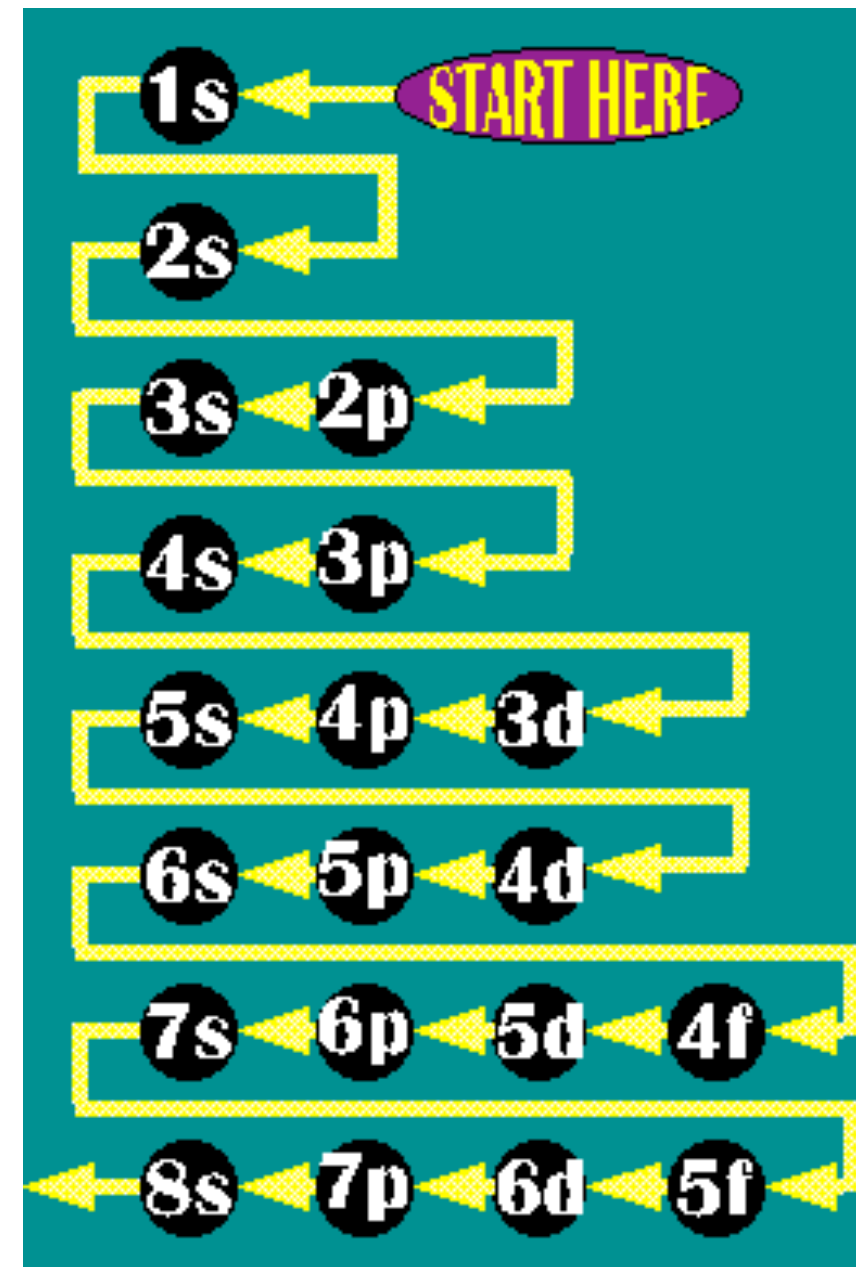
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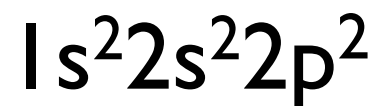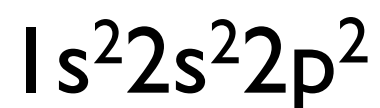**Question**: Carbon has six electrons. What is the electron configuration for carbon?

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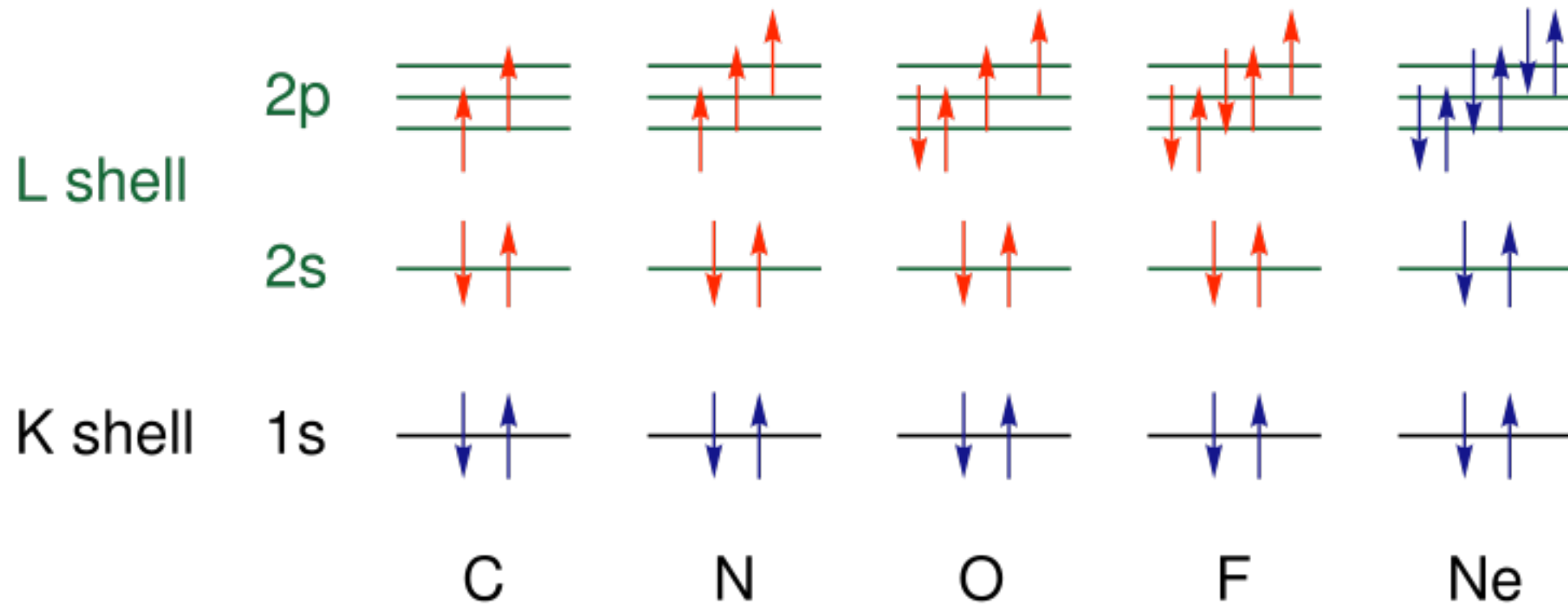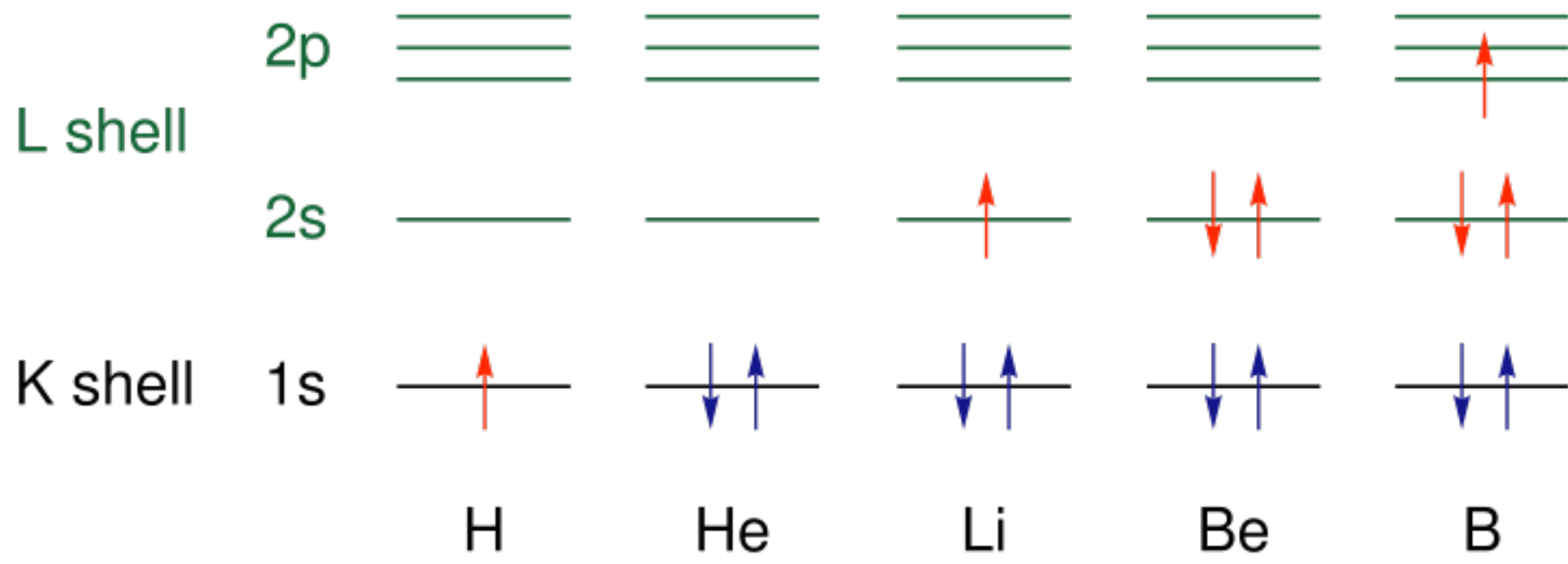**Answer**:

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The superscripts indicate the number of electrons in each shell.

Periodic Table

Angular Momentum

The total angular momentum of the electrons will be given as the sum of the angular momentum from all of the electrons. One method to do this calculation is known as Russell-Saunders coupling where the spin and orbital angular momentum are first combined individually for each electron and then added together to calculate the total angular momentum.

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

Orbital   Spin

$$\mathbf{L} = \sum l_i \qquad \mathbf{S} = \sum s_i$$

These are added together as **vectors.**

Closed shells (those which are full of electrons) have **L**=0 and **S**=0, so only open shells have to be considered.

NB: L-S coupling is applicable to non-relativistic considerations, which is the case for elements lighter than iron. In this situation, all states with the same value for L and S have the same energy. For relativistic situations, j-j coupling is the more appropriate description of the levels.

Spectroscopic Notation

Each level can be specified using spectroscopic notation. A 'term' is a state of a configuration with a specific **S** and **L** value. A 'level' is specified with the addition of the total angular momentum, as relativistic effects can give each J value a different energy.

$$^{2S+1}L_J(o)$$

J can also have different orientations (M_J) in the presence of an external magnetic field. This can produce further levels (states with different energies) and is known as the Zeeman effect.

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0 single
1/2 doublet
1 triplet

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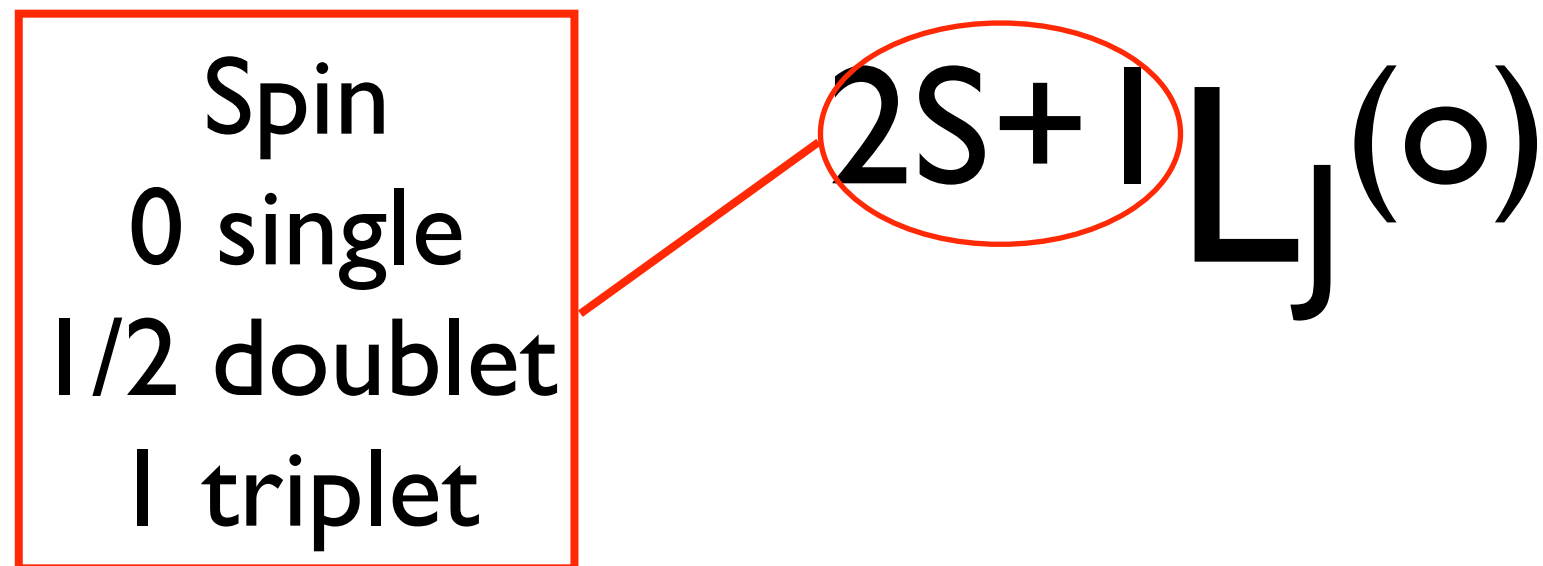
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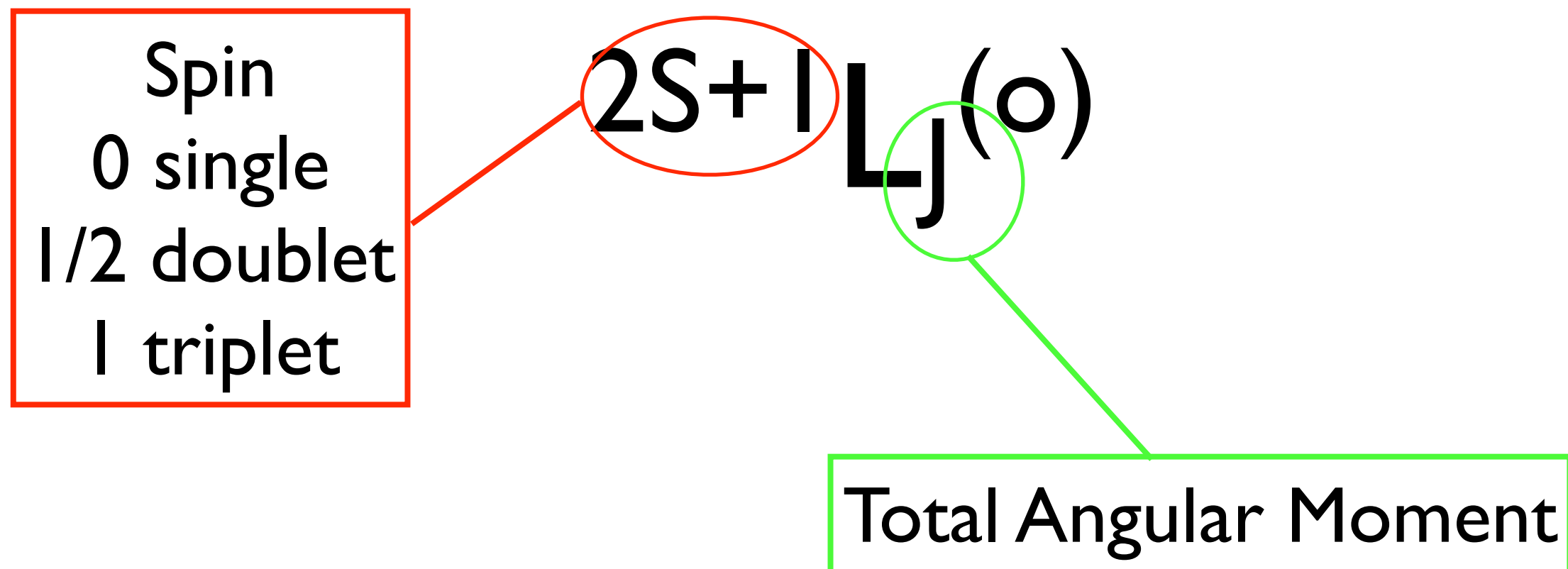
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Parity $(-1)^{\Sigma l}$

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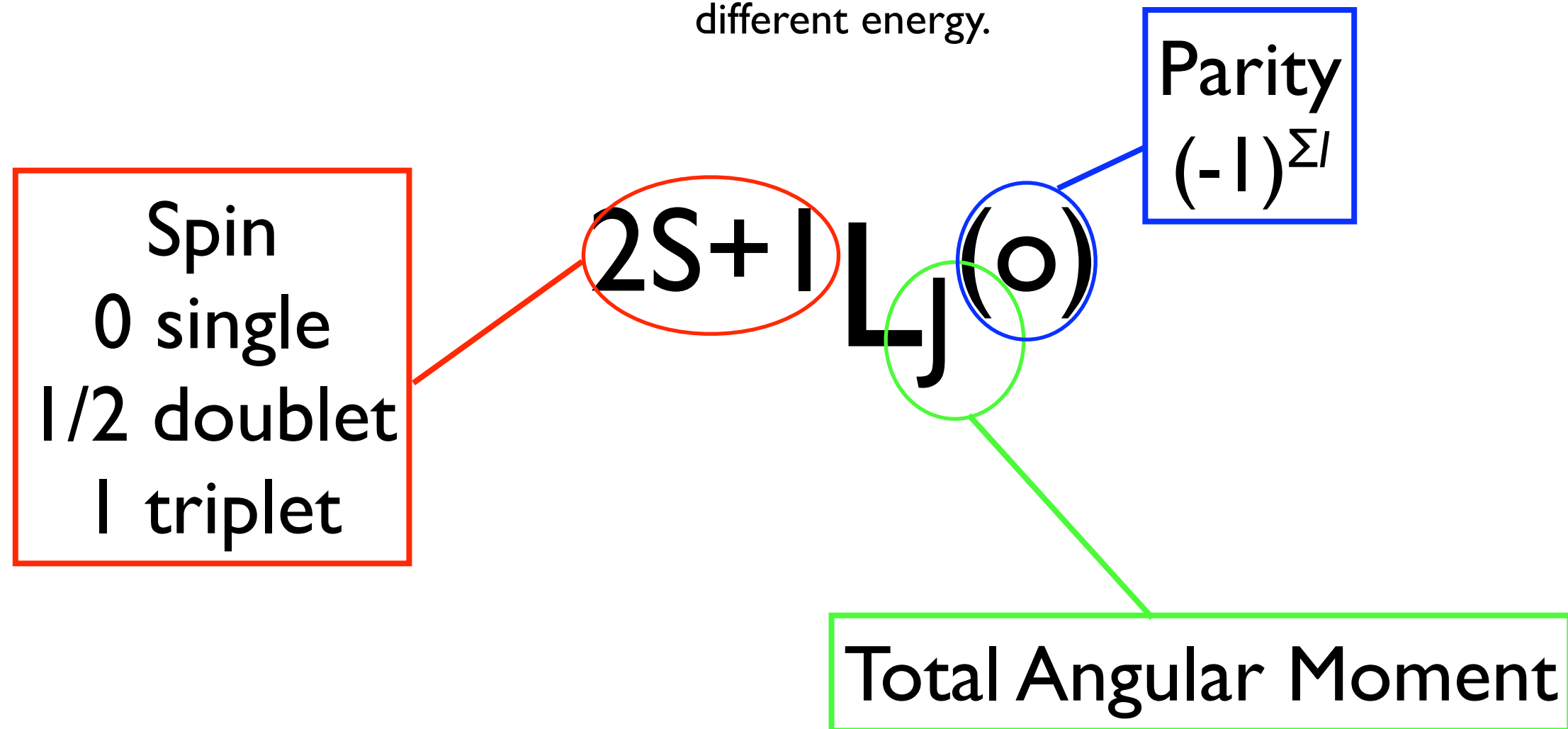
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L=1+1= 0, 1,2
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In this case, the parity is even

L	S	J	
0	0	0	$^1S_0$
0	1	1	$^3S_1$
1	0	1	$^1P_1$
1	1	0, 1, 2	$^3P_0$ $^3P_1$ $^3P_2$
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General Rule of thumb: States that have the same n and l, L+S must be even other wise the Pauli Exclusion principle will apply. So since n and l are the same here, we can eliminate the following states.

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Hund's Rules

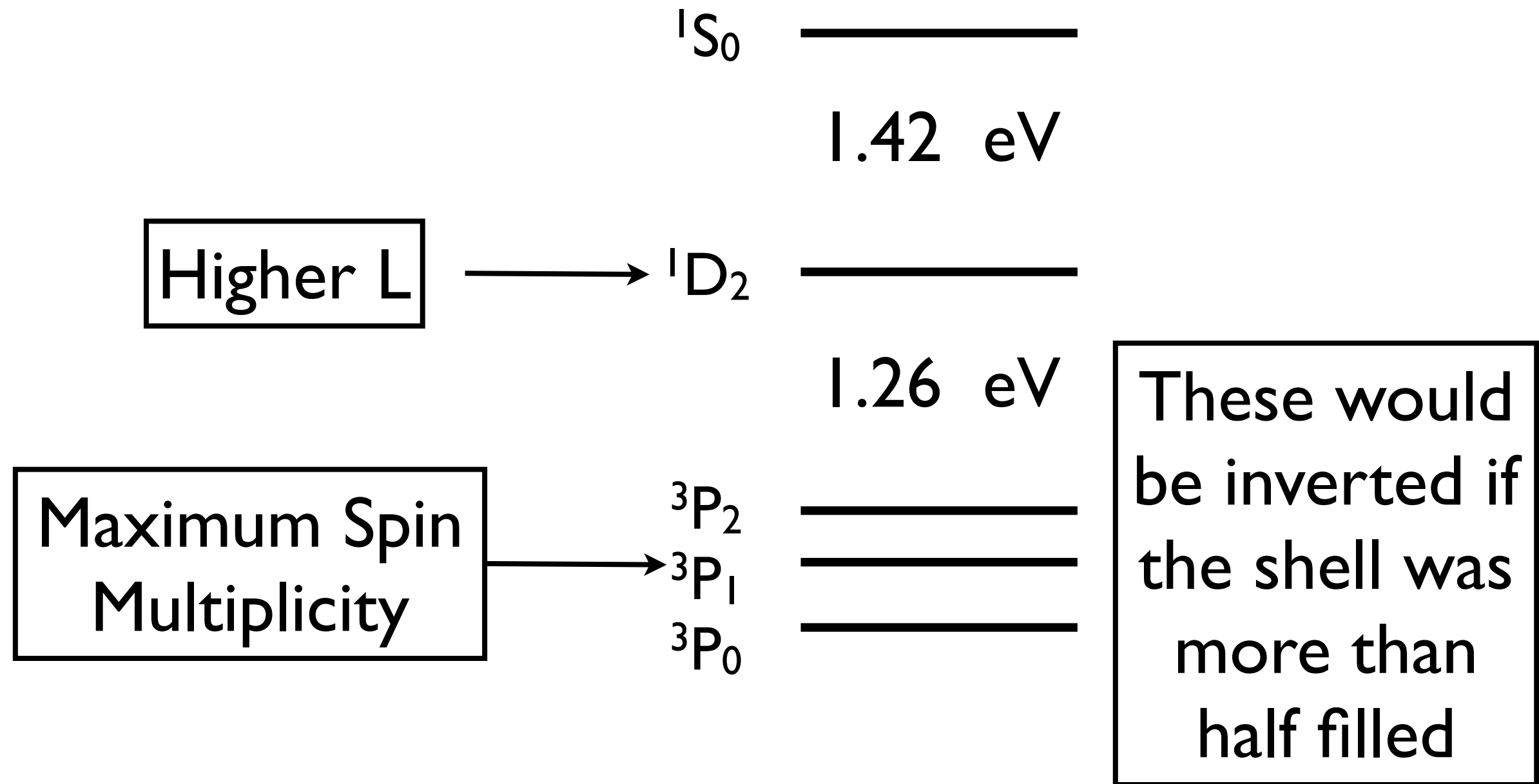Hund's rules determine the order for the different levels in complex atoms.

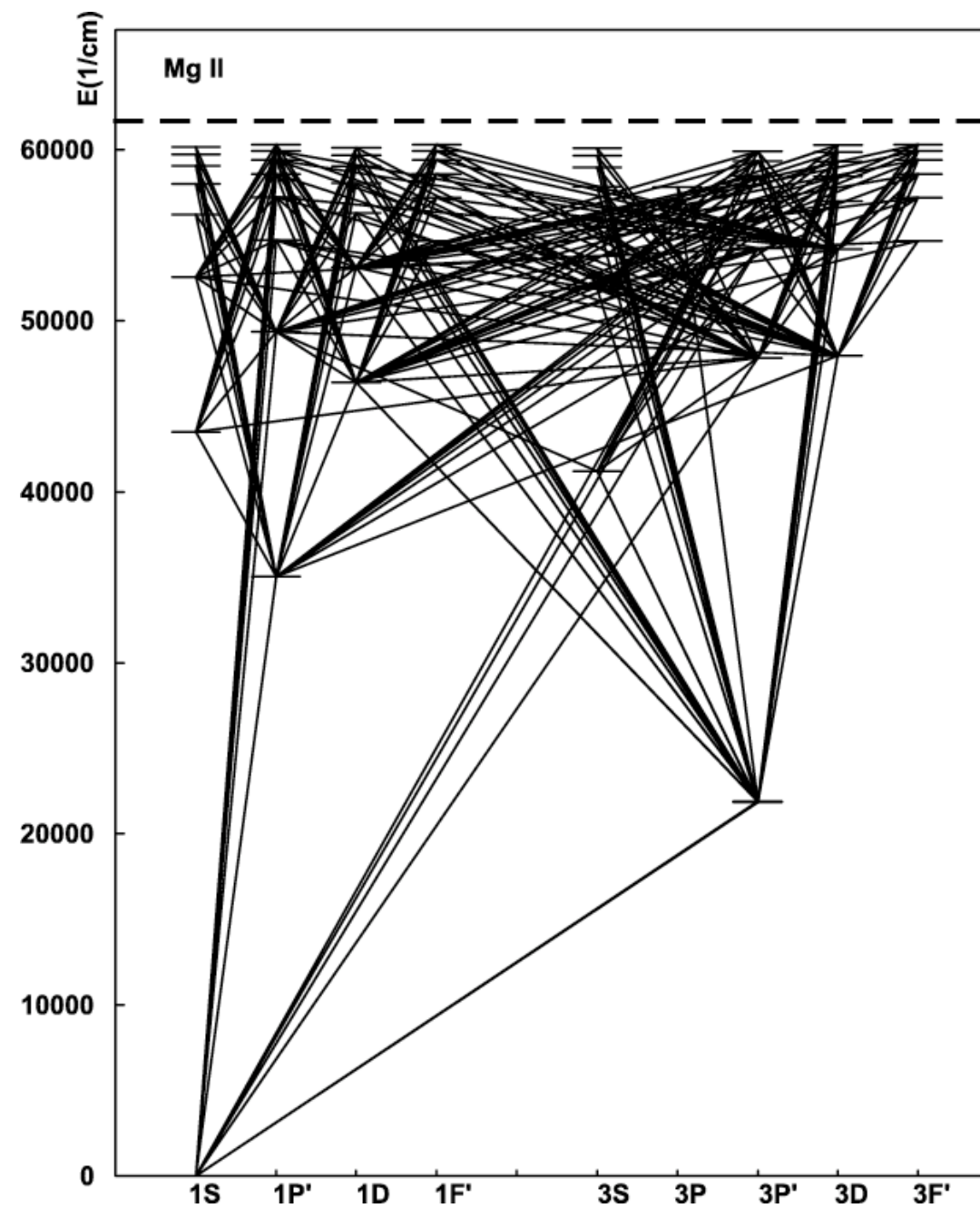| |
|---|
| 1. For a given configuration, the term with maximum spin multiplicity lies lowest in energy. |
| 2. For a given configuration and spin multiplicity, the term with the largest value of L lies lowest in energy. |
| 3. For atoms with ess than half-filled shells, the level with the lowest value of J lies lowest in energy. |
| 4. For atoms with more than half-filled shells, the level with the highest value of J lies lowest in energy. |

Energy Levels for CI

$^1S_0$ ——————

1.42 eV

Higher L → $^1D_2$ ——————

1.26 eV

Maximum Spin Multiplicity → $^3P_2$ ——————
$^3P_1$ ——————
$^3P_0$ ——————

These would be inverted if the shell was more than half filled

Grotrian Diagrams

Mishenina et al 2004

Selection Rules for Transitions

For Electric Dipole Transitions:
1. $\Delta J = 0, \pm 1$ but not 0-0
2. $\Delta M_J = 0, \pm 1$
3. Parity Changes
4. $\Delta S = 0$
5. One electron jumps, Δn any, $\Delta l = \pm 1$
6. $\Delta L = 0, \pm 1$, but not L=0-0

Allowed
Satisfy all rules
$A \sim 10^6$ s

Intercombination
Breaks #4
$A \sim 100$ s
Example: CIII]1908.7
$2s^2$ ^1S- $2s2p$ $^3P^o$

Forbidden
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There are also forbidden transitions caused by electric quadrapole and Magnetic dipole

Energy Levels

For the case of a single electron orbiting around a bare nucleus the energy is given by:

$$E_n = -\frac{\mu Z^2 e^4}{8 h^2 \varepsilon_0^2}\frac{1}{n^2} = -R\frac{Z^2}{n^2}$$

However, in the presence of multiple electrons, the energy level is shifted by the different orbital states that are available. The energy becomes a function of both n and l.

$$E_n \approx -R_\infty \frac{Z_{eff}}{n^2 - \mu_{nl}}$$

The quantum defect, μ_{nl}, involves the effect of penetration to lower energy levels by electrons with l-orbits. This involves a rather complicated equation.
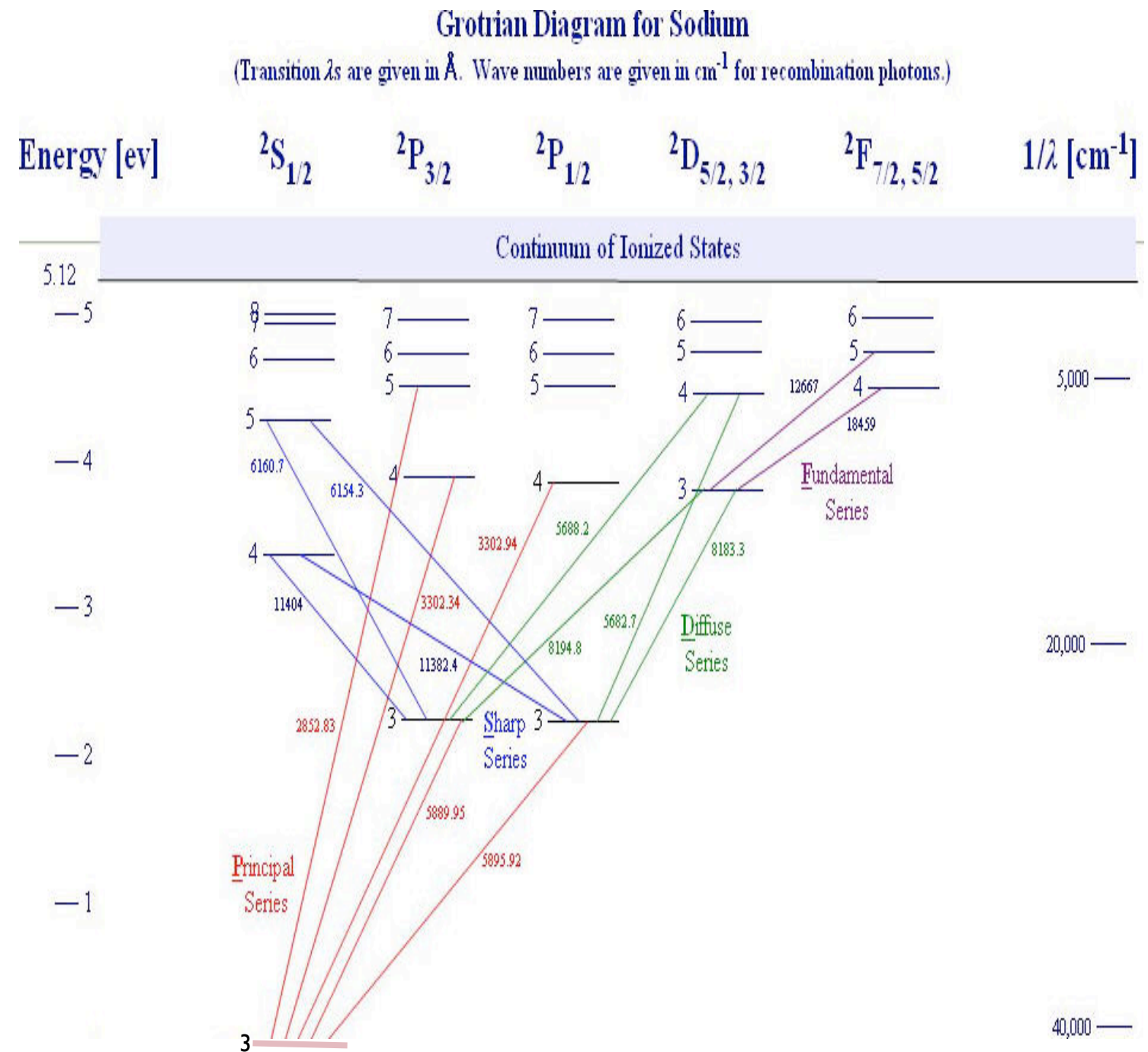
Example: NaI

Quantum Defects for NaI

l	n=3	n=4	n=5	n=6	n=∞
0=s	1.373	1.357	1.353	1.351	1.348
1=p	0.883	0.867	0.862	0.857	0.855
2=d	0.012	0.013	0.014	0.014	0.015
3=f	-	0.00	0.00	0.00	0.00

Spectral Series for NaI

Name	Transition	n values	Multiplicity
Sharp	$n\,^1S_{1/2} \rightarrow 3\,^2P^o_{3/2,1/2}$	n=4,5,6...	doublet
Principle	$n\,^2P^o_{3/2,1/2} \rightarrow 3\,^2S^o_{1/2}$	n=3,4,5,6...	doublet
Diffuse	$n\,^2D_{5/2,3/2} \rightarrow 3\,^2P^o_{3/2,1/2}$	n=3,4,5,6...	Triplet
Fundamental	$n\,^2F^o_{7/2,5/2} \rightarrow 3\,^2D_{5/2,3/2}$	n=4,5,6...	Triplet

Grotrian Diagram for Sodium
(Transition λs are given in Å. Wave numbers are given in cm⁻¹ for recombination photons.)

Spin-Orbit Interaction

In our example of neutral carbon, the lowest energy state was split into three levels. This splitting was due to the interaction between the spin of the electrons and their orbits.
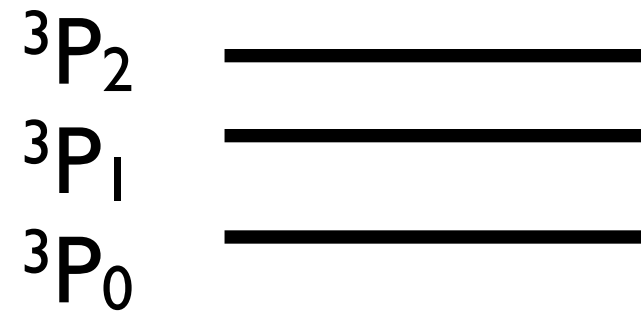
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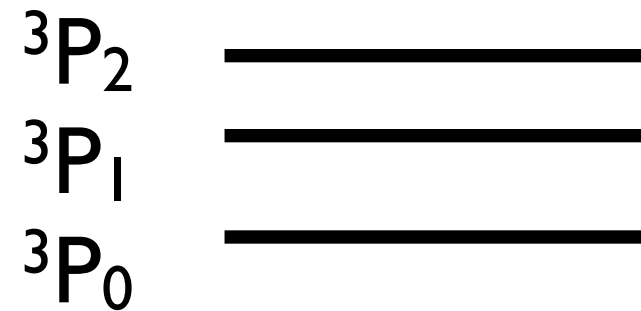
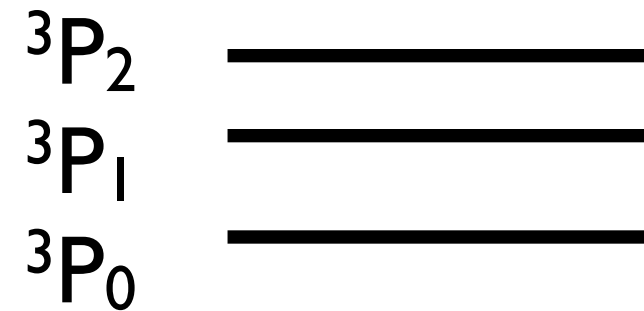**Why are there 3 levels?**

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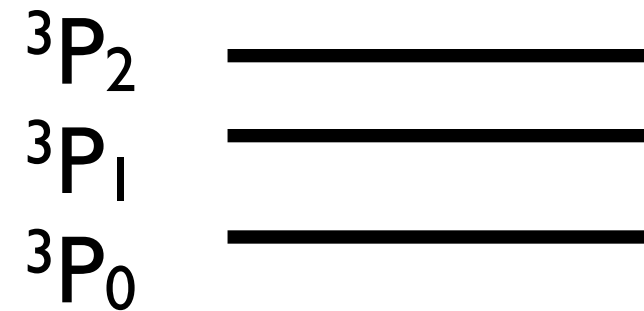
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$$E_{SO} = -\underline{\mu} \cdot \underline{B}$$

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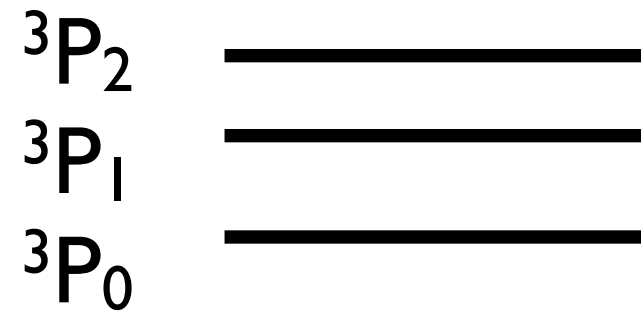$^3P_1$ ——————————

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Why are there 3 levels?

The energy for each of these levels can be estimated from the interaction between the magnetic moment generated from the electron spin and the magnetic field generated by the orbit.

$$E_{SO} = -\underline{\mu} \cdot \underline{B}$$

The magnetic moment from the electron spin is:

Spin-Orbit Interaction

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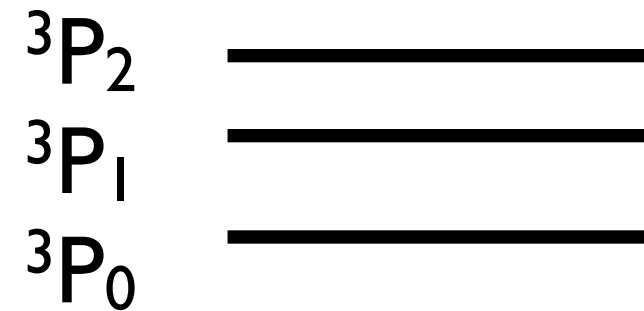
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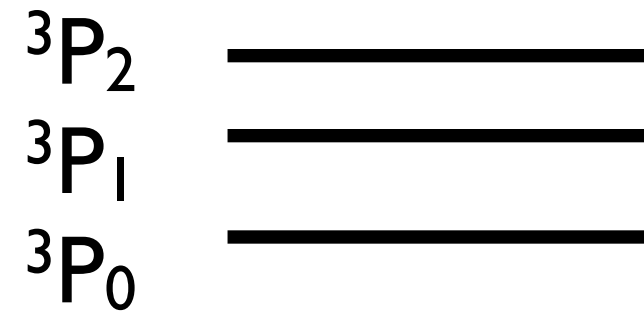
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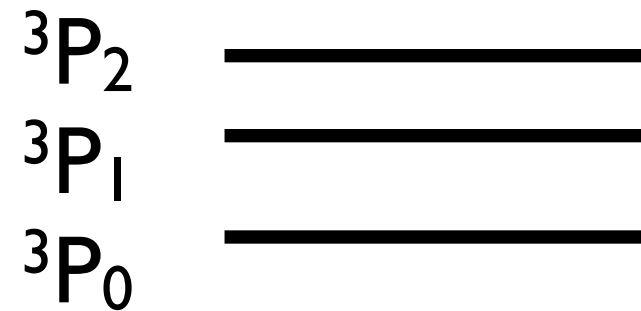$$E_{SO} = -\underline{\mu} \cdot \underline{B}$$

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$$\underline{B} = \frac{\hbar^2}{2}\frac{\underline{v} \times \underline{r}}{m_e r c^2}\frac{dV}{dr} = -\frac{\hbar^2}{2}\frac{\hat{\underline{l}}}{m_e r c^2}\frac{dV}{dr}$$

Spin-Orbit

For a single electron, the spin-orbit interaction can be treated as a perturbation to the Hamiltonian operator, such that:

$$\hat{H}_{SO} = +f(r)\underline{\hat{l}} \cdot \underline{\hat{s}}$$

However, what we care about is the interaction between a multi-electron system. This can be generalized as:

$$\hat{H}_{SO} = +\frac{A(L,S)}{\hbar^2}\hat{L} \cdot \hat{S}$$

Hence the shift in the energy will be given by

$$\Delta E_{SO} = \int \psi^* \hat{H}_{SO} \psi d\tau$$

By applying the quantization of the momentum along with a relationship between the total angular momentum, the energy shift is

$$\Delta E_{SO} = \frac{A(L,S)}{2}[J(J+1) - L(L+1) - S(S+1)]$$

Example: CI

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Applying this equation to the P levels in neutral carbon gives the following values:

Level	L	S	J	$\Delta E/A(L,S)$
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Hence the shift in the energy will be given by

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$2A - 43$ cm^{-1}

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NB: As according to Hund's rules, A(L,S) will be negative for more than half-filled shells

Fine Structure

Fine structure transitions are transitions between different spin orbital states.   For example, in the NaI transition there are the following possibilities for the triplet:

	Ratio of states
$^2D_{3/2}$->$^2P^o_{1/2}$	2
$^2D_{3/2}$->$^2P^o_{3/2}$	4
$^2D_{5/2}$->$^2P^o_{3/2}$	10
$^2D_{5/2}$->$^2P^o_{1/2}$	0

But according to the transition rule that $\Delta J = \pm 1, 0$, the last transition is not allowed. The rates of the transitions are the same, except modulated by the degeneracy of each states.

NB: However in the optically thick case, the ratio becomes nearly 1:1:1

Selection Rules for Transitions

For Electric Dipole Transitions:
1. $\Delta J = 0, \pm 1$ but not 0-0
2. $\Delta M_J = 0, \pm 1$
3. Parity Changes
4. $\Delta S = 0$
5. One electron jumps, Δn any, $\Delta l = \pm 1$
6. $\Delta L = 0, \pm 1$, but not L=0-0

<u>Allowed</u>
Satisfy all rules
$A \sim 10^6$ s

<u>Intercombination</u>
Breaks #4
$A \sim 100$ s
Example: CIII]1908.7
$2s^2\ {}^1S - 2s2p\ {}^3P^o$

<u>Forbidden</u>
Breaks #5 and #6
$A \sim 10^{-8}$ s
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There are also forbidden transitions caused by electric quadrapole and Magnetic dipole

The Einstein Coefficients

The one thing that we haven't had time to treat in this course is how to calculate the rate of transition. This requires a treatment of time-dependent perturbation theory for the quantum mechanical solution for the two level system. The probability for a electron to transition between state a and state b in the presence of an external force is:

$$P_{a->b} = \frac{|V_{ab}|^2}{\hbar^2} \frac{sin^2[(\omega_o - \omega)t/2]}{(\omega_o - \omega)^2]}$$

where the potential for an atom will be given by the electric dipole moment:

$$V_{ab} = -pE_o$$

If we sum over all possible transitions for incident photons of energy density ρ:

$$R_{a->b} = dP/dt = \frac{\pi}{3\epsilon\hbar^2}|p|^2\rho(\omega_o)$$