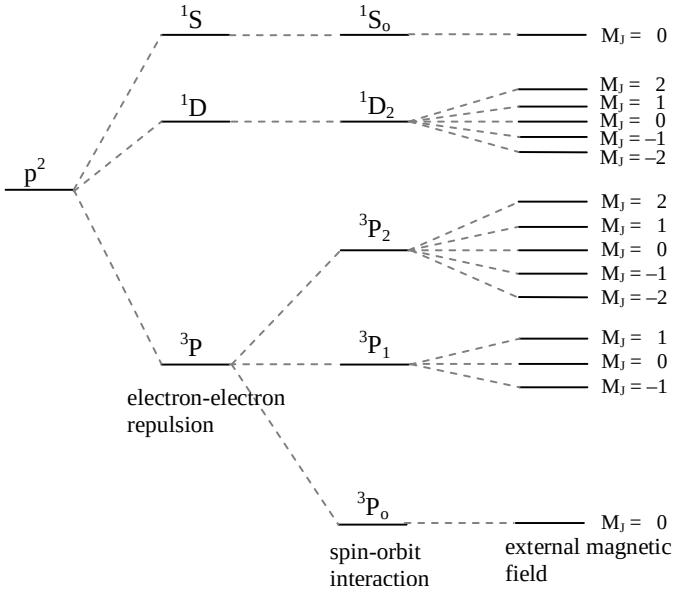
Atomic Spectroscopy



Hund's rules for a given configuration:

1). The terms with maximum S have lowest energy. (Rephrased from Sec. 25.4)
2). For a given value of S, the term with maximum L has lowest energy.
3). For a given S and L, if the open subshell is less than half-full then minimum J has lowest energy. If the open subshell is more than half-full then maximum J has lowest energy.

The energy order for excited state terms usually follow Hund's rules, but exceptions occur.

Carbon p^2 configuration:

Rule 2: $^1D_2 < {}^1S_o$. Both states have the same spin multiplicity, but the $^1D_2$ has higher L.

Rule 3: $^3P_o < {}^3P_1 < {}^3P_2$ Because the p subshell is less than half-full.

Selection Rules Govern the Intensities of Transitions: $\Delta E = h\nu$

transition dipole moment:

$$\mu_{tr} = \langle\hat{\vec{\mu}}\rangle = \int \Psi_j^* (-e\ \hat{\vec{r}})\ \Psi_i\, d\tau \qquad\qquad \hat{\vec{\mu}} = -e\ \hat{\vec{r}}$$

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gross selection rule: non-vanishing transition dipole moment

specific selection rule: conservation of angular momentum. Photon s = 1 $\rightarrow \Delta L = \pm 1$

1. $\Delta S = 0$ for example singlet to triplet transitions are not allowed
2. $\Delta L = \pm 1$ for example S $\not\leftrightarrow$ S is not allowed, but S $\leftrightarrow$ P or P $\leftrightarrow$ D is allowed
3. $\Delta J = 0, \pm 1$ except J = 0 $\not\leftrightarrow$ J = 0 for example $^2P_{½} \not\leftrightarrow {}^2D_{5/2}$ is not allowed

In addition, one n or ℓ must change for one electron: transitions between states with the same configuration are not allowed.

Ground state of Na is $^2S_{½}$: sodium doublet: $^2P_{3/2} \rightarrow {}^2S_{½}$ and $^2P_{½} \rightarrow {}^2S_{½}$

$\Delta S = 0$, $\Delta L = -1$, and $\Delta J = 1$ or 0