10.5: Atomic Configuration Wavefunctions

To express, in terms of Slater determinants, the wavefunctions corresponding to each of the states in each of the levels, one proceeds as follows:

1. For each M_S, M_L combination for which one can write down only one product function (i.e., in the non-equivalent angular momentum situation, for each case where only one product function sits at a given box row and column point), that product function **itself** is one of the desired states. For the p^2 example, the $|p_1\alpha p_0\alpha|$ and $|p_1\alpha p_{-1}\alpha|$ (as well as their four other M_L and M_S "mirror images") are members of the ^3P level (since they have M_S = ±1) and $|p_1\alpha p_1\beta|$ and its M_L mirror image are members of the ^1D level (since they have M_L = ±2).
2. After identifying as many such states as possible by inspection, one uses $L_\pm$ and $S_\pm$ to generate states that belong to the same term symbols as those already identified but which have higher or lower M_L and/or M_S values.
3. If, after applying the above process, there are term symbols for which states have not yet been formed, one may have to construct such states by forming linear combinations that are orthogonal to all those states that have thus far been found.

To illustrate the use of raising and lowering operators to find the states that can not be identified by inspection, let us again focus on the p^2 case. Beginning with three of the ^3P states that are easy to recognize, $|p_1\alpha p_0\alpha|$, $|p_1\alpha p_{-1}\alpha|$, and $|p_{-1}\alpha p_0\alpha|$, we apply S_- to obtain the $M_S = 0$ functions:

$$S_-^3P(M_L=1,M_S=1) = [S_-(1)+S_-(2)]|p_1\alpha p_0\alpha|$$

$$= \hbar\sqrt{1(2)-1(0)}\,^3P(M_L=1,M_S=0)$$

$$= \hbar\sqrt{\frac{1}{2}\left(\frac{3}{2}-\frac{1}{2}\left(-\frac{1}{2}\right)\right)}|p_1\beta p_0\alpha| + \hbar\sqrt{1}|p_1\alpha p_0\beta|,$$

so,

$$^3P(M_L=1,M_S=0) = \frac{1}{\sqrt{2}}[|p_1\beta p_0\alpha| + |p_1\alpha p_0\alpha|].$$

The same process applied to $|p_1\alpha p_{-1}\alpha|$ and $|p_{-1}\alpha p_0\alpha|$ gives

$$\frac{1}{\sqrt{2}}[|p_1\alpha p_{-1}\beta| + |p_1\beta p_{-1}\alpha|]$$

and

$$\frac{1}{\sqrt{2}}[|p_{-1}\beta p_0\beta| + |p_{-1}\beta p_0\alpha|],$$

respectively.

The $^3P(M_L=1,M_S=0) = \frac{1}{\sqrt{2}}[|p_1\beta p_0\alpha| + |p_1\alpha p_0\beta|]$ function can be acted on with L_- to generate $^3P(M_L=0,M_S=0)$:

$$L_-^3P(M_L=1,M_S=0) = [L_-(1)+L_-(2)]\frac{1}{\sqrt{2}}[|p_1\beta p_0\alpha| + |p_1\alpha p_0\beta|]$$

$$= \hbar\sqrt{1(2)-1(0)}\,^3P(M_L=0,M_S=0)$$

$$= \hbar\sqrt{\frac{1(2)-1(0)}{2}}[|p_0\beta p_0\alpha| + |p_0\alpha p_0\beta|] + \hbar\sqrt{\frac{1(2)-0(-1)}{2}}[|p_1\beta p_{-1}\alpha| + |p_1\alpha p_{-1}\beta|],$$

so,

$$^3P(M_L=0,M_S=0) = \frac{1}{\sqrt{2}}[|p_1\beta p_{-1}\alpha| + |p_1\alpha p_{-1}\beta|].$$

The ${}^1D$ term symbol is handled in like fashion. Beginning with the $M_L = 2$ state $|p_1\alpha p_1\beta|$, one applies L_- to generate the M_L = 1 state:

$$L_-^1 D(M_L=2, M_S=0) = [L_-(1)+L_-(1)]|p_1\alpha p_1\beta|$$
$$= \hbar\sqrt{2(3)-2(1)}^1 D(M_L=1, M_S=0)$$
$$= \hbar\sqrt{1(2)-1(0)}[|p_0\alpha p_1\beta| + |p_1\alpha p_0\beta|],$$

so,

$$^D(M_L=1, M_S=0) = \frac{1}{\sqrt{2}}[|p_0\alpha p_1\beta| + |p_1\alpha p_0\beta|]$$

Applying L_- once more generates the ${}^1D(M_L=0, M_S=0)$ state:

$$L_-^1 D(M_L, M_S=0) = \frac{[L_-(1)+L_-(2)]}{\sqrt{2}}[|p_0\alpha p_1\beta| + |p_1\alpha p_0\beta|]$$
$$= \hbar\sqrt{2(3)-1(0)}D(M_L=0, M_S=0)$$
$$= \sqrt{\frac{1(2)-0(-1)}{2}}[|p_{-1}\alpha p_1\beta| + |p_1\alpha p_{-1}\beta|] + \hbar\sqrt{\frac{1(2)-1(0)}{2}}[|p_0\alpha p_0\beta| + |p_0\alpha p_0\beta|]$$

so,

$$^1D(M_L=0, M_S=0) = \frac{1}{\sqrt{6}}[2|p_0\alpha p_0\beta| + |p_{-1}\alpha p_1\beta| + |p_1\alpha p_{-1}\beta|].$$

Notice that the $M_L = 0, M_S = 0$ states of ${}^3P$ and of ${}^1D$ are given in terms of the three determinants that appear in the "center" of the p^2 box diagram:

$$^1D(M_L=0, M_S=0) = \frac{1}{\sqrt{6}}[|2p_0\alpha p_0\beta| + |p_{-1}\alpha p_1\beta| + |p_1\alpha p_{-1}\beta|],$$
$$^3P(M_L=0, M_S=0)\frac{1}{\sqrt{2}}[|p_1\beta p_{-1}\alpha| + |p_1\alpha p_{-1}\beta|]$$
$$\frac{1}{\sqrt{2}}[-|p_{-1}\alpha p_1\beta| + |p_1\alpha p_{-1}\beta|].$$

The only state that has eluded us thus far is the ${}^1S$ state, which also has $M_L = 0$ and $M_S = 0$. To construct this state, which must also be some combination of the three determinants with $M_L = 0$ and $M_S = 0$, we use the fact that the ${}^1S$ wavefunction **must** be orthogonal to the ${}^3P$ and ${}^1D$ functions because ${}^1S, {}^3P$, and ${}^1D$ are eigenfunctions of the hermitian operator L^2 having different eigenvalues. The state that is normalized and is a combination of$p_0\alpha p_0\beta|$, $|p_{-1}\alpha p_1\beta|$, and $|p_1\alpha p_{-1}\beta|$ is given as follows:

$$^1S = \frac{1}{\sqrt{3}}[|p_0\alpha p_0\beta| - |p_{-1}\alpha p_1\beta| - |p_1\alpha p_{-1}\beta|].$$