2.28: A Tensor Algebra Approach to Spin-Orbit Coupling

The p^1, d^1 and f^1 electronic configurations have six, ten and fourteen microstates, respectively. The degeneracies of these microstates are split by the interaction between magnetic fields associated with spin and orbital angular momentum - the spin-orbit interaction. As is well know the p1 configuration gives rise to a $^2P_{3/2}(4)$ and $^2P_{1/2}(2)$ term under the Russell-Saunders coupling scheme. The d_1 configuration yields a $^2D_{5/2}(6)$ and $^2D_{3/2}(4)$ term. The f^1 configuration consists of $^2F_{7/2}(8)$ and $^2F_{5/2}(6)$ terms. The numbers in parentheses are the degeneracies associated with the term symbols.

In what follows, tensor algebra will be used to calculate the spin-orbit interaction in the p^1, d^1 and f^1 electronic configurations. An approximate energy level diagram for the three electronic configurations will also be presented. The required spin and angular momentum operators (in atomic units) are provided below.

Spin angular momentum operators for spin 1/2:

$$S_x = \tfrac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad S_y = \tfrac{1}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad S_z = \tfrac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Orbital angular momentum operators for L = 1 and 2 (see E. E. Anderson, *Modern Physics and Quantum Mechanics*, pp 298-300):

$$L1_x = \tfrac{1}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad L1_y = \tfrac{1}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix} \quad L1_z = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$L2_x = \tfrac{1}{2}\begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 2 & 0 & \sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & \sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & 2 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix} \quad L2_y = \tfrac{i}{2}\begin{pmatrix} 0 & -2 & 0 & 0 & 0 \\ 2 & 0 & -\sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & -\sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & -2 \\ 0 & 0 & 0 & 2 & 0 \end{pmatrix} \quad L2_z = \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -2 \end{pmatrix}$$

The spin-orbit Hamiltonian in tensor format to within a multiplicative constant which depends on the principle and angular momentum quantum numbers is as follows.

$$\hat{H}_{LS} = \hat{L} \otimes \hat{S} = \hat{L}_x \otimes \hat{S}_x + \hat{L}_y \otimes \hat{S}_y + \hat{L}_z \otimes \hat{S}_z$$

For the p^1 electronic configuration L = 1 and S = 1/2. The spin-orbit Hamiltonian and its eigenvalues are calculated as shown below. Kronecker is Mathcad's command for matrix tensor multiplication.

$$H_{LS} = \text{kronecker}\left(L1_x,\ S_x\right) + \text{kronecker}\left(L1_y,\ S_y\right) + \text{kronecker}\left(L1_z,\ S_z\right)$$

$$\text{E} = \text{sort}\left(\text{eigenvals}\left(H_{LS}\right)\right) \quad E^T = \begin{pmatrix} -1 & -1 & 0.5 & 0.5 & 0.5 & 0.5 \end{pmatrix}$$

We see that these results are as expected. We have two -1 eigenstates corresponding to the $^2P_{1/2}$ term and four 0.5 eigenstates corresponding to the $^2P_{3/2}$ term.

For the d^1 electronic configuration L = 2 and S = 1/2. The spin-orbit Hamiltonian and its eigenvalues are now calculated.

$$H_{LS} = \left(\text{kronecker}\left(L2_x,\ S_x\right) + \text{kronecker}\left(L2_y,\ S_y\right) + \text{kronecker}\left(L2_z,\ S_z\right)\right)$$

$$\text{E} = \text{sort}\left(\text{eigenvals}\left(H_{LS}\right)\right) \quad E^T = \begin{pmatrix} -1.5 & -1.5 & -1.5 & -1.5 & 1 & 1 & 1 & 1 & 1 & 1 \end{pmatrix}$$

Again the results are as expected. We have four -1.5 eigenstates corresponding to the $^2D_{3/2}$ term and a six-fold degenerate state at +1.0 corresponding to the $^2D_{5/2}$ term.

L = 3 for the f^1 configuration. The angular momentum operators for L = 3 were obtained by a study of the trends in the other angular momentum operators as L increased. To demonstrate that this procedure yielded the correct matrix operators it is shown that the x-y commutator for L = 3 is satisfied.

$$L3_x = \frac{1}{2}\begin{pmatrix} 0 & \sqrt{6} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{6} & 0 & \sqrt{10} & 0 & 0 & 0 & 0 \\ 0 & \sqrt{10} & 0 & 0 & 0 & 0 & \\ 0 & 0 & \sqrt{12} & 0 & \sqrt{12} & 0 & 0 \\ 0 & 0 & 0\sqrt{12}0 & \sqrt{12} & 0 & & \\ 0 & 0 & 0 & 0 & \sqrt{10} & 0 & \sqrt{6} \\ 0 & 0 & 0 & 0 & 0 & \sqrt{6} & 0 \end{pmatrix} \quad L3_y = \frac{i}{2}\begin{pmatrix} 0 & -\sqrt{6} & 0 & 0 & 0 & 0 & 0 \\ \sqrt{6} & 0 & -\sqrt{10} & 0 & 0 & 0 & 0 \\ 0 & \sqrt{10} & 0 & -\sqrt{12} & 0 & 0 & 0 \\ 0 & 0 & \sqrt{12} & 0 & -\sqrt{12} & 0 & 0 \\ 0 & 0 & 0 & \sqrt{12} & 0 & -\sqrt{10} & 0 \\ 0 & 0 & 0 & 0\sqrt{10} & 0 & -\sqrt{10} & \end{pmatrix}$$

$$L3_z = \begin{pmatrix} 3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3 \end{pmatrix} \quad L3_x L3_y - L3_y L3_x \to \begin{pmatrix} 3i & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2i & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & i & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -i & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -2i & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -3i \end{pmatrix}$$

The spin-orbit Hamiltonian and its eigenvalues are now calculated.

$$H_{LS} = (\text{kronecker}\,(L3_x,\ S_x) + \text{kronecker}\,(L3_y,\ S_y) + \text{kronecker}\,(L3_z,\ S - z))$$

The six states at -2 correspond to a $^2F_{5/2}$ term and the eight states at 1.5 belong to a $^2F_{7/2}$ term. These results are in agreement with expectations.

Using these results and the hydrogen atom energy equation as a function of the n and j quantum numbers, we can construct a diagram of the spin-orbit fine structure and its j-level degeneracy for the n = 4 level.

$$E = -\frac{1}{2n^2}\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

$$4f^1 \to F_{7/2}$$

$$4d^1,\ 4f^1 \to {}^2F_{5/2},\ {}^2D_{5/2}$$

$$4p^1,\ 4d^1 \to {}^2D_{3/2},\ {}^2P_{3/2}$$

$$4s^1,\ 4p^1 \to {}^2P_{1/2},\ {}^2S_{1/2}$$