A Tensor Algebra Approach to Spin-Orbit Coupling

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The \( p^1 \) and \( d^1 \) electronic configurations have six and ten 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 known the \( p^1 \) 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 numbers in parentheses are the degeneracies of the states.

In what follows, tensor algebra will be used to analyze the spin-orbit interaction in the \( p^1 \) and \( d^1 \) electronic configurations.

The required spin and angular momentum operators (in atomic units) are provided below.

Spin angular momentum operators for spin \( 1/2 \):

\[
S_x := \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y := \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad S_z := \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\]

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

\[
L_1 x := \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \end{pmatrix}, \quad L_1 y := \frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \quad L_1 z := \begin{pmatrix} 1 & 0 \\ 0 & 0 \\ 0 & -1 \end{pmatrix}
\]

\[
L_2 x := \frac{1}{2} \begin{pmatrix} 0 & 2 & 0 & 0 & 0 \\ 2 & 0 & \sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & \sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & 2 \\ 0 & 0 & 0 & 0 & 2 \end{pmatrix}, \quad L_2 y := \frac{i}{2} \begin{pmatrix} 0 & -2 & 0 & 0 & 0 \\ 2 & 0 & -\sqrt{6} & 0 & 0 \\ 0 & \sqrt{6} & 0 & -\sqrt{6} & 0 \\ 0 & 0 & \sqrt{6} & 0 & -2 \\ 0 & 0 & 0 & 0 & 2 \end{pmatrix}, \quad L_2 z := \begin{pmatrix} 2 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -2 & 0 \end{pmatrix}
\]

The spin-orbit Hamiltonian in tensor format to within a multiplicative constant 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.

\[
H_{LS} := \text{kronecker}(L1_x, S_x) + \text{kronecker}(L1_y, S_y) + \text{kronecker}(L1_z, S_z)
\]

\[
E := \text{sort(eigenvals}(H_{LS})) \quad E^T = (-1 \quad -1 \quad 0.5 \quad 0.5 \quad 0.5)
\]
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.

\[
H_{LS} := \text{kronocker}(L2_x, S_x) + \text{kronocker}(L2_y, S_y) + \text{kronocker}(L2_z, S_z)
\]

\[
E := \text{sort(eigvals}(H_{LS}))
\]

\[
E^T = (-1.5 \enspace -1.5 \enspace -1.5 \enspace -1.5 \enspace 1 \enspace 1 \enspace 1 \enspace 1 \enspace 1)
\]

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.