5.80 Small-Molecule Spectroscopy and Dynamics
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Problem Set #2

1. (a) Construct the state $|L = 2, S = 1, J = 1, M_J = 0\rangle$ from the $|LM_L\ S\ M_S\rangle$ basis using the ladder operator plus orthogonality technique.

   (b) Construct the states
   $|L = 2, S = 1, J = 1, M_J = 0\rangle \quad {}^3D_1$
   $|L = 2, S = 2, J = 1, M_J = 0\rangle \quad {}^5D_1$
   $|L = 5, S = 2, J = 3, M_J = 1\rangle \quad {}^5H_3$
   from the $|L\ M_L\ S\ M_S\rangle$ basis using Clebsch-Grodan coefficients. The ${}^3D_1$ function is the same as in Part (a) and is intended as a consistency check.

2. We know that the spin-orbit Hamiltonian, $\mathbf{H}^{\text{SO}} = AL \cdot S$, is diagonal in the $|L\ S\ J\ M_J\rangle$ basis but not in the $|L\ M_L\ S\ M_S\rangle$ basis.

   (a) Construct the full nine by nine $\mathbf{H}^{\text{SO}}$matrix in the $|L = 1\ M_L\ S = 1\ M_S\rangle$ basis.

   (b) Construct the
   $|L = 1, S = 1, J = 2, M_J = 0\rangle \quad {}^3P_2$
   $|L = 1, S = 1, J = 1, M_J = 0\rangle \quad {}^3P_1$
   and $|L = 1, S = 1, J = 0, M_J = 0\rangle \quad {}^3P_0$
   functions in the $|L\ M_L\ S\ M_S\rangle$ basis.

   (c) Show that the matrix elements
   $\left\langle L = 1, S = 1, J = 2, M_J = 0 \middle| \mathbf{H}^{\text{SO}} \middle| 1, 1, 2, 0 \right\rangle$
   $\left\langle 1, 1, 2, 0 \middle| \mathbf{H}^{\text{SO}} \middle| 1, 1, 1, 0 \right\rangle$
   $\left\langle 1, 1, 2, 0 \middle| \mathbf{H}^{\text{SO}} \middle| 1, 1, 0, 0 \right\rangle$
   $\left\langle 1, 1, 1, 0 \middle| \mathbf{H}^{\text{SO}} \middle| 1, 1, 1, 0 \right\rangle$
   $\left\langle 1, 1, 1, 0 \middle| \mathbf{H}^{\text{SO}} \middle| 1, 1, 0, 0 \right\rangle$
   $\left\langle 1, 1, 0, 0 \middle| \mathbf{H}^{\text{SO}} \middle| 1, 1, 0, 0 \right\rangle$
   expressed in terms of the $|L\ M_L\ S\ M_S\rangle$ basis in part (b) have the values expected from $L{\cdot}S = 1/2\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$ evaluated in the $|L\ S\ J\ M_J\rangle$ basis.

3. Calculate the energies for the hydrogenic systems **H** and Li^{2+} in the following states:

   $2\,^2P_{1/2}$ (means $n = 2$, $s = 1/2$, $\ell = 1$, $j = 1/2$)

   $2\,^2P_{3/2}$

   $3\,^2P_{1/2}$

   $3\,^2P_{3/2}$

   $3\,^2D_{3/2}$

   $3\,^2D_{5/2}$

   Please express "energies" in cm^{-1}: $\sigma = \frac{E}{hc}\text{cm}^{-1}$ and locate the zero of energy at $n = \infty$.

4. Consider the $(nd)^2$ configuration.

   (a) There are 10 distinct spin-orbitals associated with nd; how many Pauli-allowed $(nd)^2$ Slater determinants can you form using two of these spin-orbitals?

   (b) What are the $L - S$ states associated with the $(nd)^2$ configuration? Does the sum of their degeneracies agree with the configurational degeneracy in part (a)?

   (c) What is the lowest energy triplet state ($S = 1$) predicted by Hund's rules? Does Hund's rule predict the lowest energy singlet state?

   (d) Calculate the energies of all states (neglecting spin-orbit splitting) which arise from $(nd)^2$ in terms of the radial energy parameters F^0, F^2, and F^4. [This is a long and difficult problem. The similar $(np)^2$ problem is worked out in detail in Condon and Shortley, pages 191-193, and in Tinkham, pages 177-178. The result for $(nd)^2$ is also given, without explanation and in slightly different notation, Condon and Shortley, page 202.] What relationship between F^2 and F^4 is required by Hund's rules?

5. If an atom is in a $(2p)^2\ ^3P_0$ state, to which of the following states is an electric dipole transition allowed? Explain in each case.

   (a) $2p3d\ ^3D_2$

   (b) $2s2p\ ^3P_1$

   (c) $2s3s\ ^3S_1$

   (d) $2s2p\ ^1P_1$