5.80 Small-Molecule Spectroscopy and Dynamics
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Problem Set #2 ANSWERS

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.

ANSWER:

$|L=2, S=1, J=1, M_J=0\rangle$

We know that $|L=2, S=1, J=3, M_J=3\rangle = |L=2, S=1, M_L=2, M_S=1\rangle$

$\Rightarrow \mathbf{J}_-|2133\rangle = (\mathbf{L}_- + \mathbf{S}_-)|2121\rangle$

$\sqrt{6}|2132\rangle = 2|2111\rangle + \sqrt{2}|2120\rangle$

$|2132 = \frac{2}{\sqrt{6}}|2111\rangle + \frac{1}{\sqrt{3}}|2120\rangle$

(L S J M$_S$) (L S M$_L$ M$_S$)

$|2\ 1\ 2\ 2\rangle = a|2\ 1\ 1\ 1\rangle + b|2120\rangle$ where $a^2 + b^2 = 1$

and $\langle 2132|2122\rangle = 0 = \frac{2a}{\sqrt{6}}\langle 2111|2111\rangle + \frac{b}{\sqrt{3}}\langle 2120|2120\rangle = \frac{1}{\sqrt{16}}(2a + b\sqrt{2})$

$\Rightarrow \left\langle 2122\right| = \frac{-1}{\sqrt{3}}\left|2111\right\rangle + \sqrt{\frac{2}{3}}|2120\rangle$

$\mathbf{J}_-|2122\rangle = (\mathbf{L}_- + \mathbf{S}_-)\left[\frac{-1}{\sqrt{3}}|2121\rangle + \sqrt{\frac{2}{3}}|2120\rangle\right]$

$\Rightarrow |2121\rangle = \frac{1}{\sqrt{3}}|212-1\rangle + \frac{1}{\sqrt{6}}|2110\rangle - \frac{1}{\sqrt{2}}|2101\rangle$

Then $\mathbf{J}_-|L=2, S=1, J=3, M_J=2\rangle = (\mathbf{L}_- + \mathbf{S}_-)\left[\frac{2}{\sqrt{6}}|2111\rangle + \frac{1}{\sqrt{3}}|2320\rangle\right]$

$\Rightarrow |2131\rangle = \frac{2}{\sqrt{10}}|2101\rangle + \frac{4}{\sqrt{30}}|2110\rangle + \frac{1}{\sqrt{15}}|212-1\rangle$

We know that $|L=2, S=1, J=1, M_S=1\rangle = a|2101\rangle + b|2110\rangle + c|212-1\rangle$

$\langle L=2, S=1, J=1, M_J=1|L=2, S=1, J=2, M_J=1\rangle = 0$

and $\langle L=2, S=1, J=1, M_J=1|L=2, S=1, J=3, M_J=1\rangle = 0$

$$\left.\begin{aligned} \Rightarrow \frac{2a}{\sqrt{10}} + \frac{4b}{\sqrt{30}} + \frac{c}{\sqrt{15}} &= 0 \\ a^2 + b^2 + c^2 &= 1 \\ -\frac{a}{\sqrt{2}} + \frac{b}{\sqrt{6}} + \frac{c}{\sqrt{3}} &= 0 \end{aligned}\right\} \quad \text{so} \quad \begin{aligned} a &= \frac{1}{\sqrt{10}} \\ b &= \sqrt{\frac{3}{10}} \\ c &= -\sqrt{\frac{3}{5}} \end{aligned}$$

so $\left\langle L=2, S=1, J=1, M_J=1\right| = -\frac{1}{\sqrt{10}}\left|2101\right\rangle + \sqrt{\frac{3}{10}}|2110\rangle - \sqrt{\frac{3}{5}}|212-1\rangle$

then operating on both sides with $\mathbf{J}_- = \mathbf{S}_- + \mathbf{L}_-$ we get $|L=2, S=1, J=1, M_J=0\rangle = \sqrt{\frac{3}{10}}|21-11\rangle - \sqrt{\frac{4}{10}}|2100\rangle + \sqrt{\frac{3}{10}}|211-1\rangle$

(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-Gordan coefficients. The $^3D_1$ function is the same as in Part (a) and is intended as a consistency check.

ANSWER:

$|L = 2, S = 1, J = 1, M_J = 0\rangle$

Since $S \equiv j_2 = 1$ look in table 2^3 of Condon and Shortley,
also $J \equiv j = j_1 - 1$ look in column 3

then $|L = 2, S = 1, J = 1, M_J = 0\rangle = \sqrt{\frac{(2-0)(2-0+1)}{2 \cdot 2(2 \cdot 2+1)}}|L = 2, S = 1, M_L = -1, M_S = 1\rangle$

$+ \sqrt{\frac{(2-0)(2+0)}{2(2 \cdot 2+1)}}|L = 2, S = 1, M_L = 0, M_S = 0\rangle + \sqrt{\frac{(2+0+1)(2+0)}{2 \cdot 2(2 \cdot 2+1)}}|L = 2, S = 1, M_L = 1, M_S = -1\rangle$

$|L = 2, S = 1, J = 1, M_J = 0\rangle = \sqrt{\frac{3}{10}}|L = 2, S = 1, M_L = -1, M_S = 1\rangle$

$+ \sqrt{\frac{2}{10}}|L = 2, S = 1, M_L = 0, M_S = 0\rangle + \sqrt{\frac{3}{10}}|L = 2, S = 1, M_L = 1, M_S = -1\rangle$

$|L = 2, S = 2, J = 1, M_J = 0\rangle = \frac{-2}{\sqrt{10}}|L = 2, S = 2, M_L = -2, M_S = 2\rangle$

$+ \frac{1}{\sqrt{10}}|L = 2, S = 2, M_L = -1, M_S = 1\rangle + 0|L = 2, S = 2, M_L = 0, M_S = 0\rangle$

$- \frac{1}{\sqrt{10}}|L = 2, S = 2, M_L = 1, M_S = -1\rangle + \frac{2}{\sqrt{10}}|L = 2, S = 2, M_L = 2, M_S = -2\rangle$

$$\left.\begin{array}{l} |L = 5, S = 2, J = 3, M_S = 1\rangle = |L = 5, S = 2, M_L = -1, M_S = 2\rangle \\ -|L = 5, S = 2, M_L = 0, M_S = 1\rangle - |L = 5, S = 2, M_L = 1, M_S = 0\rangle \\ -|L = 5, S = 2, M_L = 2, M_S = -1\rangle - |L = 5, S = 2, M_L = 3, M_S = -2\rangle \end{array}\right\} \quad \text{these are not correct}$$

2. We know that the spin-orbit Hamiltonian, $\mathbf{H}^{\mathrm{SO}} = A\mathbf{L}\cdot\mathbf{S}$, 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 $\mathbf{H}^{\mathrm{SO}}$matrix in the $|L = 1\;M_L\;S = 1\;M_S\rangle$ basis.

ANSWER:
The nine basis functions are:

	$\lvert LS\,M_L M_S\rangle$
$\lvert 1\rangle$	$\lvert 11-1-1\rangle$
$\lvert 2\rangle$	$\lvert 1111\rangle$
$\lvert 3\rangle$	$\lvert 1100\rangle$
$\lvert 4\rangle$	$\lvert 111-1\rangle$
$\lvert 5\rangle$	$\lvert 11-11\rangle$
$\lvert 6\rangle$	$\lvert 110-1\rangle$
$\lvert 7\rangle$	$\lvert 1101\rangle$
$\lvert 8\rangle$	$\lvert 1110\rangle$
$\lvert 9\rangle$	$\lvert 11-10\rangle$

The diagonal matrix elements: $\langle i|A\mathbf{L}\cdot\mathbf{S}|i\rangle = \left\langle i|A(\mathbf{L}_z\mathbf{S}_z + \frac{1}{2}[\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+])|i\right\rangle = A\,\langle i|\mathbf{L}_z\mathbf{S}_z|i\rangle$
So

$$H_{11} = H_{22} = A$$
$$H_{33} = H_{66} = H_{77} = H_{88} = H_{99} = 0$$
$$H_{44} = H_{55} = -A$$

The operators $\mathbf{L}_\pm\mathbf{S}_\mp$ connect states with $\Delta M_L = \mp1$ and $\Delta M_S = \pm1$.
So

$$H_{35} = H_{53} = A$$
$$H_{34} = H_{43} = A$$
$$H_{69} = H_{96} = A$$
$$H_{78} + H_{87} = A$$

All the rest are zero!

   (b) Construct the

$|L = 1, S = 1, J = 2, M_J = 0\rangle$ $^3P_2$
$|L = 1, S = 1, J = 1, M_J = 0\rangle$ $^3P_1$
and $|L = 1, S = 1, J = 0, M_J = 0\rangle$ $^3P_0$

functions in the $|L\,M_L\,S\;M_S\rangle$ basis.

ANSWER:
$|L = 1, S = 1, J = 2, M_J = 0\rangle = \frac{1}{\sqrt{6}}\,|L = 1, S = 1, M_L = -1, M_S = 1\rangle$
$+\frac{2}{\sqrt{6}}\,|L = 1, S = 1, M_L = 0, M_S = 0\rangle + \frac{1}{\sqrt{6}}\,|L = 1, S = 1, M_L = 1, M_S = -1\rangle$
$|L = 1, S = 1, J = 1, M_J = 0\rangle = -\frac{1}{\sqrt{2}}\,|L = 1, S = 1, M_L = -1, M_S = 1\rangle$
$+\frac{1}{\sqrt{2}}\,|L = 1, S = 1, M_L = 1, M_S = -1\rangle$
$|L = 1, S = 1, J = 0, M_J = 0\rangle = \frac{1}{\sqrt{3}}\,|L = 1, S = 1, M_L = -1, M_S = 1\rangle$
$-\frac{1}{\sqrt{3}}\,|L = 1, S = 1, M_L = 0, M_S = 0\rangle + \frac{1}{\sqrt{3}}\,|L = 1, S = 1, M_L = 1, M_S = -1\rangle$

(c) Show that the matrix elements

$\left\langle L=1, S=1, J=2, M_J=0 \left|\mathbf{H}^{\mathrm{SO}}\right| 1,1,2,0\right\rangle$

$\left\langle 1,1,2,0 \left|\mathbf{H}^{\mathrm{SO}}\right| 1,1,1,0\right\rangle$

$\left\langle 1,1,2,0 \left|\mathbf{H}^{\mathrm{SO}}\right| 1,1,0,0\right\rangle$

$\left\langle 1,1,1,0 \left|\mathbf{H}^{\mathrm{SO}}\right| 1,1,1,0\right\rangle$

$\left\langle 1,1,1,0 \left|\mathbf{H}^{\mathrm{SO}}\right| 1,1,0,0\right\rangle$

$\left\langle 1,1,0,0 \left|\mathbf{H}^{\mathrm{SO}}\right| 1,1,0,0\right\rangle$

expressed in terms of the $|L\ M_L\ S\ M_S\rangle$ basis in part (b) have the values expected from $\mathbf{L}\cdot\mathbf{S} = 1/2\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$ evaluated in the $|L\ S\ J\ M_J\rangle$ basis.

ANSWER:

$\langle 1120|A\mathbf{L}\cdot\mathbf{S}|1120\rangle = \frac{1}{2}A\left\langle 1120|\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2|1120\right\rangle = \frac{1}{2}A[2(2+1) - 1(1+1) - 1(1+1)] = \frac{1}{2}A[2] = A$

$\langle 1120| = \frac{1}{\sqrt{6}}\langle 11-11| + \frac{2}{\sqrt{6}}\langle 1100| + \frac{1}{\sqrt{6}}\langle 111-1|$

$\Rightarrow \langle 1120|A\mathbf{L}\cdot\mathbf{S}|1120\rangle = \frac{1}{6}\langle 11-11|A\mathbf{L}_z\mathbf{S}_z|11-11\rangle + \frac{2}{3}\langle 1100|A\mathbf{L}_z\mathbf{S}_z|1100\rangle + \frac{1}{6}\langle 111-1|A\mathbf{L}_z\mathbf{S}_z|111-1\rangle + \frac{2}{6}\left\langle 11-11\left|\frac{1}{2}A\mathbf{L}_-\mathbf{S}_+\right|1100\right\rangle + \frac{2}{6}\left\langle 1100\left|\frac{1}{2}A\mathbf{L}_+\mathbf{S}_-\right|11-11\right\rangle + \frac{2}{6}\left\langle 111-1\left|\frac{1}{2}A\mathbf{L}_+\mathbf{S}_-\right|1100\right\rangle + \frac{2}{6}\left\langle 1100\left|\frac{1}{2}A\mathbf{L}_-\mathbf{S}_+\right|111-1\right\rangle = A\left(-\frac{1}{6} - \frac{1}{6} + \frac{2}{6} + \frac{2}{6} + \frac{2}{6} + \frac{2}{6}\right) = A$

$\left\langle 1120|\mathbf{H}^{\mathrm{SO}}|1110\right\rangle = 0$

$\langle 1120| = \frac{1}{\sqrt{6}}[\langle 11-11| + 2\langle 1100| + \langle 111-1|]$

$\langle 1110| = \frac{-1}{\sqrt{2}}[\langle 11-11| - \langle 111-1|]$

so $\langle 1120|\mathbf{H}^{\mathrm{SO}}|1110\rangle = \frac{-1}{\sqrt{12}}\langle 11-11|\mathbf{H}^{\mathrm{SO}}|11-11\rangle + \frac{1}{\sqrt{12}}\langle 111-1|\mathbf{H}^{\mathrm{SO}}|111-1\rangle - \frac{2}{\sqrt{12}}\langle 1100|\mathbf{H}^{\mathrm{SO}}|11-11\rangle + \frac{2}{\sqrt{12}}\langle 1100|\mathbf{H}^{\mathrm{SO}}|111-1\rangle = 0$

$\left\langle 1120|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle = 0$

$\langle 1120| = \frac{1}{\sqrt{6}}[\langle 11-11| + 2\langle 1100| + \langle 111-1|]$

$\langle 1100| = \frac{1}{\sqrt{3}}[\langle 11-11| - \langle 1100| + \langle 111-1|]$

so $\langle 1120|\mathbf{H}^{\mathrm{SO}}|1100\rangle = \frac{1}{\sqrt{18}}\langle 11-11|\mathbf{H}^{\mathrm{SO}}|11-11\rangle + \frac{2}{\sqrt{18}}\langle 1100|\mathbf{H}^{\mathrm{SO}}|1100\rangle - \frac{1}{\sqrt{18}}\langle 111-1|\mathbf{H}^{\mathrm{SO}}|111-1\rangle + \frac{2}{\sqrt{18}}\langle 1100|\mathbf{H}^{\mathrm{SO}}|11-11\rangle + \frac{2}{\sqrt{18}}\langle 1100|\mathbf{H}^{\mathrm{SO}}|111-1\rangle - \frac{1}{\sqrt{18}}\langle 11-11|\mathbf{H}^{\mathrm{SO}}|1100\rangle - \frac{1}{\sqrt{18}}\langle 111-1|\mathbf{H}^{\mathrm{SO}}|1100\rangle = \frac{A}{\sqrt{18}}(-1-1+2+2-1-1) = 0$

$\langle 1110|\mathbf{H}^{\mathrm{SO}}|1110\rangle = \frac{A}{2}[1(1+1) - 1(1+1) - 1(1+1)] = -A$

$\langle 1110| = \frac{-1}{\sqrt{2}}[|11-11\rangle - |111-1\rangle]$

So $\langle 1110|\mathbf{H}^{\mathrm{SO}}|1110\rangle = \frac{A}{2}[\langle 11-11|\mathbf{H}^{\mathrm{SO}}|11-11\rangle + \langle 111-1|\mathbf{H}^{\mathrm{SO}}|111-1\rangle] = \frac{A}{2}[-1-1] = -A$

$\left\langle 1110|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle = 0$

$|1110\rangle = \frac{-1}{\sqrt{2}}[|11-11\rangle - |111-1\rangle]$

$|1100\rangle = \frac{1}{\sqrt{3}}[|11-11\rangle - |1100\rangle + |111-1\rangle]$

So $\left\langle 1110|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle = \frac{-A}{\sqrt{6}}[\left\langle 11-11|\mathbf{H}^{\mathrm{SO}}|11-11\right\rangle - \left\langle 111-1|\mathbf{H}^{\mathrm{SO}}|111-1\right\rangle - \left\langle 11-11|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle + \left\langle 111-1|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle] = \frac{-A}{\sqrt{6}}(-1+1-1+1) = 0$

$\left\langle 1100|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle = \frac{A}{2}(0(0+1) - 1(1+1) - 1(1+1)) = -2A$

$|1100\rangle = \frac{1}{\sqrt{3}}[|11-11\rangle - |1100\rangle + |111-1\rangle]$

So $\left\langle 1100|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle = \frac{1}{3}[\left\langle 11-11|\mathbf{H}^{\mathrm{SO}}|11-11\right\rangle + \left\langle 111-1|\mathbf{H}^{\mathrm{SO}}|111-1\right\rangle - \left\langle 1100|\mathbf{H}^{\mathrm{SO}}|11-11\right\rangle - \left\langle 1100|\mathbf{H}^{\mathrm{SO}}|111-1\right\rangle - \left\langle 11-11|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle - \left\langle 111-1|\mathbf{H}^{\mathrm{SO}}|1100\right\rangle] = \frac{A}{3}[-1-1-1-1-1-1] = -2A$

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 $n = \infty$.

ANSWER:

$$E_{n,\ell,s,j} = E_n^\circ + E_{\text{spin-orbit}}$$
$$E_n^\circ = \frac{-\Re Z^2}{n^2}\left(\frac{\mu}{m_e}\right)(\text{cm}^{-1})$$
$$\Re = \text{Rydberg constant}$$
$$Z = \text{nuclear charge}$$
$$\frac{\mu}{m_e} = \frac{m_e m_N}{m_e(m_e + m_N)}$$

and

$$E_{\text{spin-orbit}} = \left(\frac{5.90\ \text{cm}^{-1}}{2}\right)\frac{Z^4[j(j+1) - \ell(\ell+1) - s(s+1)]}{n^3\left(\ell + \frac{1}{2}\right)(\ell+1)\ell}$$

For Hydrogen $Z = 1$, $\frac{\mu}{m_e} = 0.999456$, $\Re = 109737.42\ \text{cm}^{-1}$
For Li^{2+} $Z = 3$, $\frac{\mu}{m_e} = 0.9999218$.

Term	Hydrogen			Lithium		
	E_n°	E_{S-0}	E	E_n°	E_{S0}	E
$2^2P_{1/2}$	−27919.43	−.246	−27419.68	−246889.89	−19.91	−109798.75
$2^2P_{3/2}$	−27919.43	.123	−27419.31	−246889.89	9.96	−109718.88
$3^2P_{1/2}$	−12186.41	−.073	−12186.48	−109728.89	−5.9	−109734.79
$3^2P_{3/2}$	−12186.41	.036	−12186.37	−109728.89	2.9	−109725.99
$3^2D_{3/2}$	−12186.41	.022	−12186.39	−109728.89	−1.77	−109730.61
$3^2D_{5/2}$	−12186.41	.014	−12186.40	−109728.89	1.18	−109727.66

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?

   ANSWER:
   $(nd)^2$ available orbitals $2^+, 2^-, 1^+, 1^-, 0^+, 0^-, -1^+, -1^-, -2^+, -2^-$.

$M_L \backslash M_S$	1	0	−1
4	—	$(2^+, 2^-)$	—
3	$(2^+, 1^+)$	$(2^+, 1^-)$ $(2^-, 1^+)$	$(2^-, 1^-)$
2	$(2^+, 0^+)$	$(2^-, 0^+)$ $(2^+, 0^-)$ $(1^+, 1^-)$	$(2^-, 0^-)$
1	$(1^+, 0^+)$ $(2^+, -1^+)$	$(1^+, 0^-)$ $(1^-, 0^+)$ $(2^+, -1^-)$ $(2^-, -1^+)$	$(1^-, 0^-)$ $(2^-, 1^-)$
0	$(2^+, -2^+)$ $(1^+, -1^+)$	$(2^+, -2^-)$ $(2^-, -2^+)$ $(1^+, -1^-)$ $(1^-, -1^+)$ $(0^+, 0^-)$	$(2^-, -2^-)$ $(1^-, -1^-)$

   $\Rightarrow$ there are 45 $(nd)^2$ Slater Determinants.

   (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)?

   ANSWER: $L - S$ states: ^{1}G, ^{3}F, ^{3}P, ^{1}D, ^{1}S.

   (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?

   ANSWER: Hund's rules say ^{3}F will be lowest. Hund's rules don't really apply to other than the ground state so the lowest singlet state is not predicted.

(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?

ANSWER:

$$E(^1G) = \langle (2^+, 2^-)|\mathbf{H}|(2^+, 2^-)\rangle$$
$$E(^3F) = \langle (2^+, 1^+)|\mathbf{H}|(2^+, 1^+)\rangle$$
$$E(^3P) = \langle (1^+, 0^+)|\mathbf{H}|(1^+, 0^+)\rangle + \langle (2^+, -1^+)|\mathbf{H}|(2^+, -1^+)\rangle - E(^3F)$$
$$E(^1D) = \langle (2^-, 0^+)|\mathbf{H}|(2^-, 0^+)\rangle + \langle (2^+, 0^-)|\mathbf{H}|(2^+, 0^-)\rangle + \langle (1^+, 1^-)|\mathbf{H}|(1^+, 1^-)\rangle - E(^1G) - E(^3F)$$
$$E(^1S) = \langle (2^+, -2^-)|\mathbf{H}|(2^+, -2^-)\rangle + \langle (2^-, -2^+)|\mathbf{H}|(2^-, -2^+)\rangle + \langle (1^+, -1^-)|\mathbf{H}|(1^+, -1^-)\rangle$$
$$+ \langle (1^-, -1^+)|\mathbf{H}|(1^-, -1^+)\rangle + \langle (0^+, 0^-)|\mathbf{H}|(0^+, 0^-)\rangle - E(^1G) - E(^3F) - E(^3P) - E(^1D)$$

$$\mathbf{H} = \underbrace{\sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{r}\right)}_{\substack{\text{Equal for all terms}\\ \text{since they come from}\\ \text{same configuration}}} + \underbrace{\sum_{r>j} \frac{1}{r_{ij}}}_{\substack{\text{we only need}\\ \text{to evaluate}\\ \text{these}}}$$

These 2-electron matrix elements are of the form

$$\sum_{a>b} \left\langle (a, b) \left| \frac{1}{r_{ab}} \right| (a, b) \right\rangle = \sum_{a>b} (\langle a, b|g|a, b\rangle - \langle a, b|g|b, a\rangle)$$

since the number of electrons is 2 the sum is just one term:

$$= \langle a, b|g|a, b\rangle - \langle a, b|g|b, a\rangle \equiv J(ab) - K(ab)$$

4D ANSWER, continued:
where

$$J(ab) = \sum_{k=0}^{\infty} a^k(\ell^a m_\ell^a, \ell^b m_\ell^b) F^k(n^a \ell^a, n^b \ell^b)$$

$$K(ab) = \left[\sum_{k=0}^{\infty} b^k(\ell^a m_\ell^a, \ell^b m_\ell^b) G^k(n^a \ell^a, n^b \ell^b)\right] \delta_{m_s^a m_s^b}$$

where $b^k = (c^k)^2$

so

$$E(^1G) = F^\circ + \frac{4}{49}F^2 + \frac{1}{441}F^4$$
$$E(^3F) = F^\circ - \frac{8}{49}F^2 - \frac{9}{441}F^4$$
$$E(^3P) = F^\circ + \frac{7}{49}F^2 - \frac{84}{441}F^4$$
$$E(^1D) = F^\circ - \frac{3}{49}F^2 + \frac{36}{441}F^4$$
$$E(^1S) = F^\circ + \frac{14}{49}F^2 + \frac{126}{441}F^4$$

Since Hund's rules say that $E(^3F) < E(^3P) \Rightarrow -\frac{8}{49}F^2 - \frac{9}{441}F^4 < \frac{7}{49}F^2 - \frac{84}{441}F^4$ $\quad \therefore \frac{F^2}{F^4} > 0.56$

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) $2p3d\ ^3D_2$

   ANSWER: Forbidden since $\Delta J = 2$.

   (b) $2s2p\ ^3P_1$

   ANSWER: Allowed since $\Delta J = 1$, $\Delta\ell = -1$ & $\Delta L = 0$, $\Delta S = 0$.

   (c) $2s3s\ ^3S_1$

   ANSWER: Forbidden in the absence of configuration interaction since it is a 2–electron transition.

   (d) $2s2p\ ^1P_1$

   ANSWER: Forbidden since $\Delta S \neq 0$.