CHEMISTRY 531 EXAM II SOLUTIONS

Problem 1 (40 pts)

a) Why is the energy degeneracy of the hydrogen 2s and 2p orbitals lifted in atoms (other than hydrogenic ones)? Which energy is lower and why?

Electron-electron repulsion is greater in the 2p orbital than in the 2s one because the 2p radial distribution is more compact than the 2s. Thus the electrons are closer in the 2p than in the 2s, and so the repulsion energy is greater. This, obviously, lifts the 2s/2p energy degeneracy found in hydrogenic atoms.

b) Give the explicitly antisymmetric zero-order wave functions of the singlet and triplets of the 1s2s configuration. Give the energies to first-order. Which is lower and why

1s2s **<u>singlet</u>:** $\frac{1s(1)2s(2)+1s(2)2s(1)}{\sqrt{2}} \quad \frac{\alpha(1)\beta(2)-\beta(1)\alpha(2)}{\sqrt{2}}$

triplet: $\frac{1s(1)2s(2)+1s(2)2s(1)}{\sqrt{2}} \left\{ \begin{array}{c} \alpha(1)\alpha(2) \\ \frac{\alpha(1)\alpha(2)+\beta(1)\beta(2)}{\sqrt{2}} \\ \beta(1)\beta(2) \end{array} \right.$

$E_{1s2s} \approx E^{(0)}_{1s2s} + E^{(1)}_{1s2s_1}$ $\quad E^{(0)}_{1s2s} = -\frac{Z^2}{2} - \frac{Z^2}{8}$ **(Hartree)**

Singlet: $E^{(1)}_{1s2s} = \underset{J_{1s,2s}}{\langle 1s2s|\frac{e^2}{r_{12}}|1s2s\rangle} + \underset{K_{1s,2s}}{\langle 1s2s|\frac{e^2}{r_{12}}|1s2s\rangle}$

Triplet: $E^{(1)}_{1s2s} = J_{1s,2s} - K_{1s,2s}$. **Since** $K_{1s,2s} > 0$ **the triplet energy is below the singlet by** $2K_{1s,2s}$.

(Another answer is the node in the triplet spatial wavefunction when $r_1 = r_2$ and the absence of this node in the singlet wavefunction.)

Problem 2 (10 pts)

Give the ground state configuration and term symbol of N. What are the possible values of S, L, and J?

N: $1s^2 2s^2 2p^3$ $\quad \underset{2p_{+1}}{\uparrow} \; \underset{2p_0}{\uparrow} \; \underset{2p_{-1}}{\uparrow}$ **- highest spin state S=3/2, so ground state is ^{4}S.** $M_l = 0 \quad L = 0$

J=3/2 <u>only</u>

Other possible values: $\frac{1}{2} \le s \le \frac{3}{2}$, $0 \le L \le 2$, $\frac{1}{2} \le J \le 2.5$

$\underset{2p_{+1}}{\uparrow\downarrow} \; \underset{2p_0}{\uparrow} \; \underset{2p_{-1}}{}$ → L=2

but S=1/2

Problem 3 (10 pts)

Give the Slater determinant for the $1s^2 2p$ configuration.

Assume the 2p spin is α.

$$\frac{1}{\sqrt{3}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2p(1)\alpha(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2p(2)\alpha(2) \\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2p(3)\alpha(3) \end{vmatrix}$$

Problem 4 (10 pts)

What is the form of the wavefunction of maximum L and M_L formed from two electrons in angular momentum state $|l_1 m_1\rangle$ and $|l_2 m_2\rangle$?

$$|L_{\max} L_{\max}\rangle = |\ell_1 \ell_1\rangle |\ell_2 \ell_2\rangle; \qquad \mathrm{L} = \ell_1 + \ell_2$$

Problem 5 (30 pts)

Verify that the ground state of C is ^3P. This state is further split by spin-orbit coupling, such that $^3P_0 < {}^3P_1 < {}^3P_2$. The energies are 0.0, 16.4 cm^{-1} and 43.5 cm^{-1}. Calculate the spin-orbit coupling constant A.

$$C: 1s^2 2s^2 2p^2 \quad \underset{2p_{+1}}{\uparrow} \; \underset{2p_0}{\uparrow} \; \underset{2p_{-1}}{\_\_} \qquad {}^3\mathrm{P}$$

$\boxed{0 \le J \le 2}$ $\quad {}^3P_0 < {}^3P_1 < {}^3P_2$ **—given**

———	**43.5**
———	**16.4**
———	**0.0**

$$E_{so}^1 = \frac{A}{2\left[J(J+1) - 1(1+1) - 1(1+1)\right]}$$

$$-16.4 = -\frac{A}{2}\ (4-2) \quad A = 16.4 \text{ cm}^{-1}$$

$$43.5 = \frac{A}{2}\ (4+2) \quad A = 14.5 \text{ cm}^{-1}$$

$$\langle A \rangle = 15 \text{ cm}^{-1}$$