Chemistry 21b

Problem set # 6

Out: 22Feb2008
Due: 29Feb2008

1. Read over the crystal and ligand field theory sections of Hollas, *Modern Spectroscopy*, included as the last few pages of Lecture #16. Write down the crystal field orbital configurations of the following transition metal complexes: $[Cu(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{2+}$ – high spin, $[Co(NH_3)_6]^{3+}$ – low spin. Solutions of $[Mn(H_2O)_6]^{2+}$ are a very pale pink in color, that is, this complex has no strongly allowed visible transitions (but does have weakly allowed transitions with epsilon $\sim$ 0.01). Explain why.

2. Do problem 5-24 from Harris & Bertolucci, page 367.

3. This problem briefly reviews the so-called matrix form of the spin-1/2 problem, and so is worth going over at least once! Note that you expect the spin up and spin down functions α and β to be eigenfunctions of $\hat{I}^2$ and $\hat{I}_z$ since the latter are diagnoal. Specifically, the nuclear spin operators can be expressed as 2×2 matrices and the spin functions as column vectors. Given that

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad \text{and}$$

$$\hat{I}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \;,\; \hat{I}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \;,\; \hat{I}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \;,\; \hat{I}^2 = \left(\frac{\hbar}{2}\right)^2\begin{pmatrix} 3 & 0 \\ 0 & 3 \end{pmatrix} \;,$$

a. Show that

$$\hat{I}^2\alpha = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha \;,\; \hat{I}^2\beta = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta$$

b. And that

$$\hat{I}_x\alpha = +\frac{\hbar}{2}\beta \;,\; \hat{I}_y\alpha = +\frac{i\hbar}{2}\beta \;,\; \hat{I}_z\alpha = +\frac{\hbar}{2}\alpha$$

$$\hat{I}_x\beta = +\frac{\hbar}{2}\alpha \;,\; \hat{I}_y\beta = -\frac{i\hbar}{2}\alpha \;,\; \hat{I}_z\beta = -\frac{\hbar}{2}\beta$$

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