MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
Fall, 2002

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Problem Set #10

DUE: At the start of Lecture on Friday, December 6.

Reading: Golding Handout

Problems:

1. A. Use the method of M_L, M_S boxes to determine the L,S "terms" that belong to the d^2, d^2p, and $nd^2n'd$ electronic configurations. Use (and explain) shortcuts to deal with the d^2, d^2p, and $nd^2n'd$ configurations.

   B. What is the total degeneracy of the d^3 configuration? Use this result to direct your guesswork in determining the L–S terms that belong to d^3 by using your result for $nd^2n'd$ and eliminating inappropriate L–S terms.

   C. Use the ladders plus orthogonality method to derive the linear combination of Slater determinants that corresponds to the d^2 ^3P $M_L = 1$, $M_S = 0$ state.

   D. Use 3 – j coefficients to construct L = 1, $M_L = 1$, S = 1, $M_S = 0$ from $\left(\ell_1 = 2,\ m_{\ell_1},\ s_1 = 1/2,\ m_{s_1}\right)\left(\ell_2 = 2,\ m_{\ell_2} = 1 - m_{\ell_1},\ s_2 = 1/2,\ m_{s_2} = -m_{s_1}\right)$ combinations of spin-orbitals. The relevant coupled↔uncoupled representation formula is:

$$\left|Jj_1j_2M_J\right\rangle = \sum_{m_2=-j_2}^{j_2} (-1)^{j_1-j_2+M}(2J+1)^{1/2}\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M_J \end{pmatrix}\left|j_1m_1\right\rangle\left|j_2m_2\right\rangle.$$

   The only Slater determinants that you will need to consider are $\|2\alpha - 1\beta\|$, $\|2\beta - 1\alpha\|$, $\|1\alpha 0\beta\|$, and $\|1\beta 0\alpha\|$.

   E. Use the $\mathbf{L}^2$, $\mathbf{S}^2$ method to set up the $M_L = 0$, $M_S = 0$ block of d^2. Find the linear combination of Slater determinants that corresponds to ^3P $M_L = 0$, $M_S = 0$ and then use $\mathbf{L}_+$ to derive ^3P $M_L = 1$, $M_S = 0$.

2. A. Derive the $\mathbf{L}^2$ matrix for $M_L = 3$, $M_S = 0$ of f^2 shown on page 32-4.

   B. Derive the $\mathbf{S}^2$ matrix for $M_L = 3$, $M_S = 0$ of f^2. Find the eigenvalues and eigenvectors.

   C. Derive the four eigenvectors of the $M_L = 3$, $M_S = 0$ box of f^2 shown on page 32-4.

   D. Use the results of parts B and C to derive the relationship between the many-electron spin-orbit coupling constants

$$\zeta(4f^2;\ ^3H),\ \zeta(4f^2,\ ^3F),\ \text{and}\ \zeta(4f^2,\ ^3P)$$

and the one-electron spin-orbit coupling constant, $\zeta(4f)$.
[HINT: You are going to have to apply S_+ or S_- to your eigenvectors.]

E. This is going to involve some lengthy calculations, using some combination of ladders and/or Clebsch-Gordan algebra. Work out the diagonal and off-diagonal contributions of $\mathbf{H}^{SO}$ to the J = 4 block ($^3F_4$, $^3H_4$, $^1G_4$) of f^2.

F. Suppose, at t = 0 the single Slater determinant of f^2, $\|3\alpha 1\beta\|$ is populated. Compute the survival probability of the initially formed non-eigenstate,

$$P(t) = \left|\langle \Psi(0) | \Psi(t) \rangle\right|^2 .$$

To solve this problem you need to work out the e^2/r_{ij} energies of all L–S–J terms of f^2 that are capable of having $M_J = 4$ (i.e. $J \geq 4$). You will also need diagonal and off-diagonal matrix elements of $\mathbf{H}^{SO}$ for J = 4 (3×3), J = 5 (1×1), and J = 6 (2×2, but this is easy).