DUE: At the start of Lecture on Friday, November 22.

Reading: Angular Momentum Handouts
C-TDL, pages 999-1024, 1027-1034, 1035-1042

Spherical components of a vector operator

\[ V_{\pm 1} = \frac{1}{2} 2^{-1/2} \left[ V_x \pm i V_y \right] \]
\[ V_0 = V_z \]

Scalar product of two vector operators

\[ V \sum W = \sum (\Delta \mu) V_{-\mu} W_{\mu} \cdot \]

Scalar product of two tensor operators

\[ T_{0}^{(0)}(A_1, A_2) = \sum (\Delta \mu) T_{\mu}^{(\omega)}(A_1) T_{\mu}^{(\omega)}(A_2). \]

Problems:

1. CTDL, page 1086, #2.

2. CTDL, page 1089, #7.

3. CTDL, page 1089, #8.

4. A. d orbitals are often labeled xy, xz, yz, z^2, x^2-y^2. These labels are Cartesian tensor components. Find the linear combinations of binary products of x, y, and z that may be labeled as T_{z}^{(2)} and T_{0}^{(2)}.

B. There is a powerful formula for constructing an operator of any desired T_{M}^{(\Omega)} spherical tensor character from products of components of other operators.
\[ T^{(\Omega)}_{M}[A_1, A_2] = \sum_{\mu_1} A_{\mu_1, M-\mu_1, M}^{\omega_1, \omega_2, \Omega} T^{(\omega_1)}_{M-\mu_1}[A_1] T^{(\omega_2)}_{M}[A_2] \]

where A is a Wigner or Clebsch-Gordan coefficient, which is related to 3-j coefficients as follows:

\[
\begin{pmatrix} j_1 & j_2 & m_3 \\ m_1 & m_2 & \equiv -(m_1 + m_2) \end{pmatrix} = (-1)^{j_1 - j_2 - m_3} (2j_3 + 1)^{-1/2} A_{m_1}^{j_1 j_2 j_3} m_2 - m_3.
\]

Use the \( T^{(\Omega)}_{M}[A_1, A_2] \) formula to construct the spherical tensor \( T^{(3)}_{+2} \) and \( T^{(3)}_{0} \) components of f orbitals by combining products of linear combinations of Cartesian labeled d and p orbitals. In other words, combine \( T^{(2)} \{x, y, z\} \) with \( T^{(1)} \{x, y, z\} \) to obtain \( T^{(3)}_{M} \) as a linear combination of products of 3 Cartesian components.

5. **Angular Momenta**

Consider a two-electron atom in the “electronic configuration” 3d4p. The electronic states that belong to this configuration are \(^3\text{F} , \text{^1F}, ^3\text{D}, ^1\text{D}, ^3\text{P}, \text{^1P}.\) There are \((2\ell_1 + 1)(2\ell_2 + 1)(2s_1 + 1)(2s_2 + 1) = 60\) spin-orbital occupancies associated with this configuration. I am going to ask you to solve several angular momentum coupling problems, using 3-j coefficients and the Wigner-Eckart Theorem for states belonging to this configuration. However, I do not expect you to consider the anti-symmetrization requirement that is the subject of lectures #30 - 36.

Spin-orbitals in the uncoupled basis set are denoted by \( n\ell m s m_s(i) \) where \( n \) is the principal quantum number and \( i \) specifies the name of the assumed-distinguishable electron. Since \( s = 1/2 \) for all electrons, we can use an abbreviated notation for spin-orbitals: \( \ell \alpha/\beta \) where \( \alpha \) corresponds to \( m_s = +1/2 \) and \( \beta \) to \( m_s = -1/2 \). The two-electron basis states are denoted \( |\ell_1 \lambda_1 (\alpha/\beta)_1, \ell_2 \lambda_2 (\alpha/\beta)_2\rangle \), e.g. \( |3 -1\alpha, 2 -1\beta\rangle \) where the first three symbols are associated with \( e^- \) #1 and the second three with \( e^- \) #2.

The many-electron quantum numbers \( L, M_L, S, M_S \) are related to the one-electron spin-orbital quantum numbers by

\[
M_L = \sum_i \lambda_i \\
M_S = \sum_i \sigma_i
\]

and \( L \) and \( S \) must be constructed from the proper linear combination of spin-orbital basis states. For example,

\[
|^{3}\text{F}, M_L = 4, M_S = 1\rangle = |33\alpha , 11\alpha\rangle
\]

This is a problem of coupled↔uncoupled transformation,
where $M_L = \lambda_1 + \lambda_2$ and $\ell_2 \leq \ell_1$. The same situation obtains for the spin part

$$|S_{s_1 s_2 M_s}\rangle = \sum_{\sigma_2} |s_1 \sigma_1 s_2 \sigma_2 \rangle \langle s_1 \sigma_1 s_2 \sigma_2 |S_{s_1 s_2 M_s}\rangle.$$  

A. Use 3-j coefficients to derive the linear combination of six spin-orbital occupancies that corresponds to the $^3P_0 M_J = 0$ state. The six basis states are $|3-\alpha \ 1\beta\rangle$, $|3-\beta \ 1\alpha\rangle$, $|30\alpha \ 10\beta\rangle$, $|30\beta \ 10\alpha\rangle$, $|31\alpha \ 1-1\beta\rangle$, and $|31\beta \ 1-1\alpha\rangle$. Note that you will have to perform three uncoupled→coupled transformations:

$$\ell_1 \lambda_1 \ell_2 \lambda_2 \rightarrow L \ell_1 \ell_2 M_L$$

$$s_1 \sigma_1 s_2 \sigma_2 \rightarrow S s_1 s_2 M_s$$

and

$$LM_s SM_s \rightarrow JLSM_J.$$  

I advise against using ladders plus orthogonality to solve this problem because $M_J = 0$ is the worst possible situation for this method.

B. The atom in question has a nonzero nuclear spin, $I = 5/2$. This means that you will eventually have to perform one more uncoupled to coupled transformation:

$$\mathbf{F} = \mathbf{I} + \mathbf{J}$$

$$|JM_J I M_I\rangle \rightarrow |FJ I M_F\rangle.$$  

The nuclear spin gives rise to “Fermi-contact” and magnetic dipole hyperfine structure. The hyperfine Hamiltonian is

$$H^{\text{hf}} = \sum (a_s s_i \sum I + b_1 \ell_1 \sum I).$$

The $\Delta F = \Delta J = \Delta L = \Delta S = \Delta I = 0$ special form for the Wigner-Eckart theorem for vector operators may be used to replace the above “microscopic” form of $H^{\text{hf}}$ by a more convenient, but restricted, form

$$H^{\text{hf}} = c_{\text{hf}} \mathbf{J} \cdot \mathbf{I}$$

because the microscopic $H^{\text{hf}}$ contains $\sum_i a_i s_i$ and $\sum_i b_1 \ell_1$, both of which are vectors with respect to $\mathbf{J}$. 


\[ H_{\text{df}} = \sum (a_i \mathbf{s}_i + b_i \ell_i) \sum_{\mathbf{I}} \]
\[ = c_{\text{JLS}} \sum_{\mathbf{I}} \]

where \( c_{\text{JLS}} \) is a reduced matrix element evaluated in the \( |JLSM_j\rangle \) basis set

\[ c_{\text{JLS}} = \langle JLS | \sum_{i} (a_i \mathbf{s}_i + b_i \ell_i) \rangle |LS \rangle \]

where

\[ c_{\text{JLS}} = \langle JLSM_j | \sum_{i} (a_i \mathbf{s}_i + b_i \ell_i) \rangle |JLSM_j\rangle = c_{\text{JLS}} \langle JLSM_j | J | JLSM_j\rangle \]

\( c_{\text{JLS}} \) is a constant that depends on each of the magnitude quantum numbers \( J, L, \) and \( S \) (but not \( F \) and \( I \)). I will review this derivation and show you how to evaluate the \( J, L, S \) dependence of \( c_{\text{JLS}} \) in a handout.

Similarly, the spin-orbit Hamiltonian

\[ H_{\text{SO}} = \sum \zeta_i \ell_i \sum_{\mathbf{s}_i} \]

may be replaced by the \( \Delta L = 0, \Delta S = 0 \) restricted form,

\[ H_{\text{SO}} = \zeta_{LS} \mathbf{L} \cdot \mathbf{S}. \]

The purpose of this problem is to show that all of the fine (spin-orbit) and hyperfine structure for all of the states of the 3d4p configuration can be related to the fundamental one-electron coupling constants: \( a_{3d}, a_{4p}, b_{3d}, b_{4p}, \zeta_{3d}, \) and \( \zeta_{4p} \).

Derive simple formulas for the hyperfine and fine structure for all \( |FJLSIM_f\rangle \) states of the 3d4p configuration (consistent with neglect of \( \Delta L \neq 0, \Delta S \neq 0 \) matrix elements).

C. The six \( L-S \) states that arise from the 3d4p electronic configuration split into 12 fine-structure \( J \)-components and, in turn, into 54 hyperfine \( F \)-components. The eigenenergies are given (neglecting off-diagonal matrix elements between widely separated \( J-L-S \) fine structure components) by \( c_{\text{JLS}} \mathbf{J} \cdot \mathbf{I} \) and, alternatively, by matrix elements of the microscopic forms of the \( H_{\text{df}} \) (and \( H_{\text{SO}} \)) operators evaluated in the explicit product-of-spin-orbitals basis set. The set of 12 \( |c_{\text{JLS}}\rangle \) can be related to four of the six fundamental coupling constants listed at the end of part B. There are several tricks for expressing many-electron reduced matrix elements in terms of one-electron reduced matrix elements. One trick is to start with “extreme states”. Another is to exploit a matrix element sum rule based on the trace invariance of matrix representations of \( H \). For \( H_{\text{SO}} \) use \( ^3F_i \mathbf{M}_f = 4 \) to get \( \zeta_{3p} \), \( ^3P_0 \mathbf{M}_f = 0 \) (your answer to part A) to get \( \zeta_{3p} \), and (if you are brave: optional) the sum rule for \( J = 3, \mathbf{M}_f = 3 \) to get \( \zeta_{3p} \). For \( H_{\text{df}} \) consider only \( ^3F_i \mathbf{M}_f = (4+5/2) \) and (if you are brave: optional) \( ^3F_3 \mathbf{M}_f = (3 + 5/2) \).