MASSACHUSETTS INSTITUTE OF TECHNOLOGY

5.73 Quantum Mechanics I
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Problem Set #9

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

Spherical components of a vector operator

$$V_{\pm 1} = \mp 2^{-1/2}\left[V_x \pm iV_y\right]$$
$$V_0 = V_z$$

Scalar product of two vector operators

$$V \bullet W = \sum_{\mu}(-1)^{\mu} V_{-\mu} W_{\mu} .$$

Scalar product of two tensor operators

$$T_0^{(0)}[A_1, A_2] = \sum_{\mu}(-1)^{\mu} T_{\mu}^{(\omega)}[A_1] T_{-\mu}^{(\omega)}[A_2].$$

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 $T_{+2}^{(2)}$ 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

$$T_M^{(\Omega)}[A_1,A_2]=\sum_{\mu_1} A^{\omega_1\omega_2\Omega}_{\mu_1,M-\mu_1,M}T^{(\omega_1)}_{\mu_1}[A_1]T^{(\omega_2)}_{M-\mu_1}[A_2]$$

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

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \equiv -(m_1+m_2) \end{pmatrix} = (-1)^{j_1-j_2-m_3}(2j_3+1)^{-1/2}A^{j_1j_2j_3}_{M_1M_2-M_3}.$$

Use the $T_M^{(\Omega)}$ $[A_1,A_2]$ formula to construct the spherical tensor $T_{+2}^{(3)}$ and $T_0^{(3)}$ 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 $T_M^{(3)}$ 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 ^3F, ^1F, ^3D, ^1D, ^3P, and ^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 $n\ell m_\ell s m_s(i)$ 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: $\ell\lambda\alpha/\beta$ where α corresponds to $m_s = +1/2$ and β to $m_s = -1/2$. The two-electron basis states are denoted $\left|\ell_1\lambda_1(\alpha/\beta)_1\,\ell_2\lambda_2(\alpha/\beta)_2\right\rangle$, e.g. $\left|3-1\alpha\,2-1\beta\right\rangle$ 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,

$$\left|{}^3F, M_L = 4, M_S = 1\right\rangle = \left|33\alpha\,11\alpha\right\rangle$$

This is a problem that concerns the coupled↔uncoupled transformation,

$$\left|L\ell_1\ell_2M_L\right\rangle = \sum_{\lambda_2} \left|\ell_1\lambda_1\ell_2\lambda_2\right\rangle\left\langle\ell_1\lambda_1\ell_2\lambda_2\middle|L\ell_1\ell_2M_L\right\rangle$$

where $M_L = \lambda_1 + \lambda_2$ and $\ell_2 \le \ell_1$. The same situation obtains for the spin part

$$\left|Ss_1s_2M_s\right\rangle = \sum_{\sigma_2} \left|s_1\sigma_1s_2\sigma_2\right\rangle\left\langle s_1\sigma_1s_2\sigma_2\middle|Ss_1s_2M_S\right\rangle.$$

A. Use 3-j coefficients to derive the linear combination of six spin-orbital occupancies that corresponds to the $|{}^3P_0\ M_J = 0\rangle$ state. The six basis states are $|3{-}1\alpha\ 11\beta\rangle$, $|3{-}1\beta\ 11\alpha\rangle$, $|30\alpha\ 10\beta\rangle$, $|30\beta\ 10\alpha\rangle$, $|31\alpha\ 1{-}1\beta\rangle$, and $|31\beta\ 1{-}1\alpha\rangle$. Note that you will have to perform three uncoupled→coupled transformations:

$\ell_1\lambda_1\ \ell_1\lambda_1 \rightarrow L\ \ell_1\ \ell_2M_L$

$s_1\sigma_1s_2\sigma_2 \rightarrow S\ s_1s_2M_S$

and

$LM_LSM_S \rightarrow JLSM_J$.

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 an additional uncoupled to coupled transformation:

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

$$\left|JM_JIM_I\right\rangle \rightarrow \left|FJIM_F\right\rangle.$$

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

$$\mathbf{H}^{hf} = \sum \left(a_i\mathbf{s}_i \bullet \mathbf{I} + b_i\boldsymbol{\ell}_i \bullet \mathbf{I}\right).$$

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 $\mathbf{H}^{hf}$ by a more convenient, but restricted, form

$$\mathbf{H}^{hf} = c_{JLS}\mathbf{J}\bullet\mathbf{I}$$

because the microscopic $\mathbf{H}^{hf}$ contains $\sum_i a_i \mathbf{s}_i$ and $\sum_i b_i \ell_i$, both of which are vectors with respect to $\mathbf{J}$.

$$\mathbf{H}^{ef} = \sum (a_i \mathbf{s}_i + b_i \ell_i) \bullet \mathbf{I}$$
$$= c_{JLS} \mathbf{J} \bullet \mathbf{I}$$

where c_{JLS} is a reduced matrix element evaluated in the $|JLSM_J\rangle$ basis set

$$c_{JLS} = \left\langle JLS \left\| \sum_i (a_i \mathbf{s}_i + b_i \ell_i) \right\| JLS \right\rangle$$

where

$$c_{JLS} = \left\langle JLSM_J \left| \sum_i (a_i \mathbf{s}_i + b_i \ell_i) \right| JLSM'_J \right\rangle = c_{JLS} \langle JLSM_J | \mathbf{J} | JLSM'_J \rangle .$$

c_{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_{JLS} in a handout.

Similarly, the spin-orbit Hamiltonian

$$\mathbf{H}^{SO} = \sum_{\circ} \zeta(r_i) \ell_i \bullet \mathbf{s}_i$$

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

$$\mathbf{H}^{SO} = \zeta_{LS} \mathbf{L} \bullet \mathbf{S}.$$

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}, ζ_{3d}, and ζ_{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 $c_{JLS}\mathbf{J}\bullet\mathbf{I}$ and, alternatively, by matrix elements of the microscopic forms of the $\mathbf{H}^{hf}$ (and $\mathbf{H}^{SO}$) operators evaluated in the explicit product-of-spin-orbitals basis set. The set of 12 $\{c_{JLS}\}$ 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 $\mathbf{H}^{SO}$ use $^3F_4$ $M_J = 4$ to get $\zeta_{^3F}$, $^3P_0$ $M_J = 0$ (your answer to part A) to get $\zeta_{^3P}$, and (if you are brave: optional) the sum rule for J = 3, $M_J = 3$ to get $\zeta_{^3D}$. For $\mathbf{H}^{hf}$ consider only $^3F_4$ $M_F = (4+5/2)$ and (if you are brave: optional) $^1F_3$ $M_F = (3 + 5/2)$.