Supplement #2 to Lecture #27

Simplification of hyperfine $\mathbf{H}^{\mathrm{hf}}$ by Wigner-Eckart Theorem

There can be many angular momenta in an atom that has non–zero L, S, and I, where I is the nuclear spin. The individual angular momenta are

L	orbital angular momentum
S	electron spin angular momentum
I	nuclear spin angular momentum

and the coupled angular momenta are

$\vec{\mathbf{J}} = \vec{\mathbf{L}} + \vec{\mathbf{S}}$	total exclusive of nuclear spin
$\vec{\mathbf{F}} = \vec{\mathbf{J}} + \vec{\mathbf{I}}$	total angular momentum

and the laboratory frame projection of $\vec{\mathbf{F}}$ is

$$M_F.$$

The coupled basis states are

$$|FJLSIM_F\rangle\,.$$

If there are many electrons, we need to define the hyperfine term in the Hamiltonian as a sum over individual electron contributions

$$\mathbf{H}^{\mathrm{hf}} = \sum_i (a_i \mathbf{s}_i + b_i \boldsymbol{\ell}_i) \cdot \mathbf{I}.$$

A basis set like $|FJGLSIM_F\rangle$ would make life much simpler for evaluating matrix elements $I \cdot S$ and $I \cdot L$, but it is illegal because $[\mathbf{G}^2, \mathbf{J}^2] \neq 0$.

$$\begin{aligned} \vec{\mathbf{G}} &= \vec{\mathbf{I}} + \vec{\mathbf{S}} \\ \vec{\mathbf{J}} &= \vec{\mathbf{L}} + \vec{\mathbf{S}} \\ \vec{\mathbf{G}}^2 &= I^2 + S^2 + 2I \cdot S \\ \vec{\mathbf{J}}^2 &= L^2 + S^2 + 2L \cdot S \end{aligned}$$

$$
\begin{aligned}
[\mathbf{G}^2, \mathbf{J}^2] &= 4[I \cdot S, L \cdot S] \\
[I \cdot S, L \cdot S] &= [I_x S_x + I_y S_y + I_z S_z, L_x S_x + L_y S_y + L_z S_z] \\
&= I_x [S_x, S_y] L_y + I_x [S_x, S_z] L_z \\
&\quad + I_y [S_y, S_x] L_x + I_y [S_y, S_z] L_z \\
&\quad + I_z [S_z, S_x] L_x + I_z [S_z, S_y] L_y \\
&= i\hbar [I_x L_y S_z - I_x L_z S_y - I_y L_x S_z + I_y L_z S_x + I_z L_x S_y - I_z L_y S_x] \\
&= i\hbar I \cdot (L \times S) \neq 0.
\end{aligned}
$$

We want to replace

$$\mathbf{H}^{\mathrm{hf}} = \sum_i (a_i \mathbf{s}_i + b_i \boldsymbol{\ell}_i) \cdot \mathbf{I}$$

by

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

and to evaluate c_{JLS}. To accomplish this we must first go to an uncoupled basis set

$$|FJLSIM_F\rangle = \sum_{M_J} |JLSM_J\rangle |IM_I = M_F - M_J\rangle \underbrace{\langle JLSM_J| \langle IM_F - M_J | FJLSIM_F \rangle}_{d_{M_J}}.$$

Call the vector-coupling coefficient d_{M_J} for simplicity (we are not actually going to look up and insert values for this mixing coefficient).

We seek only the diagonal matrix elements of $\mathbf{H}^{\mathrm{hf}}$

$$
\begin{aligned}
FJLSIM_F | \mathbf{H}^{\mathrm{hf}} | FJLSIM_F \quad &= \sum_{M_J} \sum_{M_J'} d_{M_J} d_{M_J'} \times \\
&\left\langle JLSM_J \Big| \sum_i (a_i \mathbf{s}_i + b_i \boldsymbol{\ell}_i) \Big| JLSM_J' \right\rangle \langle IM_F - M_J | \mathbf{I} | IM_F - M_J' \rangle
\end{aligned}
$$

Since $\sum_i (a_i \mathbf{s}_i + b_i \boldsymbol{\ell}_i)$ is a vector with respect to $\mathbf{J}$ and we want only diagonal matrix elements with respect to J, L, and S, we can replace the microscopic operator by the corresponding matrix element of **J** times the reduced matrix element

$$\left\langle JLSM_J|\sum_i(a_i\mathbf{s}_i+b_i\boldsymbol{\ell}_i)|JLSM_J'\right\rangle$$
$$=\left\langle JLS\quad\sum_i(a_i\mathbf{s}_i+b_i\boldsymbol{\ell}_i)\quad JLS\right\rangle\times\langle JLSM_J|\mathbf{J}|JLSM_J'\rangle$$

$$c_{\rm JLS}\equiv\left\langle JLS\quad\sum_i(a_i\mathbf{s}_i+b_i\boldsymbol{\ell}_i)\quad JLS\right\rangle$$
$$FJLSIM_F\ \ \mathbf{H}^{\rm hf}\ \ FJLSIM_F\ \ =\sum_{M_J}\sum_{M_J'}c_{\rm JLS}\,\langle JLSM_J|\mathbf{J}|JLSM_J'\rangle\cdot\times$$
$$\langle IM_F-M_J|\mathbf{I}|IM_F-M_J'\rangle$$

but now we can recognize completeness and contract the product of matrix elements to one of **J**·**I** in the fully coupled basis set

$$FJLSIM_F|\mathbf{H}^{\rm hf}|FJLSIM_F\ \ =c_{JLS}\,\langle FJLSIM_F|\mathbf{J}\cdot\mathbf{I}|FJLSIM_F\rangle$$

but

$$\vec{\boldsymbol{J}}+\vec{\boldsymbol{I}}=\vec{\boldsymbol{F}}$$
$$\vec{\boldsymbol{J}}^2+\vec{\boldsymbol{I}}^2+2\vec{\boldsymbol{I}}\cdot\vec{\boldsymbol{J}}=\vec{\boldsymbol{F}}^2.$$

Thus

$$FJLSIM_F|\mathbf{H}^{\rm hf}|FJLSIM_F\ \ =\frac{\hbar^2}{2}c_{JLS}[F(F+1)-J(J+1)-I(I+1)].$$

Now the problem for the $3d4p$ configuration reduces to expressing the 12 different c_{JLS} constants in terms of single-spin-orbital integrals

$$\ell\hbar b_{n\ell}=\langle n\ell\lambda=\ell|b\ell_z|n\ell\lambda=\ell\rangle\quad\text{for 3d and 4p}$$
$$\frac{1}{2}\hbar a_{n\ell}=\langle n\ell s\alpha|as_z|n\ell s\alpha\rangle\,.$$

To accomplish this, we start with the extreme states

$$\left\langle J = L + SLSM_J = L + S \middle| \sum_i (a_i \mathbf{s}_{z_i} + b_i \boldsymbol{\ell}_{z_i}) \middle| L + SLSL + S \right\rangle =$$
$$c_{J=L+SLS} \langle J = L + SLSM_J = L + S|\mathbf{J}_z|L + SLSL + S\rangle$$

$$\text{e.g.} \quad {}^3F_4 M_J = 4 \;\; = |3d\overbrace{2\alpha4p1}^{\lambda \text{ values}}\alpha\rangle$$

$$\left\langle 4314 \;\; \sum_i (a_i \mathbf{s}_{z_i} + b_i \boldsymbol{\ell}_{z_i}) \;\; 4314 \right\rangle = c_{431}\hbar 4$$
$$= \hbar[a_{3d}/2 + a_{4p}/2 + 2b_{3d} + b_{4p}]$$

$$\boxed{c_{431} = \tfrac{1}{4}[a_{3d}/2 + a_{4p}/2 + 2b_{3d} + b_{4p}]}$$

to get the others, use the "sum rule." More on this in lecture #34. The basic idea is that the trace of a matrix is representation-invariant and the reduced matrix elements are independent of projection quantum numbers.

$$\mathbf{J}_- \;\; {}^3F_4 M_J = 4 \;\; = \sum_i (\ell_- + s_{-i})|3d\overbrace{2\alpha4p1}^{\lambda \text{ values}}\alpha\rangle$$
$$\hbar[20 - 12]^{1/2} \;\; {}^3F_4 3 \;\; = \hbar \left\{ [6 - 2]^{1/2}|3d1\alpha4p1\alpha\rangle + [2 - 0]^{1/2}|3d2\alpha4p0\alpha\rangle \right.$$
$$\left. + |3d2\beta4p1\alpha\rangle + |3d2\alpha4p1\beta\rangle \right\}$$
$$|{}^3F_4 3\rangle = 2^{-1/2}|3d1\alpha4p1\alpha\rangle + \frac{1}{2}|3d2\alpha4p0\alpha\rangle$$
$$+ 8^{-1/2}|3d2\beta4p1\alpha\rangle + 8^{-1/2}|3d2\alpha4p1\beta\rangle$$

$$3c_{431} = \frac{1}{2}\left[a_{3d}/2 + a_{4p}/2 + b_{3d} + b_{4p}\right] + \frac{1}{4}\left[a_{3d}/2 + a_{4p}/2 + 2b_{3d}\right]$$
$$+ \frac{1}{8}\left[-a_{3d}/2 + a_{4p}/2 + 2b_{3d} + 1b_{4p}\right] + \frac{1}{8}\left[a_{3d}/2 - a_{4p}/2 + 2b_{3d} + b_{4p}\right]$$

$$\boxed{c_{431} = \tfrac{1}{8}a_{3d} + \tfrac{1}{8}a_{4p} + \tfrac{1}{2}b_{3d} + \tfrac{1}{4}b_{4p}} \quad \text{confirmed as expected}$$

$$
\begin{aligned}
{}^1F_3 3 &= 2^{1/2}\left[|3d2\alpha 4p1\beta\rangle - |3d2\beta 4p1\alpha\rangle\right] \\
3c_{330} &= \frac{1}{2}\left[a_{3d}/2 - a_{4p}/2 + 2b_{3d} + b_{4p}\right] \\
&+ \frac{1}{2}\left[-a_{3d}/2 + a_{4p}/2 + 2b_{3d} + b_{4p}\right]
\end{aligned}
$$

$$\boxed{c_{330} = \tfrac{2}{3}b_{3d} + \tfrac{1}{3}b_{4p}}$$

The $J = 3, M_J = 3$ box contains entries from

$${}^3F_4 3 \quad , \quad {}^3F_3 3 \quad , \quad {}^1F_3 3 \quad , \text{and} \quad {}^3D_3 3$$

$$
\begin{aligned}
&3c_{431} + 3c_{331} + 3c_{330} + 3c_{321} \\
&\quad = \langle 3d1\alpha 4p1\alpha\rangle + \langle 3d2\alpha 4p0\alpha\rangle + \langle 3d2\beta 4p1\alpha\rangle + \langle 3d2\alpha 4p1\beta\rangle \\
&\quad = a_{3d}/2 + a_{3d}/2 - a_{3d}/2 + a_{3d}/2 + a_{4p}/2 + a_{4p}/2 + a_{4p}/2 - a_{4p}/2 \\
&\quad + b_{3d} + b_{4p} + 2b_{3d} + 2b_{3d} + b_{4p} + 2b_{3d} + b_{4p} \\
&\quad = a_{3d} + a_{4p} + 7b_{3d} + 3b_{4p}
\end{aligned}
$$

We know c_{431} and c_{330}. Need to do a bit of algebra to get c_{331} and c_{321}.

$${}^3D_3 3 \;=\; {}^3DM_L = 2M_S = 1 \;= -\left(\frac{1}{3}\right)^{1/2}|3d1\alpha 4p1\alpha\rangle + \left(\frac{2}{3}\right)^{1/2}|3d2\alpha 4p0\alpha\rangle$$

$$
\begin{aligned}
3c_{321} &= \frac{1}{3}\left[a_{3d}/2 + a_{4p}/2 + b_{3d} + b_{4p}\right] \\
&+ \frac{2}{3}\left[a_{3d}/2 + a_{4p}/2 + 2b_{3d}\right]
\end{aligned}
$$

$$\boxed{c_{321} = \tfrac{1}{6}a_{3d} + \tfrac{1}{6}a_{4p} + \tfrac{5}{9}b_{3d} + \tfrac{1}{9}b_{4p}}$$

$$\therefore \boxed{c_{331} = \tfrac{1}{24}a_{3d} + \tfrac{1}{24}a_{4p} + \tfrac{11}{18}b_{3d} + \tfrac{11}{36}b_{4p}}$$

(steps omitted)