5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #20: Transformations between Basis Sets: 3-j, 6-j, and Wigner-Eckart Theorem

Last time: effects of "Remote Perturbers". What terms must we add to the effective **H** so that we can represent all usual behaviors with minimum number of parameters.

Today: A taste of spherical tensor algebra.

Suppose we want to evaluate matrix elements of $\mathbf{H}^{SO}$ for atoms. We have a choice between two basis sets:

coupled	$\|L\ S\ J\ M_J\rangle$
uncoupled	$\|\ L\ M_L\ S\ M_S\rangle$

If we take the simplified form of $\mathbf{H}^{SO}$

$$\mathbf{H}^{SO} = \zeta(nLS)\mathbf{L}\cdot\mathbf{S} = \zeta(nLS)\left[\mathbf{L}_z\mathbf{S}_z + \frac{1}{2}\left(\mathbf{L}_+\mathbf{S}_- + \mathbf{L}_-\mathbf{S}_+\right)\right],$$

we can set up a matrix for $\mathbf{H}^{SO}$ in either the coupled or uncoupled basis. One basis is more convenient than the other but all necessary matrix elements are explicitly evaluable because all of the quantum numbers we need to evaluate the matrix elements appear explicitly in either basis set. But

$$\left[\mathbf{H}^{SO}, \mathbf{J}^2\right] = 0 \qquad \left[\mathbf{H}^{SO}, \mathbf{J}_z\right] = 0$$
$$\left[\mathbf{H}^{SO}, \mathbf{L}_z\right] \neq 0 \qquad \left[\mathbf{H}^{SO}, \mathbf{S}_z\right] \neq 0 .$$

This means that $\mathbf{H}^{SO}$ is fully diagonal in $|\ L\ S\ J\ M_J\rangle$ but massively off-diagonal in $|\ L\ M_L\ S\ M_S\ \rangle$. We see that $\mathbf{H}^{SO}$ is diagonal in $|LSJM_J\rangle$ here:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$
$$\mathbf{J}^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L}\cdot\mathbf{S}$$
$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$$
$$\left\langle \mathbf{LSJM}_J \left| \mathbf{H}^{SO} \right| \mathbf{LSJM}_J \right\rangle = \frac{1}{2}\zeta(nLS)\left[J(J+1) - L(L+1) - S(S+1)\right].$$

There are cases when it is not possible to evaluate matrix elements in the "wrong" basis set because the necessary quantum numbers do not appear explicitly in the basis set. A famous example is the Zeeman Hamiltonian that cannot be expressed in the coupled basis set, which is best for $\mathbf{H}^{SO}$.

$$\mathbf{H}^{\text{Zeeman}} = \mu_{\text{Bohr}}\left[\mathbf{L}_Z + 2\mathbf{S}_Z\right]B_Z \qquad (B_Z \text{ is magnetic field})$$

$$\left\langle \text{LSJM}_J \middle| \mathbf{L}_Z \middle| \text{L}'\text{SJ}'\text{M}'_J \right\rangle = ?$$

So we need to transform between coupled and uncoupled basis sets

$$\left|\text{LSJM}_J\right\rangle = \sum \underbrace{\left|\text{LM}_L\text{SM}_S\right\rangle\overbrace{\left\langle \text{LM}_L\text{SM}_S \middle| \text{LSJM}_J \right\rangle}^{\text{transformation coefficient}}}_{\text{completeness}}.$$

What do we sum over?

We are replacing J (range $|L - S| \le J \le L + S$, that includes $2L + 1$ or $2S + 1$ values of J, whichever is smaller) in the coupled representation by M_S ($M_S = M_J - M_L$) (range $-S \le M_S \le S$, that includes $2S + 1$ or $2L + 1$ values, whichever is smaller).

$$\left|\text{LSJM}_J = \text{M}_L + \text{M}_S\right\rangle = \sum_{\substack{\text{M}_S=-S \\ (L\ge S)}}^{S} \left|\text{LM}_L\text{SM}_S\right\rangle\left\langle \text{LM}_L\text{SM}_S \middle| \text{LSJM}_J \right\rangle$$

and, in the reverse direction,

$$\left|\text{LM}_L\text{SM}_S = \text{M}_J - \text{M}_L\right\rangle = \sum_{J=|L-S|}^{L+S} \left|\text{LSJM}_J\right\rangle\left\langle \text{LSJM}_J \middle| \text{LM}_L\text{SM}_S = \text{M}_J - \text{M}_L \right\rangle.$$

The transformation coefficients are universal. It does not matter what kinds of angular momenta are involved. All that matters is that each angular momentum is defined by the standard angular momentum commutation rule.

$$\left[\mathbf{A}_i, \mathbf{A}_j\right] = i\hbar\sum_k \varepsilon_{ijk}\mathbf{A}_k.$$

So we can expect these transformation coefficients to be tabulated. The most convenient form for the transformation coefficients is 3-j coefficients, because of their symmetry properties.

$$\langle j_1 m_1 j_2 m_2 | j_1 j_2 j_3 - m_3 \equiv m_1 + m_2 \rangle = (-1)^{j_1 - j_2 - m_3} (2j_3 + 1)^{1/2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 = -m_1 - m_2 \end{pmatrix}$$

$$m_1 + m_2 + m_3 \equiv 0$$

$$|j_1 - j_2| \le j_3 \le j_1 + j_2 \quad (\text{triangle rule})$$

For example

$$|LM_L SM_S\rangle = \sum_{J=|L-S|}^{L+S} |LSJM_J = M_L + M_S\rangle (-1)^{L-S+M_L+M_S} (2J+1)^{1/2} \underbrace{\begin{pmatrix} L & S & J \\ M_L & M_S & -(M_L + M_S) \end{pmatrix}}_{3-j}.$$

All basis set transformations may be broken down into a series of coupled↔decoupled↔recoupled transformations. Two examples:

1. Hyperfine: nuclear spin I
   total angular momentum **F** = **J** + **I** = **L** + **S** + **I**
   total spin **G** = **S** + **I**

   two routes to **F**, **F** = **J** + **I**
   F = **G** + **L**
   (there is one other route) **F** = (**L** + **I**) + **S** (never used)

whenever 3 angular momenta are coupled to form a fourth, there will always be 3 coupling schemes. Often one is particularly convenient. Suppose a hyperfine coupling term a**I** · **S** is larger than the spin-orbit term **AL** · **S** (perhaps because L = 0), then

$$G = I + S$$

$$I \cdot S = \frac{1}{2}\left[G^2 - I^2 - S^2\right].$$

This means that the $|LSIGFM_F\rangle$ basis is more convenient than the $|LSJIF\rangle$ basis set.

2. Molecular Rydberg states, Watson's

$$\left|(\text{ion-core})^+ \left(\text{Rydberg } e^-\right)(\text{combined core and Rydberg angular momenta})\right\rangle \text{ basis set.}$$

The ion-core can be in Hunds cases a^+, b^+, c^+, respectively

a^+: $|(L^+)\Lambda^+ S^+ \Sigma^+ J^+ \Omega^+\rangle$

b^+: $|(L^+)\Lambda^+ S^+ N^+ J^+\rangle$

c^+: $|(L^+)\ S^+ \left(J_a^+\right)\ R^+ J^+\rangle$

and the Rydberg electron can be in any Hund's case, but since spin-orbit for a Rydberg electron is always small, cases a and c are irrelevant. Usually one is concerned about cases b and d, and e when the ion-core is in case a^+.

Many angular momenta are being coupled together in various sequences.

We need a way to deal with transformations between different coupling sequences.

Suppose we have 3 angular momenta coupled together to make a total angular momentum. We have 3 different coupling sequences.

$$\left|\, j_1 j_2 j_3 j_{1,2} (\mathbf{j}_1 + \mathbf{j}_2) J M_J \right\rangle$$
$$\left|\, j_1 j_2 j_3 j_{1,3} (\mathbf{j}_1 + \mathbf{j}_3) J M_J \right\rangle$$
$$\left|\, j_1 j_2 j_3 j_{2,3} (\mathbf{j}_2 + \mathbf{j}_3) J M_J \right\rangle$$

To transform between any two of these we need to perform two coupled→uncoupled transformations followed by two uncoupled→coupled transformations.

For example:

$$\left|\, j_1 j_2 j_3 j_{12} J M_J \right\rangle \rightarrow \left|\, j_1 j_2 j_3 m_3 j_{12} m_{12} = M_J - m_3 \right\rangle$$

uncouple j_3 from j_{12} (kill J)

$$\rightarrow \left|\, j_1 m_1 j_2 m_2 = m_{12} - m_1 j_3 m_3 = M_J - m_1 - m_2 \right\rangle$$

uncouple j_1 from j_2 (kill j_{12})

$$\rightarrow \left|\, j_1 j_2 m_2 j_3 j_{13} m_{13} \right\rangle \rightarrow \left|\, j_1 j_2 j_3 j_{13} J M_J \right\rangle$$

couple j_1 to j_3 (create j_{13})

couple j_2 to j_{13} (create J)

This sequence of transformations requires four sums over a product of *four* 3-j coefficients. These four transformations may be re-expressed as one transformation by exploiting 6-j coefficients.

$$\left|\, j_1 j_2 j_3 j_{12} J M_J \right\rangle = \sum_{j_{13}=|j_1-j_3|}^{j_1+j_3} \left|\, j_1 j_2 j_3 j_{13} J M_J \right\rangle \left\langle j_1 j_2 j_3 j_{13} J M_J \,\middle|\, j_1 j_2 j_3 j_{12} J M_J \right\rangle$$

$$\left\langle j_1 j_2 j_3 j_{13} J M_J \,\middle|\, j_1 j_2 j_3 j_{12} J M_J \right\rangle \equiv (-1)^{j_1+j_2+j_3+J} \left[(2j_{12}+1)(2j_{13}+1)\right]^{1/2} \begin{Bmatrix} j_1 & j_2 & j_3 \\ \underbrace{j_3 \quad J}_{\text{four unchanged quantum numbers}} & & \underbrace{j_{12}}_{\text{one for one replacement}} \end{Bmatrix}$$

The 6-j coefficients are invariant with respect to all six permutations of columns and to all upper/lower permutations within each of two columns. This is a total of $6 \times 4 = 24$ permutations.

There are some details about reversed angular momenta that affect the use of 3-j and 6-j coefficients. I do not fully understand these details. CAUTION!

Next we ask about evaluating matrix elements. We classify operators according to their spherical tensor character with respect to various angular momenta.

$$\left[\mathbf{J}_z, \mathbf{T}^{(\omega)}_\mu\right] = \mu \mathbf{T}^{(\omega)}_\mu$$

$$\left[\mathbf{J}_\pm, \mathbf{T}^{(\omega)}_\mu\right] = \left[\omega(\omega+1) - \mu(\mu \pm 1)\right]^{1/2} \mathbf{T}^{(\omega)}_{\mu\pm1}$$

ω is the rank and μ is the component. The $\mathbf{T}^{(\omega)}_\mu$ are analogous to an angular momenta of magnitude, ω, and z-component, μ. Since the spherical tensor classification of the operator does not depend on the specific nature of the operator, one expects that some sort of general statement might be made about matrix elements of $\mathbf{T}^{(\omega)}_\mu$ operators in a $|JM_J\rangle$ basis set. This is the Wigner-Eckart Theorem,

$$\left\langle N' j' m' \left| \mathbf{T}^{(\omega)}_\mu \right| N j m \right\rangle = (-1)^{j'-m'} \begin{pmatrix} j' & \omega & j \\ -m' & \mu & m \end{pmatrix} \left\langle N' j' \left\| T^{(k)} \right\| N j \right\rangle.$$

The non-zero matrix elements must satisfy the selection rule and triangle condition.

$-m' + \mu + m = 0$ OR $\mu = m' - m$

$|j' - \omega| \le j \le j' + \omega$

N′, N are all "other" quantum numbers needed to specify a state. $\left\langle N' j' \left\| T^{(k)} \right\| N j \right\rangle$ is called a *reduced matrix element*. All projection (component) quantum numbers have been "removed" via the Wigner-Eckart Theorem.

In order to use the Wigner-Eckart Theorem most effectively it is necessary to learn how to do two things:

1. Decompose $\mathbf{T}^{(\omega)}_{\mu}(\mathbf{A},\mathbf{B})$ in terms of products of tensor components of **A** and **B**. For example, **H** is a scalar quantity $\left(\mathbf{T}^{(0)}_0\right)$ with respect to the total angular momentum. If **A,B** are vector operators:

$$\mathbf{T}^{(0)}_0(\mathbf{A},\mathbf{B}) = \sum_{i=x,y,z} \mathbf{A}_i \cdot \mathbf{B}_i = \sum_{\mu=-1}^{1} (-1)^{\mu} \mathbf{A}_{\mu} \cdot \mathbf{B}_{-\mu} \qquad \text{(e.g. } \mathbf{H})$$

$$\mathbf{T}^{(1)}_{\pm 1}(\mathbf{A},\mathbf{B}) = \mathbf{A}_{\pm 1}\mathbf{B}_0 - \mathbf{A}_0\mathbf{B}_{\pm 1}$$

$$\mathbf{T}^{(1)}_0(\mathbf{A},\mathbf{B}) = \mathbf{A}_1\mathbf{B}_{-1} - \mathbf{A}_{-1}\mathbf{B}_1$$

$$\mathbf{T}^{(2)}_{\pm 2}(\mathbf{A},\mathbf{B}) = \mathbf{A}_{\pm 1}\mathbf{B}_{\pm 1}$$

$$\mathbf{T}^{(2)}_{\pm 1}(\mathbf{A},\mathbf{B}) = \mathbf{A}_{\pm 1}\mathbf{B}_0 + \mathbf{A}_0\mathbf{B}_{\pm 1}$$

$$\mathbf{T}^{(2)}_0(\mathbf{A},\mathbf{B}) = 2\mathbf{A}_0\mathbf{B}_0 + \mathbf{A}_1\mathbf{B}_{-1} + \mathbf{A}_{-1}\mathbf{B}_1$$

where $\mathbf{A}_0 = \mathbf{A}_z$, $\mathbf{A}_{\pm 1} = \mp 2^{-1/2}(\mathbf{A}_x \pm i\mathbf{A}_y)$.

More generally, for combinations of tensorial operators

$$\mathbf{T}^{(\omega)}_{\mu}(\mathbf{A}_1,\mathbf{A}_2) = \sum (-1)^{\omega_1-\omega_2-\mu}(2\omega+1)^{1/2} \begin{pmatrix} \omega_1 & \omega_2 & \omega \\ \mu_1 & \mu_2 = \mu - \mu_1 & -\mu \end{pmatrix} \mathbf{T}^{(\omega_1)}_{\mu_1}(\mathbf{A}_1)\mathbf{T}^{(\omega_2)}_{\mu-\mu_1}(\mathbf{A}_2)$$

2. Uncouple the basis functions into factors operated on exclusively by $\mathbf{T}^{(\omega_1)}_{\mu_1}(\mathbf{A}_1)$ and $\mathbf{T}^{(\omega_2)}_{\mu_2}(\mathbf{A}_2)$. For example:

$$\mathbf{H}^{SO} = \sum_{\substack{i \\ \text{electrons}}} \mathrm{T}^{(0)}_0\left(a(r_i)\ell_i, \mathbf{s}_i\right) = \sum_i \sum_{\mu=-1}^{1} (-1)^{\mu} \mathrm{T}^{(1)}_{\mu}\left(a(r_i)\ell_i\right) \mathrm{T}^{(1)}_{-\mu}(\mathbf{s}_i)$$

and the matrix elements are

$$\left\langle L'M'_L S'M'_S \right| \mathbf{H}^{SO} \left| LM_L SM_S \right\rangle = \sum_i \sum_{\mu=-1}^{1} \left\langle L'M'_L \right| \mathrm{T}^{(1)}_{\mu}(a(r_i)\ell_i) \left| LM_L = M'_L + \mu \right\rangle$$
$$\times \left\langle S'M'_S \right| \mathrm{T}^{(1)}_{-\mu}(\mathbf{s}_i) \left| SM_S = M_{S'} - \mu \right\rangle$$