Secular dipole-dipole derivation PhL 2.2.08

Start with the full result shown page 204 in (7.34). Omit the b factor, we add it back at the end.
We can write the Hamiltonian in this manner:

$$H = [3e_i e_j - \delta_{ij}]\, I_{1i} I_{2j}$$

Now, the sum for H has nine terms and we can *just write them out*:

$$(3e_x e_x - 1)\, I_{1x} I_{2x} + (3e_x e_y)\, I_{1x} I_{2y} + (3e_x e_z)\, I_{1x} I_{2z}$$

$$+ (3e_y e_x)\, I_{1y} I_{2x} + (3e_y e_y - 1)\, I_{1y} I_{2y} + (3e_y e_z)\, I_{1y} I_{2z}$$

$$+ (3e_z e_x)\, I_{1z} I_{2x} + (3e_z e_y)\, I_{1z} I_{2y} + (3e_z e_z - 1)\, I_{1z} I_{2z}$$

The four terms in red have an I_z with a transverse I component, and we know these are going to have a single raising or lowering operator so we throw them out in a secular approximation. Two of the remaining terms can be combined, and we get

$$H = (3e_x^2 - 1)\, I_{1x} I_{2x} + (3e_y^2 - 1)\, I_{1y} I_{2y} + (3e_z^2 - 1)\, I_{1z} I_{2z} + (3e_x e_y)\, [I_{1x} I_{2y} + I_{1y} I_{2x}]$$

Now from Levitt page 159 (13.6) we see that $[I_{1x} I_{2y} + I_{1y} I_{2x}] = (1/2)\ \{ -i\, I_1^+ I_2^+ + i\, I_1^- I_2^- \}$ just to save us recomputing it. Clearly we want to dump this term in any secular action. So we are left with

$$H = (3e_x^2 - 1)\, I_{1x} I_{2x} + (3e_y^2 - 1)\, I_{1y} I_{2y} + (3e_z^2 - 1)\, I_{1z} I_{2z}$$

Now we want to form the two transverse products shown, but throw out ++ and -- combinations, so we get

$$I_{1x} I_{2x} = I_{1y} I_{2y} = (1/4)\ (\ I_1^+ I_2^- + I_1^- I_2^+\ ) \qquad \text{// given that we throw those things out}$$

We want to KEEP these terms because they are zero-quantum terms. They will have matrix elements close to the other terms so secular says to keep them! So we now have

$$H = \{(3e_x^2 - 1) + (3e_y^2 - 1)\}\ (1/4)\ (\ I_1^+ I_2^- + I_1^- I_2^+\ ) + (3e_z^2 - 1)\, I_{1z} I_{2z}$$

The first factor in {} is $\{3(1-e_z^2) - 2\} = -(3e_z^2 - 1)$. So now we have:

$$H = (3e_z^2 - 1)\ \{\ I_{1z} I_{2z} - (1/4)\ (\ I_1^+ I_2^- + I_1^- I_2^+\ )\}$$
$$(1/2)(3e_z^2 - 1)\ \{\ 2 I_{1z} I_{2z} - (1/2)\ (\ I_1^+ I_2^- + I_1^- I_2^+\ )\}$$

now we use our little identity from our ang mom page which says $(1/2)(\ I_1^+ I_2^- + I_1^- I_2^+\ ) = I_1 \bullet I_2 - I_{1z} I_{2z}$ so we then get

$$H = (1/2)(3e_z^2 - 1)\{ 2I_{1z}I_{2z} - [\mathbf{I_1 \bullet I_2} - I_{1z}I_{2z}] \}$$

$$= (1/2)(3e_z^2 - 1)\,[3I_{1z}I_{2z} - \mathbf{I_1 \bullet I_2}]$$

QED. We have shown that by throwing out all but zero-quantum terms, we get (7.37).

Comment 1. Notice a similar tensor structure in (7.30) page 201 where $I_1 = I_2$. And notice similarity to the quadrupole moment 2,0 factor ($3z^2$-r^2). Situations are different, but it is how things *transform* that determines the spherical tensor aspect.

Comment 2: In the *hetero*nuclear case, the ($I_1^+I_2^- + I_1^-I_2^+$) type terms are "far away" because the absorption gaps are very different for the two different nuclei, so you can throw these terms out as well, even though they are nominally zero quantum. This is the same as saying $\mathbf{I_1 \bullet I_2} = I_{1z}I_{2z}$ and we then get the result on page 207 top. We make the exact same replacement top of page 213 for heteronuclear.

Comment 3: This very same idea is applied in the "weak coupling" situation described page 233. If you do a photon up and another one down, where you land is far from where you started if $\omega_1 - \omega_2$ is large relative to J, so can throw out the ($I_1^+I_2^- + I_1^-I_2^+$) type terms and use $\mathbf{I_1 \bullet I_2} = I_{1z}I_{2z}$ in this case. We of course made this assumption in all our AX system work.

Tensor Stuff

We could define two symmetric Cartesian rank-2 tensors as follows

$$A_{ij} = 3e_ie_j - \delta_{ij} \qquad B_{ij} = I_{1i}I_{2j} \qquad \mathrm{tr}(A) = 0 \qquad \mathrm{tr}(B) = \mathbf{I_1 \bullet I_2}$$

and then H is the contraction of these two things, $H = A_{ij}B_{ij}$. We are not surprised to find that such a contraction yields a scalar.

Tinkham on page 126 discusses the relation between Cartesian and Spherical rank-2 tensors, his writing is very good, I am fortunate to have this book of his.

In general, he says, if you have a Cartesian rank-2 tensor T_{ij}, you can break it into its j = 0,1 and 2 components as follows:

j=0	tr(T)		1 indep var
j=1	$A_i = \varepsilon_{ijk}(T_{jk} - T_{kj})$		3 indep vars
` j=2	$S_{ij} = (1/2)(T_{ij} + T_{ji}) - (1/3)\,\mathrm{tr}(T)$	// traceless	5 indep vars

These are not exactly the spherical operator components, but each set is a linear combination of them within its j world. For example, we can see that A_i is a Cartesian vector, so we know from our separate document on this subject how to turn it into it into a spherical ℓ=1 tensor component set. A similar thing can be done with the S_{ij} terms to make the 5 components of an ℓ=2 spherical tensor, but Tinkham does not write these down as far as I can tell.

However, on page 129, he does write down these 5 components if you take a direct product of two j=1 spherical tensors which he calls U and V. You can convert these things back to x,y,z by using the usual substitutions as shown on page 126. (see // comments below about his U,V forms)

Now what can we say about the spherical content of our two Cartesian tensors A and B above?

Since A and B are both symmetric, neither of them has a j=1 component.

Since tr(A) = 0, A is also missing its j=0 component. A is entirely j=2, and you can see that the 5 independent components can be written as [e_{xx}, e_{yy}, e_{xy}, e_{xz}, e_{yz}] .

So here are our conclusions:

A	j=0	0
	j=1	0
	j=2	[$e_x e_x$, $e_y e_y$, $e_x e_y$, $e_x e_z$, $e_y e_z$]
B	j=0	$\mathbf{I_1 \bullet I_2}$
	j=0	0
	j=2	$I_{1i} I_{2j}$ - (1/3) $\mathbf{I_1 \bullet I_2}$

In the last case we just wrote out S_{ij} and we know it has 3 diag + 2 off diag = 5 independent elements.

Now, suppose we actually had the various spherical tensors all written out. We would find that our scalar result $H = A_{ij}B_{ij}$ is equal to the contraction of the j=2 part of A with the j=2 part of B. In this regard, it is somewhat like our electric quadrupole stuff.

Notice that we really have $\hat{e} = \hat{e}(\theta,\phi)$, and functions like $e_x = \sin\phi\sin\theta$, $e_z = \cos\theta$. If we shuffled the five terms shown above around to the right linear combinations for a j=2 spherical tensor, we end up exactly with the functions $Y_{2,m}(\theta,\phi)$, the ℓ=2 spherical harmonics.

Tinkham shows us exactly how we should "contract" two tensors of the same rank to get the scalar component of the result, see page 129 (5.65). So if our B spherical tensor were $B_{2,m}$ then we would have

$$\text{scalar piece} = \Sigma_m \ (-1)^m A_{2,m} B_{2,-m} = \Sigma_m (-1)^m Y_{2,m}(\theta,\phi) B_{2,-m} = \text{constant} * H$$

So this gives an interesting way to write our same Hamiltonian! At first, we might have wondered why it contains only the ℓ=2 spherical harmonics, but now we know why!

Here is how you can construct the B tensor. You know that the +2 component will be $I_1^+ I_2^+$ and similarly for the - 2 component. So just apply the rule:

$$[\ I_1^- + I_2^-,\ I_1^+ I_2^+\ ] = \sqrt{6 - 2}\ B_{2,1} = 2\, B_{2,1}$$

The commutator can be evaluated

$$[\ I_1^- + I_2^-,\ I_1^+ I_2^+\ ] = [\ I_1^-,\ I_1^+ I_2^+\ ] + [\ I_2^-,\ I_1^+ I_2^+\ ] = [\ I_1^-,\ I_1^+\ ]\, I_2^+ + I_1^+ [\ I_2^-, I_2^+\ ]$$

$$= -2 I_{1z}\, I_2^+ - 2\, I_1^+ I_{2z} = -2(I_{1z}\, I_2^+ + I_1^+ I_{2z}) = 2\, B_{,1}$$

So far then we have:

$B_{2,2} = I_1^+ I_2^+$

$B_{2,1} = -(I_{1z} I_2^+ + I_1^+ I_{2z})$ // compare to Tinkham (5-63c) p 129

This agrees with my (19) and (20) in the electric quadrupole Q's, apart from overall constant. So from that I would predict that we have

$B_{2,0} = +\sqrt{2/3}\ (\ 3\ I_{1z}\ I_{2z} - \mathbf{I_1 \bullet I_2}\ )$ // compare to Tinkham (5-63c) p 129

which is in fact our secular Hamiltonian. So what we now realize is that the "secular approximation" is doing this:

$H_{full} = \Sigma_m\ (-1)^m\ A_{2,m}\ B_{2,-m}$ = contraction of our two j=2 parts of A and B

$H_{secular} = A_{2,0}\ B_{2,0}$ only $= (1/2)(3\cos^2\theta - 1)\ [3 I_{1z} I_{2z} - \mathbf{I_1 \bullet I_2}]$

So the term $B_{2,0}$ contains all the "zero quantum" stuff, and the other $B_{2,m}$ are 1 and 2 quantum stuff which we are throwing out. [I have not tracked constants in this discussion.]

Along the way I ran into a "Zamar" pdf (saved) which happens to talk about exactly this subject. Here the spins of interest are I_ℓ and I_k instead of my I_1 and I_2. The authors have shuffled constants and signs between their A and F factors causing some confusion, such that the A and F are not really the tensors any more, but fine. We confirm the idea that $A^0\ F^0$ is the secular approximation. The authors are talking about spin-lattice relaxation and this is happening with the dipole-dipole interaction.

$$\begin{aligned} \mathcal{H}_S &= \mathcal{H}_Z + \overline{\mathcal{H}_{SI}} \quad \text{with} \\ \mathcal{H}_Z &= -\gamma\hbar H_0 \textstyle\sum_j I_{jz}\ , \quad \text{and} \\ \overline{\mathcal{H}_{SI}} &= \tfrac{1}{2} \textstyle\sum_{lk} \sum_q A_{lk}^q \overline{F_{lk}^q}\ , \end{aligned} \qquad (2)$$

$$\begin{aligned} A_{lk}^0 &= -\gamma\hbar\{-I_l^z I_k^z + \tfrac{1}{4}(I_l^+ I_k^- + I_k^+ I_l^-)\} & F_{lk}^0 &= \tfrac{1}{r_{lk}^3}(1 - 3\cos^2\theta_{lk}) \\ A_{lk}^{\pm 1} &= -\tfrac{3}{2}\gamma\hbar(I_l^z I_k^\pm + I_l^\pm I_k^z) & F_{lk}^{\pm 1} &= \tfrac{1}{r_{lk}^3}\sin\theta_{lk}\cos\theta_{lk} e^{\pm i\phi_{lk}} \\ A_{lk}^{\pm 2} &= -\tfrac{3}{4}\gamma\hbar I_l^\pm I_k^\pm\ ; & F_{lk}^{\pm 2} &= \tfrac{1}{r_{lk}^3}\sin^2\theta_{lk} e^{\pm 2i\phi_{lk}}\ . \end{aligned} \qquad (3)$$