A B

Spin $\frac{1}{2}$ + Spin 1

$\mathcal{H}_A = \text{span}\{|\uparrow\rangle, |\downarrow\rangle\}$ $\mathcal{H}_B = \text{span}\{|1\rangle, |0\rangle, |-1\rangle\}$

$\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B = \mathcal{H}_{\frac{1}{2}} \oplus \mathcal{H}_{3/2}$ b.c. $\frac{1}{2} \otimes 1 = \frac{1}{2} \oplus \frac{3}{2}$

↳ $\mathcal{H}_{1/2} = \text{span}\{|1\tfrac{1}{2}, \tfrac{1}{2}\rangle, |1\tfrac{1}{2}, -\tfrac{1}{2}\rangle\}$ & $\mathcal{H}_{\frac{3}{2}} = \text{span}\{|\tfrac{3}{2}, m\rangle\}$

$\dim \mathcal{H} = \dim \mathcal{H}_A \times \dim \mathcal{H}_B = 2 \times 3 = 6$ w/ $m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$

$= \dim \mathcal{H}_{\frac{1}{2}} + \dim \mathcal{H}_{3/2} = 2 + 4 = 6$ ✓

Each factor has $\vec{S}_A$ and $\vec{S}_B$ w/ $\vec{S}^2_{A/B} = s(s+1)\mathbb{1}$ b.c irrep

so $\vec{S}_A^2 = \frac{3}{4}\mathbb{1}$ and $\vec{S}_B^2 = 2\mathbb{1}$

Define $\vec{S} = \vec{S}_A + \vec{S}_B \Rightarrow \vec{S}^2 = \vec{S}_A^2 + \vec{S}_B^2 + 2\vec{S}_A \cdot \vec{S}_B$

$= \frac{11}{4}\mathbb{1} + 2\vec{S}_A \cdot \vec{S}_B$

Because whole $\mathcal{H}$ is a reducible representation $\vec{S}^2 = \sum_s s(s+1) P^{(s)}$

where s is adding the spins appearing in the combination

and $P^{(s)}$ is the projector into the s-spin subspace

For us, $\vec{S}^2 = \frac{3}{4} P^{(\frac{1}{2})} + \frac{15}{4} P^{(3/2)}$ where $P^{(\frac{1}{2})} = |\tfrac{1}{2}, \tfrac{1}{2}\rangle\langle\tfrac{1}{2}, \tfrac{1}{2}| + |\tfrac{1}{2}, -\tfrac{1}{2}\rangle\langle\tfrac{1}{2}, -\tfrac{1}{2}|$ for ex.

In the $|s, m\rangle$ basis this is diagonal, but not in the tensor product basis

↳ $\vec{S}^2 = \begin{pmatrix} \frac{3}{4} & & & & & \\ & \frac{3}{4} & & & & \\ & & 15/4 & & & \\ & & & 15/4 & & \\ & & & & 15/4 & \\ & & & & & 15/4 \end{pmatrix}$

The two bases can be interchanged w/ "6-j coefficients"

ex $|\frac{3}{2}, \frac{3}{2}\rangle = |1\rangle|\uparrow\rangle$ but $|\frac{3}{2}, \frac{1}{2}\rangle = \sqrt{\frac{1}{3}}|1\rangle|\downarrow\rangle + \sqrt{\frac{2}{3}}|0\rangle|\uparrow\rangle$

More on projectors, the $P^{(S)}$ can always be written as polynomials in $\vec{S}^2$; $P^{(S)} \propto \prod_{S' \neq S} \left(\vec{S}^2 - S'(S'+1)\right)$

so that a factor vanishes when $\vec{S}^2 |S', m\rangle = S'(S'+1)|S', m\rangle$

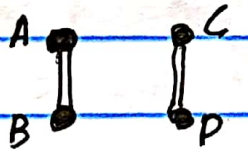
Ex: $P^{(1/2)} \propto \left(\vec{S}^2 - \frac{15}{4}\mathbb{1}\right)$ where the proportionality coefficient is determined by $P^{(S)}|S,m\rangle = |S,m\rangle$

$P^{(1/2)}|\tfrac{1}{2},m\rangle = \lambda\left(\tfrac{3}{4} - \tfrac{15}{4}\right)|\tfrac{1}{2},m\rangle$

$\hookrightarrow \lambda = -\frac{4}{12} = -\frac{1}{3}$

This can give non-trivial operators when substituting $\vec{S}^2 = \#\mathbb{1} + 2\vec{S}_A \cdot \vec{S}_B$

Suppose we have two molecules w/ two sites



we model an electron on this system as a 4-state QM problem

$\mathcal{H} = \text{span}\{|A\rangle, |B\rangle, |C\rangle, |D\rangle\}$

At first the two molecules are independent w/ Hamiltonian

$$\hat{H} = \hat{H}_{AB} + \hat{H}_{CD} = \left(\begin{matrix} U|A\rangle\langle A| + U|B\rangle\langle B| \\ + \\ t|A\rangle\langle B| + t|B\rangle\langle A| \end{matrix}\right) + \left(\begin{matrix} \varepsilon|C\rangle\langle C| + \varepsilon|D\rangle\langle D| \\ + \\ \tilde{t}|C\rangle\langle D| + \tilde{t}|D\rangle\langle C| \end{matrix}\right)$$

Written as a matrix in this basis

$$\hat{H} = \begin{pmatrix} U & t & & \\ t & U & & \\ & & \varepsilon & \tilde{t} \\ & & \tilde{t} & \varepsilon \end{pmatrix}$$

We can diagonalize H by diagonalizing each $\hat{H}_{AB}$, $\hat{H}_{CD}$ seperately

$\hat{H}_{AB} = U\mathbb{1} + t\sigma^x \Rightarrow E_{\pm}^{AB} = U \pm t \qquad |AB,\pm\rangle = \frac{1}{\sqrt{2}}(|A\rangle \pm |B\rangle)$

$H_{CD} = \varepsilon\mathbb{1} + \tilde{t}\sigma^x \Rightarrow E_{\pm}^{CD} = \varepsilon \pm \tilde{t} \qquad |CD,\pm\rangle = \frac{1}{\sqrt{2}}(|C\rangle \pm |D\rangle)$

In the energy basis above

$$H = \begin{pmatrix} U-t & & & \\ & U+t & & \\ & & \varepsilon-\tilde{t} & \\ & & & \varepsilon+\tilde{t} \end{pmatrix}$$

Suppose $U = \varepsilon$ and $t = \tilde{t}$ and define $U - t = \varepsilon - \tilde{t} = g$

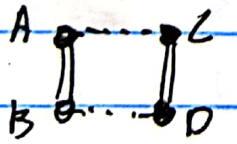
↳ $U + t = \varepsilon + \tilde{t} = G$

↳ $$H = \begin{pmatrix} g & & & \\ & G & & \\ & & g & \\ & & & G \end{pmatrix} \Rightarrow H = \begin{pmatrix} g & & & \\ & g & & \\ & & G & \\ & & & G \end{pmatrix}$$

in the $|AB,-\rangle, |CD,-\rangle, |AB,+\rangle, |CD,+\rangle$ basis

With this tuning the system is degenerate

Suppose we add hoppings across the molecules



$H = H_0 + s(|A\rangle\langle C| + |C\rangle\langle A|) + s(|B\rangle\langle D| + |D\rangle\langle B|)$

$= H_0 + V$

~~where V can be treated as a perturbation~~

Question: How do we write $\hat{V}$ in the unperturbed energy eigen basis?

$$|A\rangle = \frac{1}{\sqrt{2}}\left(|AB,+\rangle + |AB,-\rangle\right) \qquad |B\rangle = \frac{1}{\sqrt{2}}\left(|AB,+\rangle - |AB,-\rangle\right)$$

$$|C\rangle = \frac{1}{\sqrt{2}}\left(|CD,+\rangle + |CD,-\rangle\right) \qquad |D\rangle = \frac{1}{\sqrt{2}}\left(|CD,+\rangle - |CD,-\rangle\right)$$

↳ $$|A\times C| = \frac{1}{2}\left(\begin{matrix} |AB,+\times CD,+1 + |AB,+\times CD,-1 \\ |AB,-\times CD,+1 + |AB,-\times CD,-1 \end{matrix}\right)$$

$|C\times A|$ is the same w/ bras $\Rightarrow$ kets

Similarly we have

$$|B\times D| = \frac{1}{2}\left(\begin{matrix} |AB,+\times CD,+1 - |AB,+\times CD,-1 \\ -|AB,-\times C,D+1 + |AB,-\times CD,-1 \end{matrix}\right)$$

So $$|A\times C| + |B\times D| = |AB,+\times CD,+1 + |AB,-\times CD,-1$$

So in the basis of original energy eigenstates

$$H = \begin{pmatrix} g & s & & \\ s & g & & \\ & & G & s \\ & & s & G \end{pmatrix}$$

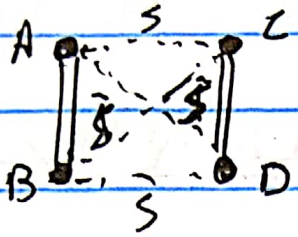
and we can still solve it exactly!

$$E_0 = g - s \qquad E_1 = g + s$$

$$|E_0\rangle = \frac{1}{\sqrt{2}}\left(|AB,-\rangle - |CD,-\rangle\right) \qquad |E_1\rangle = \frac{1}{\sqrt{2}}\left(|AB,-\rangle + |CD,-\rangle\right)$$

and so on

What if we added diagonal hoppings as well



and got a matrix like

$$\tilde{V} = \tilde{s}\,(|A\rangle\langle D| - |B\rangle\langle C| + h.c.)$$

$$H = \begin{pmatrix} g & s & 0 & \tilde{s} \\ s & g & -\tilde{s} & 0 \\ 0 & -\tilde{s} & G & s \\ \tilde{s} & 0 & s & G \end{pmatrix}$$

This ruins the nice block structure and means we'd need to diagonalize the full 4x4 to solve exactly

What is $\tilde{s} \ll 1$ so that $\tilde{V}$ is a perturbation?

Let $s = 0$ for a moment. We're doing degenerate perturbation theory

$$H = H_0 + \tilde{V} = \begin{pmatrix} g & 0 & 0 & \tilde{s} \\ 0 & g & -\tilde{s} & 0 \\ 0 & -\tilde{s} & G & 0 \\ \tilde{s} & 0 & 0 & G \end{pmatrix}$$

Suppose we want the correction to the ground states to second order in $\tilde{s}$

At first order in perturbation theory the effective Hamiltonian is

$$H_{eff} = \begin{pmatrix} g & 0 \\ 0 & g \end{pmatrix}$$ which has no $\tilde{s}$ so the correction only appears at second order

There's a slick way of writing H_{eff} to second order

Consider $$H = \begin{pmatrix} H_L & T_{LH} \\ T_{HL} & H_H \end{pmatrix}$$ where all of these are matrices

H_L describes the "low-energy" states and has eigenvalues E_0
H_H describes "high-energy" states and $\{T_{LH}, T_{HL}\}$ connect them

To second order in perturbation theory in $\|T\|$

$$H_{eff} = H_L + T_{LH}(E_0 - H_H)^{-1} T_{HL}$$

So in our case: $H_L = \begin{pmatrix} g & 0 \\ 0 & g \end{pmatrix}$ $H_H = \begin{pmatrix} G & 0 \\ 0 & G \end{pmatrix}$

$$T_{LH} = \begin{pmatrix} 0 & \tilde{s} \\ -\tilde{s} & 0 \end{pmatrix} \quad T_{HL} = \begin{pmatrix} 0 & -\tilde{s} \\ \tilde{s} & 0 \end{pmatrix}$$

$$H_{eff} = \begin{pmatrix} g & 0 \\ 0 & g \end{pmatrix} + \begin{pmatrix} 0 & \tilde{s} \\ -\tilde{s} & 0 \end{pmatrix} \begin{pmatrix} (g-G)^{-1} & \\ & (g-G)^{-1} \end{pmatrix} \begin{pmatrix} 0 & -\tilde{s} \\ \tilde{s} & 0 \end{pmatrix}$$

$$= \begin{pmatrix} g + \frac{s^2}{g-G} & 0 \\ 0 & g + \frac{s^2}{g-G} \end{pmatrix}$$ Degeneracy not split at second order

Some times this method isn't the simplest, it's best when you already have the matrix elements this away

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Consider a $d=3$ spin-1 particle in a SHO potential with this spin coupling

$$H = \frac{p^2}{2} + \frac{1}{2}\omega^2 r^2 + \lambda \vec{r}\cdot\vec{S}$$

where $\vec{S} = (S_x, S_y, S_z)$ are spin-1 matrices

Suppose $\lambda \ll \omega$ so the last term can be treated perturbatively, compute the correction to the groundstate energy to second order

The groundstate is 3-fold degenerate $|n=0\rangle \otimes |m\rangle$ where $m = \{1, 0, -1\}$ for spin states

The first order correction vanishes as $\langle n=0 | \vec{r} | n=0 \rangle = 0$ so we need to go to second order degenerate PT

$$H_{eff} = P\left(\sum_k \frac{\hat{V}|k\rangle\langle k|\hat{V}}{E_0 - E_k}\right)P$$

where P is the projector into the degenerate subspace

$\{|k\rangle\}$ includes every thing outside this subspace

V is the perturbation, E_0 and E_k are unperturbed energies

To Let's look at position space first

$\langle 0,0,0| \hat{r} |n_1, n_2, n_3\rangle$ $\qquad r_i = \frac{1}{\sqrt{2\omega}}(a_i + a_i^\dagger)$

↑ From P ↑ From $|k\rangle$

So $\langle 0,0,0| \hat{r}_i |n_1, n_2, n_3\rangle = \frac{1}{\sqrt{2\omega}}$ From the $|k\rangle$ state with $n_i = 1$ else 0

↳ $E_k = \omega\left(1 + \frac{3}{2}\right) = \frac{5}{2}\omega$ $\qquad (E_0 = \frac{3}{2}\omega)$

$$H_{eff} = \frac{\lambda^2}{2\omega}\left(-\frac{1}{\omega}\right) P \sum_m (\vec{S}\cdot\hat{n})\,|m\rangle\langle m|\,(\vec{S}\cdot\hat{n})\, P$$

Spin part of perturbation

But this looks like $S_x\left(\sum_m |m\rangle\langle m|\right) S_x + S_y\left(\sum_m |m\rangle\langle m|\right) S_y + S_z\left(\sum_m |m\rangle\langle m|\right) S_z$

$= S_x^2 + S_y^2 + S_z^2 = \vec{S}^2$

$= 2\mathbb{1}$ for spin-1

and $P = \sum_m |m\rangle\langle m| = \mathbb{1}_{spin}$

↳ $H_{eff} = -\frac{\lambda^2}{\omega^2}\mathbb{1}$ $\Rightarrow$ degeneracy not lifted