WEEK 3 : Spherical Tensors

Formal definition of spherical tensor operators :

- First, a Cartesian tensor : For vectors $\vec{v}$ and $\vec{w}$, a cartesian tensor $T_{ij} = v_i w_j \longrightarrow \hat{R} : T'_{ij} = v'_i w'_j = \sum_{\ell n} R_{i\ell} R_{jn} V_\ell W_n$.

Basically, a tensor (seems) to be defined based on it's transformation under rotation.

Where does this come from? A rotation $R(\alpha, \beta, \gamma)$ can be represented as a matrix:

$$\mathbb{R}(\alpha,\beta,\gamma) = \mathbb{R}_z(\alpha)\,\mathbb{R}_y(\beta)\,\mathbb{R}_z(\gamma)$$

where:

$\mathbb{R}_z(\alpha)$ for $\hat{R}_z(\alpha)\vec{r} = \vec{r}\,'$ where $\left.\begin{matrix} x' = x\cos\alpha - y\sin\alpha \\ y' = x\sin\alpha + y\cos\alpha \end{matrix}\right\}$

$$\overset{!}{=} \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and so on.

So that $x'_i = \sum_j \underset{\text{element from } \mathbb{R}(\alpha,\beta,\gamma)}{R_{ij}} x_i$.

Demonstration (?):

$$x'_i \equiv \underset{\text{unit vector}}{\hat{x}_i} \cdot \vec{r}\,' = \hat{x}_i \cdot \hat{R}\vec{r} = \hat{x}_i \cdot \hat{R}\left(\sum_j \hat{x}_j x_j\right)$$

$$= \sum_j \underbrace{(\hat{x}_i \cdot \hat{R}\hat{x}_j)}_{\text{physical}} x_j = \sum_j \mathbb{R}_{ij} x_j$$

"A vector is a quantity whose three (cartesian) components transform as the component of the position vector under rotations"

$\vec{A}$ is a vector $\Leftrightarrow A'_i = \sum_j R_{ij} A_j$

"A cartesian tensor is a collection of multi-index quantities T_{ijk} which transform as:

$$T'_{ijk} = \sum_{i'j'k'} R_{ii'} R_{jj'} R_{kk'} T_{i'j'k'}$$

- The cartesian components of the position vector are linear combinations of spherical harmonics with $\ell = 1$:

$$Y_{1\pm1}(\hat{r}) = \mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\underbrace{\sin\theta\, e^{\pm i\phi}}_{} = \mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\overset{\text{a scalar!}}{\frac{1}{r}}(x \pm iy)$$

$$= \frac{1}{r}(r\sin\theta\cos\phi \pm i r\sin\theta\sin\phi) = (x \pm iy)/r$$

and $Y_{10}(\hat{r}) = \sqrt{\frac{3}{4\pi}} \cos\theta$

meaning we can also write cartesian components x, y, z as combinations of spherical tensors.

- As a result! We can connect the transformation of a Cartesian tensor to the transformation of a "spherical tensor".

Say $A_{1,0} \equiv A_z$, $A_{1,\pm 1} = \mp \frac{A_x \pm i A_y}{\sqrt{2}}$

Then $A_{1,\mu} = \sqrt{\frac{4\pi}{3}} |\vec{A}| Y_{1\mu}(\hat{A})$

↖ unit vector along $\vec{A}$.

$A_{1,\mu}$ is a spherical tensor with <u>rank</u> $j=1$. Furthermore:

$Y_{\ell m}(\theta, \phi) = \langle \hat{r} | \ell m \rangle$, $\hat{R} | \ell m \rangle = \sum_{m'} | \ell m' \rangle \langle \ell m' | \hat{R} | \ell m \rangle$

($| \ell m \rangle$ form $2\ell+1$ space invariant under rotations)

$= \sum_{m'} | \ell m' \rangle D^{(\ell)}_{m'm}(\alpha, \beta, \gamma)$ ①

where $A_{1\mu} = | \ell m \rangle |\vec{a}|$.

We already know $[\hat{J}_i, \hat{A}_j] = i\hbar \varepsilon_{ijk} A_k$ for vector (tensor of rank 1) operator $\hat{A}$ and $[\hat{J}_i, \hat{S}] = 0$ for scalar $\hat{S}$ (rank 0 tensor)

Thus we infer these can be extended to tensors of all ranks.

Say $\hat{T}_{k\mu}$, with rank k and projection $\mu = -k, -k+1, \ldots, k$ is a family of ~~tensor~~ operators.

$\hat{R} | \psi_{JM} \rangle = \sum_{M'} | \psi_{JM'} \rangle D^{(J)}_{M'M}$

This is how the <u>object</u> w/ angular momentum J transforms under rotation.

What about:

$\hat{R}(\hat{T}_{k\mu} | \psi_{JM} \rangle)$? We expect it to be like: $\hat{R}(\hat{T}_{k\mu})\hat{R}|\psi\rangle$

And of course, the expression is equal to: $\hat{R}\hat{T}_{k\mu}\hat{R}^{-1}\hat{R}|\psi\rangle$.

which implies:

$\hat{R}\hat{T}_{k\mu}\hat{R}^{-1} = \hat{R}\hat{T}_{k\mu}$ this is how the <u>operators</u> transform under rotation.

<u>IF</u> $\hat{R}\hat{T}_{k\mu}$ fits the form of ① so that

$$\hat{R}\hat{T}_{k\mu}\hat{R}^{-1} = \sum_{\mu'} \hat{T}_{k\mu'} D^{(k)}_{\mu'\mu}(\hat{R})$$

<u>THEN</u> $\{\hat{T}_{k\mu}\}$ is a spherical tensor of rank k.

with this definition, we can define the generic commutators.

$\hat{R} = e^{-i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar}$ $\hat{R}\hat{T}_{k\mu}\hat{R}^{-1}$ is:

$$e^{-i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar}\hat{T}_{k\mu}e^{i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar} = \sum_{\mu'}\hat{T}_{k\mu'}\langle k\mu'|e^{-i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar}|k\mu\rangle$$

if we pick $\phi \ll 1$ and expand to $O(\phi^2)$:

$$(1-i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar)\hat{T}_{k\mu}(\hat{1}+i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar) = \sum_{\mu'}\hat{T}_{k\mu'}\langle k\mu'|\hat{1}-i\phi\hat{n}\cdot\hat{\vec{J}}/\hbar|k\mu\rangle$$

$$\hat{T}_{k\mu} - \frac{i\phi}{\hbar}[\hat{n}\cdot\hat{\vec{J}},\hat{T}_{k\mu}] = \hat{T}_{k\mu} - \frac{i\phi}{\hbar}\sum_{\mu'}\hat{T}_{k\mu'}\langle k\mu'|\hat{n}\cdot\hat{\vec{J}}|k\mu\rangle$$

$$[\hat{n}\cdot\hat{\vec{J}},\hat{T}_{k\mu}] = \sum_{\mu'}\hat{T}_{k\mu'}\langle k\mu'|\hat{n}\cdot\hat{\vec{J}}|k\mu\rangle$$

the $\hat{n}$ can be $\hat{x},\hat{y},\hat{z}$, so we can make $\hat{J}_{x,y,z}$ and find commutators with $\hat{J}_\pm$

$$[\hat{J}_z,\hat{T}_{k\mu}] = \sum_{\mu'}\hat{T}_{k\mu'}\underbrace{\langle k\mu'|\hat{J}_z|k\mu\rangle}_{=\hbar\mu\,\delta_{\mu'\mu}} = \hbar\mu\,\hat{T}_{k\mu}$$

$$[\hat{J}_\pm,\hat{T}_{k\mu}] = \sum_{\mu'}\hat{T}_{k\mu'}\underbrace{\langle k\mu'|\hat{J}_\pm|k\mu\rangle}_{\hbar\sqrt{k(k+1)-\mu(\mu\pm1)}\,|k\mu\pm1\rangle} = \hbar\sqrt{k(k+1)-\mu(\mu\pm1)}\,\hat{T}_{k\mu\pm1}$$

Any $\{\hat{T}_{k\mu}\}$ that fills these commutation relations are spherical tensors (definition).

Wigner-Eckhart Thm again:

$\langle\alpha,J\underline{M}|\hat{T}_{k\underline{\mu}}|\alpha',J'\underline{M'}\rangle$ has 3 different magnetic quantum numbers, which define how each component is oriented in space. WE thm says

$$= \underbrace{C^{JM}_{J'M'k\mu}}/\sqrt{2J+1}\;\langle\alpha J\|\hat{T}_k\|\alpha' J'\rangle$$

↖ no dependence on magnetic #s.

The magnetic #s are all here!

On its own, $\hat{T}_{k\mu}|\alpha',J'M'\rangle$ is not well defined. It is projected to a specific value with $\langle JM|$.

We can demonstrate the WE thm using our commutation relations.

$$\underbrace{\langle \alpha j m | \hat{T}_{kk} | \alpha' j' j' \rangle}_{} = \delta_{j, k+j'} \delta_{m, k+j'} \cdot (??)$$
← some #.

μ and m' are as large as possible. This is also an eigenstate of $\hat{J}_z$ where $m = k+j'$ and $j_{total} = k+j'$.

$\delta_{j, k+j'} \delta_{m, k+j'}$ is indeed $C^{j'+k \; j'+k}_{jj' kk} = 1$.

If we know $\langle \alpha j m | \hat{T}_{k\mu} | \alpha' j' m' \rangle$ for $m, m+1, \ldots, m=j$ then we can do:

$$\langle \alpha j m | [\hat{J}_+, \hat{T}_{k\mu}] | \alpha' j' m' \rangle = \hbar \sqrt{k(k+1) - \mu(\mu+1)} \langle \alpha j m | \hat{T}_{k\mu+1} | \alpha' j' m' \rangle$$

$$= \langle \alpha j m | \hat{J}_+ \hat{T}_{k\mu} | \alpha' j' m' \rangle - \langle \alpha j m | \hat{T}_{k\mu} \hat{J}_+ | \alpha' j' m' \rangle$$

$\hat{J}_-$

$$\hbar \sqrt{j(j+1) - m(m-1)} \langle \alpha j m-1 | \hat{T}_{k\mu} | \alpha' j' m' \rangle$$

$$= \hbar \sqrt{j'(j'+1) - m'(m'+1)} \langle \alpha j m | \hat{T}_{k\mu} | \alpha' j' m'+1 \rangle + \hbar \sqrt{k(k+1) - \mu(\mu+1)} \langle \cdots \rangle$$

So:

$$\langle \alpha j (m-1) | \hat{T}_{k\mu} | \alpha' j' m' \rangle$$

$$= \sqrt{\frac{j'(j'+1) - m'(m'+1)}{j(j+1) - m(m-1)}} \langle \alpha j \underline{\underline{m}} | \hat{T}_{k\mu} | \alpha' j' m'+1 \rangle$$

$$+ \sqrt{\frac{k(k+1) - \mu(\mu+1)}{j(j+1) - m(m-1)}} \langle \alpha j m | \underline{\underline{\hat{T}_{k\mu+1}}} | \alpha' j' m' \rangle$$

This is the SAME as the Clebsch-Gordan recurrence relation. so indeed:

$$\langle \alpha j m | \hat{T}_{k\mu} | \alpha' j' m' \rangle \propto C^{jm}_{j'm' k\mu}$$

<u>Why is this interesting?</u>

Some transitions, e.g. $|i\rangle \xrightarrow[\hbar, \gamma, \omega]{\text{excited!}} |f\rangle$ that occur with probabilities

$P_{f \leftarrow i} \propto |\langle f | \hat{H}_I | i \rangle|^2$ (first order TDPT) or $|i\rangle \xrightarrow[\hbar, \gamma']{\hbar, \gamma} |f\rangle$

$P_{f \leftarrow i} \propto |\langle f | \hat{H}_I \hat{G}_0^+ (E_i + \hbar\omega) \hat{H}_I | i \rangle|^2$ (2nd order TDPT)

Basically if $\hat{H}_I = -\vec{\mathcal{E}} \cdot \hat{\vec{\mu}}$, $\hat{\vec{\mu}} = \sum_i q_i \hat{\vec{r}}_i$, $\hat{\mu}_{\pm} = \mp \frac{\hat{\mu}_x \pm i \hat{\mu}_y}{\sqrt{2}}$ etc. & the Hamiltonian is rotationally invariant (eg from a nucleus)

Then: Transition amplitude $A_{f \leftarrow i} = \langle f, JM | \hat{\mu}_{1\tau} | i, J_0 M_0 \rangle$ which via the Clebsch-Gordan / WE thm is:

$$C^{JM}_{J_0 M_0 1 \tau} \Big/ \sqrt{2J+1} \quad \langle f, J \| \hat{\mu}_1 \| i, J_0 \rangle$$

$\tau = -1, 0, \text{or } 1 \rightarrow M = M_0, M_0+1, \text{or } M_0-1$ and
$J = J_0, J_0+1, \text{or } J_0-1$

IF you have $\tau = M_0 = 0$, The coefficient is:

$$C^{J0}_{J_0 0 1 0} = (-1)^{J_0+1-J} C^{J0}_{J_0 0 1 0} \quad \text{(by def.)}$$

so if we want the transition probability to be non-zero (so the transition is possible):

$$(-1)^{J_0+1-J} \neq -1 \longrightarrow J \neq J_0$$

Take the hydrogen atom: $|n \ell m\rangle$ can emit/absorb a photon.

$$|n \ell 0\rangle \xrightarrow[\hat{\mu}_{10}]{\gamma} |n \underline{\ell \pm 1}\, 0\rangle$$

why?

$|n\ell 0\rangle$ is proportional to spherical harmonics with angular momentum ℓ:

$\langle \vec{r} | n \ell m \rangle = R_{n\ell}(r) Y_{\ell m}(\hat{r})$ and this spherical harmonic has a parity of $\Pi(\ell) = (-1)^{\ell}$.

$\hat{\mu}_{10}$ is odd, so $\Pi_{\mu} = -1$. Thus the final parity must be:

$\Pi(\ell)\Pi_{\mu} = (-1)^{\ell}(-1) = (-1)^{\ell+1}$ (or $(-1)^{\ell-1}$). so the final state must have $\ell' = \ell \pm 1$ and not ℓ.

Thus the transition of $J \to J$ (or in this case $\ell \to \ell$) is forbidden. (Tho only for one particle. It's possible with multiple!).

Intro to time-independent perturbation theory

Last semester we saw that you can solve for the eigenvalues/states of the Hamiltonian in a few very specific cases. It's actually not very common to be able to do that in realistic cases.

For example, sometimes the associated Hilbert space has billions or trillions of dimensions, so $\hat{H}|\Psi_n\rangle = E|\Psi_n\rangle$ is prohibitively difficult to solve.

In some of these, we can write $\hat{H}$ as:

$$\underset{\substack{\uparrow \\ \text{unperturbed} \\ \text{"model" Hamiltonian}}}{\hat{H} = \hat{H}_0} + \underbrace{\lambda \hat{V}}_{\text{a perturbation}}, \quad \lambda \in [0,1]$$

"scaling factor" often used to see transition from $\hat{H}_0$ to $\hat{H}$.

We can then solve $\hat{H}(\lambda)|\Psi_n(\lambda)\rangle = E_n(\lambda)|\Psi_n(\lambda)\rangle$ where the model Hamiltonian follows $\hat{H}_0|\Psi_n^{(0)}\rangle = E_n^{(0)}|\Psi_n^{(0)}\rangle$.

We should know $|\Psi_n^{(0)}\rangle$ and $E_n^{(0)}$ from the outset. Pick:

$$\lim_{\lambda\to 0}|\Psi_n(\lambda)\rangle = |\Psi_n^{(0)}\rangle \text{ and } \lim_{\lambda\to 0} E_n(\lambda) = E_n^{(0)}$$

where $\hat{H}_0$ has degenerate eigenvalues. And of course we want to find $|\Psi_n(\lambda)\rangle$ and $E_n(\lambda)$. We typically find these as expansions in powers of λ.

Brillouin-Wigner Method : easier, but not size consistent, meaning $E_{A+B}^{[N]} \neq E_A^{[N]} + E_B^{[N]}$ so you can't model bringing together indep. particles until they're close enough to interact.

The non-degenerate case is as follows: We introduce projector $\hat{P}$ onto the unperturbed state $|\varphi_0\rangle$, where:

$$\hat{H}_0|\varphi_n\rangle = E_n^{(0)}|\varphi_n\rangle, \quad \langle\varphi_n|\varphi_m\rangle = \delta_{nm}$$

$$\hat{P} \equiv |\varphi_0\rangle\langle\varphi_0|$$

and $\hat{P}$'s orthogonal complement $\hat{1} - \hat{P} = \sum_{n\neq 0} |\varphi_n\rangle\langle\varphi_n| = \hat{Q}$.

Note that in BW we assume $\lambda = 1$, and choose <u>intermediate</u> normalization

so $\langle \varphi_0 | \Psi \rangle = 1$.

$$[\hat{H} = (\hat{H}_0 + \hat{V})] \underset{\text{perturbed}}{|\Psi\rangle} = E|\Psi\rangle, \quad \hat{P}|\Psi\rangle = |\varphi_0\rangle\langle\varphi_0|\Psi\rangle = \underset{\text{unperturbed}}{|\varphi_0\rangle}$$

$\hat{Q} + \hat{P} = \hat{1}$, so: ↙ projects orthogonal to $|\varphi_0\rangle$ & $\hat{P}$.

$$|\Psi\rangle = (\hat{P} + \hat{Q})|\Psi\rangle = \underbrace{|\varphi_0\rangle}_{=\text{known!}} + \underbrace{\hat{Q}|\Psi\rangle}_{=\text{correction term}}$$

What is $\hat{Q}|\Psi\rangle$?

$$(\hat{H}_0 + \hat{V})|\Psi\rangle = E|\Psi\rangle$$

$$\hat{V}|\Psi\rangle = (E - \hat{H}_0)|\Psi\rangle$$

$$\hat{V}|\Psi\rangle = (E - \hat{H}_0)(|\varphi_0\rangle + \hat{Q}|\Psi\rangle)$$

Apply $\hat{Q}$ on both sides:

$$\hat{Q}\hat{V}|\Psi\rangle = \underbrace{\hat{Q}(E - \hat{H}_0)|\varphi_0\rangle}_{\substack{|\varphi_0\rangle \text{ not in } \hat{Q}\text{'s} \\ \text{subspace.}}} + \hat{Q}(E - \hat{H}_0)\hat{Q}|\Psi\rangle$$

$$= 0 + \hat{Q}E\hat{Q}|\Psi\rangle - \underbrace{\hat{Q}\hat{H}_0\hat{Q}|\Psi\rangle}_{\text{in } \hat{Q}\text{'s subspace already}}$$

$$= E\hat{Q}|\Psi\rangle - \hat{H}_0\hat{Q}|\Psi\rangle$$

$$\hat{Q}\hat{V}|\Psi\rangle = (E - \hat{H}_0)\hat{Q}|\Psi\rangle$$

<u>IF</u> we assume E can <u>only</u> coincide with $E_0^{(0)}$

Now, $(E - \hat{H}_0)$ is invertible in the range of $\hat{Q}$:

$$(E - \hat{H}_0)\hat{Q} = \sum_{i=1}^{\infty} \underbrace{(E - E_i)|\varphi_i\rangle\langle\varphi_i|}_{\text{will never be } E_0}$$ will never be 0. so we

can define:

$$\hat{G}_Q(E) = \frac{1}{E - \hat{H}_0}\hat{Q}$$

So $\hat{Q}\hat{V}|\Psi\rangle = (E - \hat{H}_0)\hat{Q}|\Psi\rangle$ becomes

$$\hat{G}_Q(E)\hat{V}|\Psi\rangle = \hat{Q}|\Psi\rangle$$

Now we know $\hat{Q}|\Psi\rangle$, so we can do:

$$|\Psi\rangle = |\varphi_0\rangle + \hat{G}_Q(E)\,\underline{\underline{\hat{V}|\Psi\rangle}}$$

Reference state — term is "linear" in perturbation

$$= |\varphi_0\rangle + \hat{G}_Q(E)\hat{V}\,\underline{\underline{(|\varphi_0\rangle + \hat{G}_Q(E)\hat{V}|\Psi\rangle)}}$$

$$= |\varphi_0\rangle + \hat{G}_Q(E)\hat{V}|\varphi_0\rangle + (\hat{G}_Q(E)V)^2\,\underline{|\Psi\rangle}$$

$$= |\varphi_0\rangle + \hat{G}_Q(E)\hat{V}|\varphi_0\rangle + (\hat{G}_Q(E)\hat{V})^2\,\underline{\underline{(|\varphi_0\rangle + \hat{G}_Q(E)\hat{V}|\Psi\rangle)}}$$

and so on, which produces the expansion: (if the series converges)

$$|\Psi\rangle = \left\{\sum_{n=0}^{\infty}(\hat{G}_Q(E)\hat{V})^n\right\}|\varphi_0\rangle$$

This is often written as:

$$|\Psi\rangle = \sum_{n=0}^{\infty}|\Psi^{(n)}\rangle, \quad |\Psi^{(n)}\rangle = (\hat{G}_Q(E)\hat{V})^n|\varphi_0\rangle$$

Great; all we need to do now is find E:

We said $\langle\varphi_0|\Psi\rangle = 1$, so $E = \langle\varphi_0|\Psi\rangle E$
$= \langle\varphi_0|\underline{\underline{A|\Psi\rangle}} = \langle\varphi_0|\hat{H}_0 + \hat{V}|\Psi\rangle$

Splitting terms:

$$E = \underline{\underline{\langle\varphi_0|\hat{H}_0|\Psi\rangle}} + \langle\varphi_0|\hat{V}|\Psi\rangle = E_0^{(0)} + \langle\varphi_0|\hat{V}|\Psi\rangle$$

$$= E_0^{(0)} + \langle\varphi_0|\hat{V}\sum_{n=0}^{\infty}(\hat{G}_Q(E)\hat{V})^n|\varphi_0\rangle = E_0^{(0)} + \sum_{n=0}^{\infty}\langle\varphi_0|\hat{V}|\Psi^{(n)}\rangle$$

$$= E_0 + \sum_{n=1}^{\infty}E^{(n)}$$

Where $E^{(n)} = \langle\varphi_0|\hat{V}|\Psi^{(n)}\rangle$. We can do this last step because $\sum_{n=0}^{\infty}\langle\varphi_0|\hat{V}|\Psi^{(n)}\rangle = 0 + \sum_{n=1}^{\infty}\langle\varphi_0|\hat{V}|\Psi^{(n)}\rangle$. The first term, which is the "zero-th order correction" is always 0. This makes sense because the correction to the unperturbed state (zero-th order state) is 0.

Then, also: $E^{(n)} = \langle \varphi_0 | \hat{V} (\hat{G}_Q(E) \hat{V})^{n-1} | \varphi_0 \rangle$

and, as before: $|\psi\rangle = \left\{ \sum_{n=0}^{\infty} (\hat{G}_Q(E)\hat{V})^n \right\} |\varphi_0\rangle = \sum_n |\psi^{(n)}\rangle$

Thus we can do, as an example:

$$|\psi^{(1)}\rangle = (\hat{G}_Q(E)\hat{V})^1 |\varphi_0\rangle$$

$$= \sum_{i \neq 0} |\varphi_i\rangle\langle\varphi_i| \frac{\hat{V}}{E - \hat{H}_0} |\varphi_0\rangle$$

$$= \sum_{i \neq 0} |\varphi_i\rangle\langle\varphi_i|\hat{V}|\varphi_0\rangle / E - E_i^{(0)}$$

def of $\hat{Q}$

$$|\psi^{(2)}\rangle = \sum_{i,j \neq 0} |\varphi_j\rangle \frac{\langle\varphi_j|\hat{V}|\varphi_i\rangle\langle\varphi_i|\hat{V}|\varphi_0\rangle}{(E - E_j^{(0)})(E - E_i^{(0)})}$$

Note: true energy E appears in the expansion!

And:

$$E^{(1)} = \langle\varphi_0|\hat{V}|\varphi_0\rangle$$

$$E^{(2)} = \langle\varphi_0|\hat{V}(\hat{G}_Q(E)\hat{V})|\varphi_0\rangle = \frac{\langle\varphi_0|V\hat{Q}V|\varphi_0\rangle}{E - E_i^{(0)}}$$

$$= \sum_{i \neq 0} \frac{\langle\varphi_0|\hat{V}|\varphi_i\rangle\langle\varphi_i|\hat{V}|\varphi_0\rangle}{E - E_i^{(0)}}$$

$$= \sum_{i \neq 0} \frac{V_{0i} V_{i0}}{E - E_i^{(0)}} = \sum_{i \neq 0} \frac{|V_{i0}|^2}{E - E_i^{(0)}}$$

Rayleigh-Schrödinger Perturbation Theory

- This method gives perturbative terms not in terms of the perturbed energy, $E^{(n)}(\lambda)$ scales exactly with λ^n, and the method is size extensive. My pen is dying =-

We once again start with $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{V}$, $\hat{H}(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$ and want to write $E(\lambda)$ and $|\psi(\lambda)\rangle$ in terms of some expansion of λ^n terms:

$$E(\lambda) = \sum_{n=0}^{\infty} E^{(n)}\lambda^n \quad \text{and} \quad |\psi(\lambda)\rangle = \sum_{n=0}^{\infty} |\psi^{(n)}\rangle\lambda^n$$

This time, we can substitute in $|\psi(\lambda)\rangle$ to our TISE:

$(\hat{H}_0 + \lambda\hat{V})|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle$

$= (\hat{H}_0 + \lambda\hat{V})\sum_{n=0}^{\infty}|\psi^{(n)}\rangle\lambda^n = \left(\sum_{n=0}^{\infty}E^{(n)}\lambda^n\right)\left(\sum_{n=0}^{\infty}|\psi^{(n)}\rangle\lambda^n\right)$

$\sum_{n=0}^{\infty}\hat{H}_0|\psi^{(n)}\rangle\lambda^n + \sum_{n=0}^{\infty}\hat{V}|\psi^{(n)}\rangle\lambda^{n+1} = \sum_{n,m}^{\infty}E^{(n)}|\psi^{(m)}\rangle\lambda^{n+m}$

We can use $\sum_{n=0}^{\infty}\hat{V}|\psi^{(n)}\rangle\lambda^{n+1} = \sum_{n=1}^{\infty}\hat{V}|\psi^{(n-1)}\rangle\lambda^n$

and $\sum_{n,m}E^{(n)}|\psi^{(m)}\rangle\lambda^{n+m} = \sum_{n=0}^{\infty}\lambda^n\sum_{k=0}^{n}|\psi^{(k)}\rangle E^{(n-k)}$

So overall:

$\sum_{n=0}^{\infty}\hat{H}_0|\psi^{(n)}\rangle\lambda^n + \sum_{n=1}^{\infty}\hat{V}|\psi^{(n-1)}\rangle\lambda^n = \sum_{n=0}^{\infty}\lambda^n\sum_{k=0}^{n}|\psi^{(k)}\rangle E^{(n-k)}$

We evaluate this equation <u>order by order</u>:

$n=0: \hat{H}_0|\psi^{(0)}\rangle(1) + 0 = \lambda^0|\psi^{(0)}\rangle E^{(0)}$

$\hat{H}_0|\psi^{(0)}\rangle = E^{(0)}|\psi^{(0)}\rangle$ of course!

$n>0: H_0|\psi^{(n)}\rangle + \hat{V}|\psi^{(n-1)}\rangle = \sum_{k=0}^{n}|\psi^{(k)}\rangle E^{(n-k)}$

$= \sum_{k=0}^{n-1}|\psi^{(k)}\rangle E^{(n-k)} + |\psi^{(n)}\rangle E^{(0)}$

$\hat{V}|\psi^{(n-1)}\rangle - \sum_{k=0}^{n-1}|\psi^{(k)}\rangle E^{(n-k)} = (E^{(0)} - \hat{H}_0)|\psi^{(n)}\rangle$

We can once again use $\hat{Q}$ like we did in the Brillouin-Wigner method; $\langle\varphi_0|\psi\rangle = 1$ and so on:

$\hat{Q}(E^{(0)} - \hat{H}_0)|\psi^{(n)}\rangle = \hat{Q}\hat{V}|\psi^{(n-1)}\rangle - \underbrace{\hat{Q}\sum_{k=0}^{n-1}|\psi^{(k)}\rangle E^{(n-k)}}_{\hat{Q}|\psi^{(0)}\rangle = 0 \text{ by def. of } \hat{Q}}$

$\hat{Q}|\psi^{(n)}\rangle = \hat{G}_Q(E_0^{(0)})\hat{V}|\psi^{(n-1)}\rangle - \hat{G}_Q(E_0)\sum_{k=1}^{n-1}|\psi^{(k)}\rangle E^{(n-k)}$

and for $n>0$, $\hat{Q}|\psi^{(n)}\rangle = |\psi^{(n)}\rangle$.

To find the energies, we project onto $|\varphi_0\rangle$:

$$\underbrace{\langle\varphi_0|E^{(0)}-\hat{H}_0|\psi^{(n)}\rangle}_{\text{this is } \perp \text{ to } |\varphi_0\rangle} = -\sum_{k=0}^{n-1} \underbrace{\langle\varphi_0|\psi^{(k)}\rangle}_{=\delta_{0,k}} E^{(n-k)} + \langle\varphi_0|\hat{V}|\psi^{(n-1)}\rangle$$

$$0 = -E^{(n-0)} + \langle\varphi_0|\hat{V}|\psi^{(n-1)}\rangle$$

$$E^{(n)} = \langle\varphi_0|\hat{V}|\psi^{(n-1)}\rangle$$

This matches Brillouin-Wigner to 1st and 2nd order.