Degenerate Rayleigh-Schroedinger perturbation theory

$$\hat{H} = \hat{H}_0 + \hat{V}$$

$$\hat{H}_0 |k, n_k\rangle_0 = E_k^0 |k, n_k\rangle \qquad n_k = 1, 2, \ldots d(k)$$

$d(k)$ = degeneracy of level k

We assume each $|k, n_k\rangle$ state is an orthonormal basis set
we can always achieve this via Gram-Schmidt orthogonalization from a set of eigenvectors which span the degenerate subspace.

Our eigenvalue equation is

$$(\hat{H}_0 + \hat{V}) |k, n_k\rangle = E_{k, n_k} |k, n_k\rangle$$

The perturbation $\hat{V}$ may totally lift the degeneracy, partially lift it, or not lift it at all.

Follow the Rayleigh-Schroedinger strategy

$$(E_k^0 - \hat{H}_0) |k, n_k\rangle = (\hat{V} - \Delta E_{k, n_k}) |k, n_k\rangle$$

Need to "protect" with projection operators to invert

Define $\hat{P}_k = \sum_{n_k=1}^{d(k)} |k, n_k\rangle_0 \, {}_0\langle k, n_k|$ projects onto the E_k^0 subspace

$$\hat{P}_k^2 = \sum_{n_k=1}^{d(k)} \sum_{n_k'=1}^{d(k)} |k, n_k\rangle_0 \, \underbrace{{}_0\langle k, n_k | k, n_k'\rangle_0}_{\delta_{n_k, n_k'} \text{ because orthonormal}} \, {}_0\langle k, n_k'|$$

$$= \sum_{n_k=1}^{d(k)} |k, n_k\rangle_0 \, {}_0\langle k, n_k| = \hat{P}_k$$

so $\hat{P}_k^2 = \hat{P}_k \Rightarrow$ projection operator $\qquad \hat{Q}_k = 1 - \hat{P}_k$ = proj operator too
projects $\perp$ to deg subspace

Note further that

$$[\hat{P}_k, \hat{H}_0]_- = [\hat{Q}_k, \hat{H}_0]_- = 0$$

so multiply Schroedinger equation by $\hat{Q}_k$

$$(E_k^0 - \hat{H}_0)\underbrace{\hat{Q}_k |k, n_k\rangle}_{|k,n_k\rangle_\perp} = \hat{Q}_k(\hat{V} - \Delta E_{k,n_k})|k, n_k\rangle$$

$$|k,n_k\rangle_\perp = \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})|k, n_k\rangle$$

But $|k,n_k\rangle = |k,n_k\rangle_\parallel + |k,n_k\rangle_\perp = \hat{P}_k|k,n_k\rangle + \hat{Q}_k|k,n_k\rangle$

$$= |k,n_k\rangle_\parallel + \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})|k,n_k\rangle$$

Solving for $|k,n_k\rangle$ gives

$$\boxed{|k,n_k\rangle = \left[\mathbb{1} - \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})\right]^{-1} |k,n_k\rangle_\parallel}$$

in non deg PT $|k,n_k\rangle_\parallel$ was known since there was only one state

$$|k\rangle_\parallel = \hat{P}_k|k\rangle = |k\rangle_0 \underbrace{{}_0\langle k|k\rangle}_{=1} = |k\rangle_0$$

But in degenerate PT, we don't know a priori the direction in the E_k^0 subspace for the wave functions

$$|k,n_k\rangle_\parallel = \sum_{n_k'=1}^{d(k)} |k,n_k'\rangle_0 \, {}_0\langle k,n_k'|k,n_k\rangle$$

← don't know these numbers

so we need an equation to find them!

recall

$$|k,n_k\rangle_\perp = \hat{Q}_k \left[1 - \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})\right]^{-1} |k,n_k\rangle_\parallel$$

For the parallel space we try

$$\hat{P}_k \hat{V} |k,n_k\rangle = \hat{P}_k (\underset{\substack{\uparrow \\ E_k}}{\hat{H}} - \underset{\substack{\uparrow \\ E_k^0}}{\hat{H}_0}) |k,n_k\rangle$$

$\rightarrow$ because $\hat{P}_k \hat{H}_0 |k,n_k\rangle = \hat{H}_0 \hat{P}_k |k,n_k\rangle = E_k^0 |k,n_k\rangle$

$$= \Delta E_{k,n_k} \hat{P}_k |k,n_k\rangle = \Delta E_{k,n_k} |k,n_k\rangle_\parallel$$

so we get

$$\hat{P}_k \hat{V} \left[1 - \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})\right]^{-1} |k,n_k\rangle_\parallel = \Delta E_{k,n_k} |k,n_k\rangle_\parallel$$

$\uparrow$ can add $\hat{P}_k$ here since $\hat{P}_k$ projects $\parallel$ to k subspace

$$\boxed{\begin{aligned} &\text{so } \left\{\hat{P}_k \hat{V} \left[1 - \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})\right]^{-1} \hat{P}_k - \Delta E_{k,n_k}\right\} |k,n_k\rangle_\parallel = 0 \\ &(\hat{L}_{k,n_k} - \Delta E_{k,n_k}) |k,n_k\rangle_\parallel = 0 \\ &\hat{L}_{k,n_k} = \hat{P}_k \hat{V} \left[1 - \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0}(\hat{V} - \Delta E_{k,n_k})\right]^{-1} \hat{P}_k \end{aligned}}$$

this equation allows us to find $\Delta E_{k,n_k}$ and $|k,n_k\rangle_\parallel$

To see how this works we write an expansion in powers of $\hat{V}$

$$\Delta E_{k,n_k} = E_k - E_k^0 = E_{k,n_k}^{(1)} + E_{k,n_k}^{(2)} + E_{k,n_k}^{(3)}$$

$$\hat{L}_{k,n_k} = \hat{L}_{k,n_k}^{(1)} + \hat{L}_{k,n_k}^{(2)} + \cdots$$

$$|k, n_k\rangle_{\parallel} = |k, n_k\rangle_{\parallel}^{(1)} + |k, n_k\rangle_{\parallel}^{(2)} + \cdots$$

convention to start from (1) here.

Lowest order

$$\Delta E_{k,n_k} = \Delta E_{k,n_k}^{(1)}$$

$$\hat{L}_{k,n_k} = \hat{L}_{k,n_k}^{(1)} = \hat{P}_k \hat{V} \hat{P}_k$$

$$(\hat{L}_{k,n_k}^{(1)} - E_{k,n_k}^{(1)}) |k, n_k\rangle_{\parallel}^{(1)} = 0$$

$$\hat{P}_k \hat{V} \hat{P}_k |k, n_k\rangle_{\parallel}^{(1)} = E_{k,n_k}^{(1)} |k, n_k\rangle_{\parallel}^{(1)}$$

Schroedinger-like Equation in the degenerate subspace

expand in terms of $\{|k, n_k\rangle_0\}$ to get

$$\boxed{\sum_{n_k''} {}_0\langle k, n_k' | \hat{V} | k, n_k''\rangle_0 \; {}_0\langle k, n_k'' | k, n_k\rangle_{\parallel}^{(1)} = E_{k,n_k}^{(1)} \; {}_0\langle k, n_k' | k, n_k\rangle_{\parallel}}$$

matrix × vector = number * vector

This is a matrix equation for the first-order energy shift and for the parallel directions.

Let's take a break to look at the simplest example.

$$\hat{H}_0 = \begin{pmatrix} a & 0 \\ 0 & a \end{pmatrix} \qquad \hat{V} = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}$$

The first-order matrix equation is

$$\det\left[\hat{V} - E^{(1)} \mathbb{1}\right] = 0$$

$$\det\begin{bmatrix} V_{11} - E^{(1)} & V_{12} \\ V_{21} & V_{22} - E^{(1)} \end{bmatrix} = 0$$

$$E^{(1)2} - (V_{11} + V_{22}) E^{(1)} + V_{11} V_{22} - V_{12} V_{21} = 0$$

$$E^{(1)} = \frac{V_{11} + V_{22}}{2} \pm \frac{1}{2}\sqrt{(V_{11} + V_{22})^2 - 4V_{11}V_{22} + 4V_{12}V_{21}}$$

$$\boxed{E^{(1)} = \frac{V_{11}+V_{22}}{2} \pm \frac{1}{2}\sqrt{(V_{11}-V_{22})^2 + 4V_{12}V_{21}}}$$

We find the directions of $|k, n_k\rangle_{11}$ by finding the eigenvectors (see homework).

Now, suppose the first order perturbation theory lifts all of the degeneracies

$$E^{(1)}_{k,n_k} \neq E^{(1)}_{k,n_k'} \quad \text{for all } n_k, n_k'$$

so $\hat{P}_k \hat{V} \hat{P}_k |k, n_k\rangle^{(1)}_{11} = E^{(1)}_{k,n_k} |k, n_k\rangle_{11}$ with all $E^{(1)}_{k,n_k}$ different

Now look at second order

$$\hat{L}_k = \hat{L}_k^{(1)} + \hat{L}_k^{(2)} = \hat{P}_k \hat{V} \hat{P}_k + \hat{P}_k \hat{V} \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0} (\hat{V} - \Delta E^{(1)}_{k,n_k}) \hat{P}_k$$

can ignore since $\hat{Q}_k \hat{P}_k = 0$

$$= \hat{P}_k \hat{V} \hat{P}_k + \hat{P}_k \hat{V} \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0} \hat{V} \hat{P}_k$$

and the second-order equation is

$$(\hat{P}_k \hat{V} \hat{P}_k - E^{(1)}_{k,n_k}) |k, n_k\rangle^{(1)}_{11} + (\hat{P}_k \hat{V} \hat{P}_k - E^{(1)}_{k,n_k}) |k, n_k\rangle^{(2)}_{11}$$

$$+ \left(\hat{P}_k \hat{V} \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0} \hat{V} \hat{P}_k - E^{(2)}_{k,n_k}\right) |k, n_k\rangle^{(1)}_{11} = 0$$

multiply by ${}^{(1)}_{11}\langle k, n_k'|$ to get

$${}^{(1)}_{11}\langle k, n_k' | \hat{P}_k \hat{V} \hat{P}_k - E^{(1)}_{k,n_k}) |k, n_k\rangle^{(1)}_{11} + {}^{(1)}_{11}\langle k, n_k' | (\hat{P}_k \hat{V} \hat{P}_k - E^{(1)}_{k,n_k}) |k, n_k\rangle^{(2)}_{11}$$

$$+ {}^{(1)}_{11}\langle k, n_k' | \left(\hat{P}_k \hat{V} \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0} \hat{V} \hat{P}_k - E^{(2)}_{k,n_k}\right) |k, n_k\rangle^{(1)}_{11} = 0$$

note $\;{}_{\text{II}}^{(1)}\langle k, n_k | k, n_k' \rangle_{\text{II}}^{(1)} = \delta_{n_k, n_k'}$ (by convention!)

and $\hat{P}_k \hat{V} \hat{P}_k |k, n_k\rangle_{\text{II}}^{(1)} = E_{k,n_k}^{(1)} |k, n_k\rangle_{\text{II}}^{(1)}$ so

$$\cancelto{0}{\left(E_{k,n_k}^{(1)} - E_{k,n_k}^{(1)}\right)} \delta_{n_k n_k'} + \left(E_{k,n_k'}^{(1)} - E_{k,n_k}^{(1)}\right) {}_{\text{II}}^{(1)}\langle k, n_k' | k, n_k \rangle_{\text{II}}^{(2)}$$

$$+ {}_{\text{II}}^{(1)}\langle k, n_k' | \hat{P}_k \hat{V} \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0} \hat{V} \hat{P}_k | k, n_k \rangle_{\text{II}}^{(1)} - E_{k,n_k}^{(2)} \delta_{n_k, n_k'} = 0$$

To find $E_{k,n_k}^{(2)}$, set $n_k' = n_k$ to get

$$E_{k,n_k}^{(2)} = {}_{\text{II}}^{(0)}\langle k, n_k | \hat{P}_k \hat{V} \frac{\hat{Q}_k}{E_k^0 - \hat{H}_0} \hat{V} \hat{P}_k | k, n_k \rangle_{\text{II}}^{(1)}$$

which is the formula for nondeg second-order perturbation theory within the basis found at first order

$\Rightarrow$ once the degeneracy is lifted, subsequent PT expansions look like the nondegenerate PT formulas

To get $|k, n_k\rangle_{\text{II}}^{(2)}$ need to look at $n_k' \neq n_k$

we won't do that here, but see the HW for examples.