Set up the problem again

$$\hat{H}\psi_q = E_q\psi_q$$

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$$

$$E_q = E_q^{(0)} + \lambda E_q^{(1)} + \lambda^2 E_q^{(2)} + \ldots$$

$$\psi_q = \phi_q^{(0)} + \lambda\psi_q^{(1)} + \ldots$$

But, there are some g-fold degenerate states such that

$$E_{q,1}^{(0)} = E_{q,2}^{(0)} = \ldots = E_{q,g}^{(0)} = E_q^{(0)}$$

and $\psi_{q,j}^{(0)} = \phi_{q,j}^{(0)} + \lambda\psi_{q,j}^{(1)} + \lambda^2\psi_{q,j}^{(2)} + \ldots$

with $\phi_{q,j}^{(0)} = \sum_{j=1}^{g} c_j \psi_{q,j}^{(0)}$

Choose these to be Schmidt orthogonalized although they not be

Since we are always examining state q, drop this index

$$\Rightarrow \hat{H}\psi_{q,j} = E_{q,j}\psi_{q,j} \Leftrightarrow \hat{H}\psi_j = E_j\psi_j \quad 1 \le j \le g$$

$E_q^{(0)}$ = energy of the unperturbed degenerate state

$$\therefore\ E_j = E_q^{(0)} + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + \ldots$$

$$\psi_j = \phi_j^{(0)} + \lambda\psi_j^{(1)} + \lambda^2\psi_j^{(2)} + \ldots$$

$$\phi_j^{(0)} = \sum_{j=1}^{g} c_j\psi_j^{(0)}$$

Derivation ahead

Substitute into the eigenvalue problem:

$$\hat{H}\psi_j = E_j\psi_j$$

$$\Rightarrow\left(\hat{H}^{(0)} + \lambda\hat{H}^{(1)}\right)\left(\phi_j^{(0)} + \lambda\psi_j^{(1)} + \ldots\right) = \left(E_q^{(0)} + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + \ldots\right)\left(\phi_j^{(0)} + \lambda\psi_j^{(1)} + \ldots\right)$$

Collect term in λ^n:

$$\lambda^0: \left(\hat{H}^{(0)} - E_q^{(0)}\right)\phi_j^{(0)} = 0 \qquad (1)$$

$$\lambda^1: \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_j^{(1)} + \left(\hat{H}^{(1)} - E_j^{(1)}\right)\phi_j^{(0)} = 0 \qquad (2)$$

$$\lambda^2: \left(\hat{H}^{(0)} - E_q^{(0)}\right)\psi_j^{(2)} + \left(\hat{H}^{(1)} - E_j^{(1)}\right)\psi_j^{(1)} - E_j^{(2)}\phi_j^{(0)} = 0 \text{ ... etc.}$$

Consider equation (1):

$$\phi_j^{(0)} = \sum_{j=1}^{g} c_j \psi_j^{(0)} \Rightarrow \left(\hat{H}^{(0)} - E_q^{(0)}\right)\left(\sum_{j=1}^{g} c_j \psi_j^{(0)}\right) = 0$$

as demanded by superposition principle. Not new!

Consider equation (2):

Use $\phi_j^{(0)} = \sum_{j=1}^{g} c_j \psi_j^{(0)}$ **Note: $\mathbf{c_j}$ values still unknown**

and $\psi_j^{(1)} = \sum_{k=1}^{\infty} a_k \psi_k^{(0)}$ As for non-degenerate perturbation theory. $\mathbf{a_k}$ **values still need to be determined.**

$$\Rightarrow (2) \equiv$$

$$\left(\hat{H}^{(0)} - E_q^{(0)}\right)\sum_{k=1}^{\infty} a_k \psi_k^{(0)} = \left(\hat{H}^{(1)} - E_j^{(1)}\right)\sum_{j=1}^{g} c_j \psi_j^{(0)}$$

Sum over **all** states

Sum over all degenerate states

$$\Rightarrow \sum_{k=1}^{\infty} a_k \left(E_k^{(0)} - E_q^{(0)}\right)\psi_k^{(0)} = \sum_{j=1}^{g} c_j \left(\hat{H}^{(1)} - E_j^{(1)}\right)\psi_j^{(0)}$$

Multiply by $\Phi_q^{(0)\star}$ and integrate. Remember q is the state for which we want to solve the problem.

$$\therefore \sum_{k=1}^{\infty} a_k \left(E_k^{(0)} - E_q^{(0)}\right)\left\langle \phi_q^{(0)} \mid \psi_k^{(0)} \right\rangle = \sum_{j=1}^{g} c_j \left[\left\langle \phi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_j^{(0)} \right\rangle - E_j^{(1)} \left\langle \phi_q^{(0)} \mid \psi_j^{(0)} \right\rangle\right]$$

Case I: q is a non-degenerate state → j = q and g =1

As before a_q =0 and $<\Phi_q^{(0)}|\Psi_k^{(0)}>$ = 0 for q ≠k

Therefore the LHS = 0 and $E_q^{(1)} = \left\langle \phi_q^{(0)} \mid \hat{H}^{(1)} \mid \phi_q^{(0)} \right\rangle = H_{qq}^{(1)};\ and\ \ \phi_q^{(0)} = \psi_q^{(0)}$

Case II: q is a g-fold degenerate state.

Write LHS as two terms:

$$\sum_{k=q_1}^{q_g} a_k \left(E_k^{(0)} - E_q^{(0)}\right)\left\langle \phi_q^{(0)} \mid \psi_k^{(0)} \right\rangle + \sum_{k \neq q_1,\ldots,q_g}^{\infty} a_k \left(E_k^{(0)} - E_q^{(0)}\right)\left\langle \phi_q^{(0)} \mid \psi_k^{(0)} \right\rangle$$

$$\sum_{k=q_1}^{q_g} a_k \left(E_k^{(0)} - E_q^{(0)}\right)\left\langle \phi_q^{(0)} \mid \psi_k^{(0)} \right\rangle + \sum_{k \neq q_1,\ldots,q_g}^{\infty} a_k \left(E_k^{(0)} - E_q^{(0)}\right)\left\langle \phi_q^{(0)} \mid \psi_k^{(0)} \right\rangle$$

Sum over all degenerate levels within q^{th} state → $E_k^{(0)}=E_q^{(0)}$ always → sum = 0

Sum over all other states ($k \neq q_j$). Here k and q are orthogonal →$<\Phi_q^{(0)}|\Psi_k^{(0)}>=0$ → sum = 0.

In all cases LHS =0. Therefore, in general:

$$\sum_{j=1}^{g} c_j \left[\left\langle \phi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_j^{(0)} \right\rangle - E_j^{(1)} \left\langle \phi_q^{(0)} \mid \psi_j^{(0)} \right\rangle\right] = 0$$

Note: this looks like the non-degenerate case, but there are g Φs which if they Schmidt orthogonalized → $<\Phi_q^{(0)}|\Phi_j^{(0)}> = \delta_{qj}$

Use earlier definition:

$$\hat{H}_{qj}^{(1)} = \left\langle \phi_q^{(0)} \mid \hat{H}^{(1)} \mid \psi_j^{(0)} \right\rangle$$

Introduce "Overlap Integral": $S_{qj} = <\phi_q^{(0)} \mid \psi_j^{(0)}>$

$$\Rightarrow \sum_{j=1}^{g} c_j \left[H_{qj}^{(1)} - E_j^{(1)} S_{qj} \right] = 0$$

This represents g equations in g unknowns: $\{c_1, c_2, \ldots, c_g\}$ with coefficients $H_{qj}^{(1)} - E_j^{(1)} S_{qj}$

Need to solve for each 1.) $E_j^{(1)}$, and then 2.) for c_j where $\phi_j^{(0)} = \sum_{j=1}^{g} c_j \psi_j^{(0)}$

Key steps to solve this.

1.) Make certain that the original wave functions $\Phi_j^{(0)}$ are orthonormal for all degenerate states. $\rightarrow S_{qj} = \delta_{qj}$

This reduces equations to:

$$\sum_{j=1}^{g} c_j \left[H_{qj}^{(1)} - E_j^{(1)} \delta_{qj} \right] = 0 \qquad 1 \le q \le g;\, 1 \le j \le g$$

2.) For the set of equations to have a non-trivial solution ($c_j \neq 0$), the determinant of the coefficients must vanish.

1.) Write out equations in detail.

$$\Rightarrow \sum_{j=1}^{g} c_j \left[H_{qj}^{(1)} - E_j^{(1)} \delta_{qj} \right] = 0 \qquad q = 1, 2, \ldots, g$$

$$q = 1: \left(H_{11}^{(1)} - E_1^{(1)} \right) c_1 + H_{12}^{(1)} c_2 + H_{13}^{(1)} c_3 + \ldots + H_{1g}^{(1)} c_g = 0$$

$$q = 2: H_{21}^{(1)} c_1 + \left(H_{22}^{(1)} - E_2^{(1)} \right) c_2 + H_{23}^{(1)} c_3 + \ldots + H_{2g}^{(1)} c_g = 0$$

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$$q = g: H_{g1}^{(1)} c_1 + H_{g2}^{(1)} c_2 + H_{g3}^{(1)} c_3 + \ldots + \left(H_{gg}^{(1)} - E_g^{(1)} \right) c_g = 0$$

The determinant of the coefficients is:

$$\begin{vmatrix} \left(H_{11}^{(1)} - E_1^{(1)}\right) & H_{12}^{(1)} & H_{13}^{(1)} & \cdots & H_{1g}^{(1)} \\ H_{21}^{(1)} & \left(H_{22}^{(1)} - E_2^{(1)}\right) & H_{23}^{(1)} & \cdots & H_{2g}^{(1)} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ H_{g1}^{(1)} & H_{g2}^{(1)} & H_{g3}^{(1)} & \cdots & \left(H_{gg}^{(1)} - E_g^{(1)}\right) \end{vmatrix}$$

2.) Can solve this equation (a polynomial in $E_j^{(1)}$) to get $E_1^{(1)}$, $E_2^{(1)}$, …$E_g^{(1)}$ since the matrix elements $H_{ij}^{(1)}$'s are known= numbers obtained by doing integrations

3.) For each root $E_j^{(1)}$, j = 1,2,…,g, there will be a different set of coefficients $\{c_j\}$ giving a different correct zeroth order wave function.

4.) Determine the coefficients a_k such that we get:

$$\psi_j^{(1)} = \sum_{k=1}^{\infty} a_k \psi_k^{(0)}$$

and thus:

$$\psi_j = \phi_j^{(0)} + \psi_j^{(1)} + \psi_j^{(2)} + \ldots.$$

$$= \sum_{j=1}^{g} c_j \psi_j^{(0)} + \sum_{\substack{k=1 \\ k \neq j}}^{\infty} a_k \psi_k^{(0)} + \ldots.$$

5.) Determine 2^{nd} order energy correction as before **using correct 0^{th} order wave functions**.

Procedure requires:

1.) Schmidt orthogonalization procedure

2.) matrix algebra where matrix elements $H_{ij}^{(1)} = \langle \Psi_i | \mathbf{H}^{(1)} | \Psi_j \rangle$

3.) patience

Example: Given the following Hamiltonian matrix:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \begin{pmatrix} 20 & 0 & 0 \\ 0 & 20 & 0 \\ 0 & 0 & 30 \end{pmatrix} + \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 2 \\ 0 & 2 & 0 \end{pmatrix}$$

Determine the eigenvalues correct to second order

Answer: First note that $|\Psi_1^{(0)}>$ and $|\Psi_2^{(0)}>$ are degenerate but $|\Psi_3^{(0)}>$ is not part of the degeneracy

$\therefore E_3^{(1)} = 0$ This is read right off $\mathbf{H}^{(1)}$

To find the correct first order corrections to the energy for the degenerate set one must solve the following secular determinant:

$$\begin{vmatrix} H_{11}^{(1)} - E^{(1)} & H_{12}^{(1)} \\ H_{21}^{(1)} & H_{22}^{(1)} - E^{(1)} \end{vmatrix} = 0$$

$$\Rightarrow \begin{vmatrix} -E^{(1)} & 1 \\ 1 & -E^{(1)} \end{vmatrix} = 0 \Rightarrow \left(E^{(1)}\right)^2 - 1 = 0$$

$$\Rightarrow E^{(1)} = \pm 1$$

To find the correct first order wave functions for the degenerate levels, substitute (one by one) each $E^{(1)}$ in the secular determinant.

<u>$E^{(1)} = 1$:</u> $$\Rightarrow \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow c_2 = c_1 \Rightarrow \tilde{c} = c_1 \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

Normalize: $$\tilde{c}^{+}\tilde{c} = 1 \Rightarrow 2c_1^2 = 1 \Rightarrow c_1 = \frac{1}{\sqrt{2}}$$

$$\therefore \phi_1^{(0)} = \frac{1}{\sqrt{2}}\left(\psi_1^{(0)} + \psi_2^{(0)}\right)$$

Similarly for $E^{(1)}=-1$:

$$\Rightarrow \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow c_2 = -c_1 \Rightarrow \tilde{c} = c_1 \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Normalize: $\tilde{c}^{+}\tilde{c} = 1 \Rightarrow 2c_1^2 = 1 \Rightarrow c_1 = \dfrac{1}{\sqrt{2}}$

$$\therefore \phi_2^{(0)} = \frac{1}{\sqrt{2}}\left(\psi_1^{(0)} - \psi_2^{(0)}\right)$$

These are the wave functions which must be used to calculate $E_q^{(2)}$!