Chapter 9

Non-degenerate Perturbation Theory

Problem :

$$\underline{H}\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle$$

can't solve exactly.

But

$$\underline{H} = \underline{H}^0 + \lambda\underline{H}' + \lambda^2\underline{H}'' + \cdots$$

with

$$\text{Lim } \lambda \to 0 \quad \underline{H}^0\left|\varphi_n^0\right\rangle = E_n^0\left|\varphi_n^0\right\rangle$$

Unperturbed eigenvalue problem.
Can solve exactly.

Therefore, know E_n^0 **and** $\left|\varphi_n^0\right\rangle$.

$$\lambda\underline{H}' + \lambda^2\underline{H}'' + \cdots$$

called perturbations

Solutions of

$$\underline{H}^0 \left|\varphi_n^0\right\rangle = E_n^0 \left|\varphi_n^0\right\rangle$$

complete, orthonormal set of ket vectors

$$\left\{\left|\varphi_n^0\right\rangle\right\} \Rightarrow \left|\varphi_0^0\right\rangle, \left|\varphi_1^0\right\rangle, \left|\varphi_2^0\right\rangle \cdots$$

with eigenvalues $E_0^0, E_1^0, E_2^0, \cdots$
and

$$\left\langle \varphi_n^0 \middle| \varphi_m^0 \right\rangle = \delta_{mn}$$

Kronecker delta

$$\delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}$$

Expand wavefunction

$$\left|\varphi_n\right\rangle = \left|\varphi_n^0\right\rangle + \lambda\left|\varphi_n'\right\rangle + \lambda^2\left|\varphi_n''\right\rangle + \cdots$$

and

$$E_n = E_n^0 + \lambda E_n' + \lambda^2 E_n'' + \cdots$$

also have

$$\underline{H} = \underline{H}^0 + \lambda \underline{H}' + \lambda^2 \underline{H}'' + \cdots$$

Have series for

$$\underline{H} \qquad \left|\varphi_n\right\rangle \qquad E_n$$

Substitute these series into the original eigenvalue equation

$$\underline{H}\left|\varphi_n\right\rangle = E_n\left|\varphi_n\right\rangle$$

Sum of infinite number of terms for all powers of λ equals 0.

$$\left(\underline{H}^0\left|\varphi_n^0\right\rangle - E_n^0\left|\varphi_n^0\right\rangle\right)\lambda^0 + \left(\underline{H}^0\left|\varphi_n'\right\rangle + \underline{H}'\left|\varphi_n^0\right\rangle - E_n^0\left|\varphi_n'\right\rangle - E_n'\left|\varphi_n^0\right\rangle\right)\lambda$$

$$+\left(\underline{H}^0\left|\varphi_n''\right\rangle + \underline{H}'\left|\varphi_n'\right\rangle + \underline{H}''\left|\varphi_n^0\right\rangle - E_n^0\left|\varphi_n''\right\rangle - E_n'\left|\varphi_n'\right\rangle - E_n''\left|\varphi_n^0\right\rangle\right)\lambda^2$$

$$+\cdots = 0$$

Coefficients of the individual powers of λ must equal 0.

zeroth order - λ^0 $$\underline{H}^0\left|\varphi_n^0\right\rangle - E_n^0\left|\varphi_n^0\right\rangle = 0$$

first order - λ^1 $$\underline{H}^0\left|\varphi_n'\right\rangle + \underline{H}'\left|\varphi_n^0\right\rangle - E_n^0\left|\varphi_n'\right\rangle - E_n'\left|\varphi_n^0\right\rangle = 0$$

second order - λ^2 $$\underline{H}^0\left|\varphi_n''\right\rangle + \underline{H}'\left|\varphi_n'\right\rangle + \underline{H}''\left|\varphi_n^0\right\rangle - E_n^0\left|\varphi_n''\right\rangle - E_n'\left|\varphi_n'\right\rangle - E_n''\left|\varphi_n^0\right\rangle = 0$$

First order correction

$$\underline{H}^0\left|\varphi_n'\right\rangle - E_n^0\left|\varphi_n'\right\rangle = \left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

Want to find E_n' and $\left|\varphi_n'\right\rangle$.

Expand $\left|\varphi_n'\right\rangle$

$$\left|\varphi_n'\right\rangle = \sum_i c_i\left|\varphi_i^0\right\rangle$$

also substituting

Then

$$\underline{H}^0\left|\varphi_n'\right\rangle = \sum_i c_i\,\underline{H}^0\left|\varphi_i^0\right\rangle = \sum_i c_i E_i^0\left|\varphi_i^0\right\rangle$$

Substituting this result.

After substitution

$$\sum_i c_i\left(E_i^0 - E_n^0\right)\left|\varphi_i^0\right\rangle = \left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

After substitution

$$\sum_i c_i\left(E_i^0 - E_n^0\right)\left|\varphi_i^0\right\rangle = \left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

Left multiply by

$$\left\langle \varphi_n^0 \right|$$

$$\left\langle \varphi_n^0 \right| \sum_i c_i\left(E_i^0 - E_n^0\right)\left|\varphi_i^0\right\rangle = \left\langle \varphi_n^0 \right|\left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

$$\sum_i c_i\left(E_i^0 - E_n^0\right)\left\langle \varphi_n^0 \middle| \varphi_i^0\right\rangle = \left\langle \varphi_n^0 \right|\left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

$$\left\langle \varphi_n^0 \middle| \varphi_i^0\right\rangle = 0$$

unless $n = i$,
but then

$$E_n^0 - E_n^0 = 0$$

Therefore, the left side is 0.

We have

$$\left\langle \varphi_n^0 \middle| \left(E_n' - \underline{H}' \right) \middle| \varphi_n^0 \right\rangle = 0$$

$$\Rightarrow \left\langle \varphi_n^0 \middle| E_n' \middle| \varphi_n^0 \right\rangle - \left\langle \varphi_n^0 \middle| \underline{H}' \middle| \varphi_n^0 \right\rangle = 0$$

E_n' number, kets normalized, and transposing,

$$E_n' = \left\langle \varphi_n^0 \middle| \underline{H}' \middle| \varphi_n^0 \right\rangle$$

The first order correction to the energy.
(Expectation value of $\underline{H}'$ in zeroth order state φ_n^0)

Then

$$E_n = E_n^0 + \lambda E_n'$$

Absorbing λ into H_{nn}' and E_n'

$$E_n = E_n^0 + E_n'$$

$$E_n' = \left\langle \varphi_n^0 \middle| \underline{H}' \middle| \varphi_n^0 \right\rangle = H_{nn}'$$

The first order correction to the energy is the expectation value of $\underline{H}'$.

First order correction to the wavefunction

Again using the equation obtained after substituting series expansions

$$\sum_i c_i \left(E_i^0 - E_n^0\right)\left|\varphi_i^0\right\rangle = \left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

Left multiply by $\left\langle\varphi_j^0\right|$

$$\left\langle\varphi_j^0\right|\sum_i c_i \left(E_i^0 - E_n^0\right)\left|\varphi_i^0\right\rangle = \left\langle\varphi_j^0\right|\left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

Equals zero unless *i* = *j*.

$$c_j\left(E_j^0 - E_n^0\right) = \left\langle\varphi_j^0\right|\left(E_n' - \underline{H}'\right)\left|\varphi_n^0\right\rangle$$

$$c_j\left(E_j^0 - E_n^0\right) = -\left\langle\varphi_j^0\right|\underline{H}'\left|\varphi_n^0\right\rangle$$

$$c_j = \frac{\left\langle\varphi_j^0\right|\underline{H}'\left|\varphi_n^0\right\rangle}{\left(E_n^0 - E_j^0\right)} \qquad j \neq n$$

Coefficients in expansion of ket in terms of the zeroth order kets.

$$c_j = \frac{\langle \varphi_j^0 | \underline{H}' | \varphi_n^0 \rangle}{\left(E_n^0 - E_j^0\right)} \qquad j \neq n$$

$$c_j = \frac{H'_{jn}}{\left(E_n^0 - E_j^0\right)}$$

H'_{jn} is the bracket of $\underline{H}'$ with $\langle \varphi_j^0 |$ and $| \varphi_n^0 \rangle$.

correction to zeroth order ket

Therefore

$$|\varphi_n\rangle = |\varphi_n^0\rangle + {\sum_j}' \frac{H'_{jn}}{(E_n^0 - E_j^0)} |\varphi_j^0\rangle$$

The prime on the sum mean $j \neq n$.

zeroth order ket

energy denominator

First order corrections

$$E_n = E_n^0 + H'_{nn} + \cdots \qquad H'_{nn} = \left\langle \varphi_n^0 \middle| H' \middle| \varphi_n^0 \right\rangle$$

$$\left|\varphi_n\right\rangle = \left|\varphi_n^0\right\rangle + \sum_j{}' \frac{H'_{jn}}{(E_n^0 - E_j^0)} \left|\varphi_j^0\right\rangle + \cdots \qquad H'_{jn} = \left\langle \varphi_j^0 \middle| H' \middle| \varphi_n^0 \right\rangle$$

Second Order Corrections

Using λ^2 coefficient

Expanding $|\varphi_n'\rangle \quad |\varphi_n''\rangle$

Substituting and following same type of procedures yields

$$E_n'' = \sum_i{}' \frac{H'_{ni}H'_{in}}{\left(E_n^0 - E_i^0\right)} + H''_{nn}$$

λ^2 coefficients have been absorbed.

$$H'_{ni}H'_{in} = \langle \varphi_n^0 | \underline{H}' | \varphi_i^0 \rangle \langle \varphi_i^0 | \underline{H}' | \varphi_n^0 \rangle$$

Second order correction due to first order piece of *H*.

Second order correction due to an additional second order piece of *H*.

$$|\varphi_n''\rangle = \sum_k{}' \left[\sum_m{}' \frac{H'_{km}H'_{mn}}{\left(E_n^0 - E_k^0\right)\left(E_n^0 - E_m^0\right)} - \frac{H'_{nn}H'_{kn}}{\left(E_n^0 - E_k^0\right)^2} \right] |\varphi_k^0\rangle + \sum_k{}' \frac{H''_{kn}}{(E_n^0 - E_k^0)} |\varphi_k^0\rangle$$

Second order correction due to first order piece of *H*.

Second order correction due to an additional second order piece of *H*.

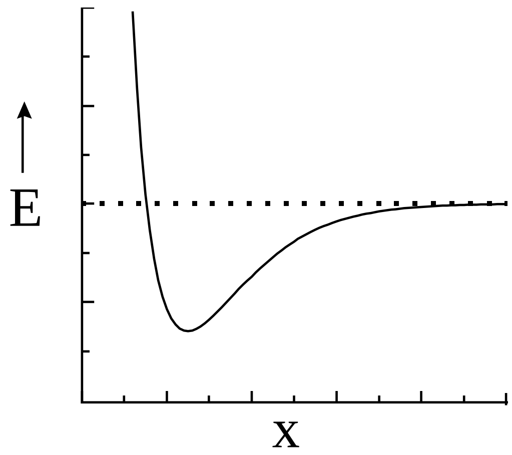
Energy and Ket Corrected to First and Second Order

$$E = E^0 + H'_{nn} + \sum_i{}' \frac{H'_{ni} H'_{in}}{\left(E_n^0 - E_i^0\right)} + H''_{nn} + \cdots$$

$$\left|\varphi_n\right\rangle = \left|\varphi_n^0\right\rangle + \sum_j{}' \frac{H'_{jn}}{(E_n^0 - E_j^0)} \left|\varphi_j^0\right\rangle + \sum_k{}' \left[\sum_m{}' \frac{H'_{km} H'_{mn}}{\left(E_n^0 - E_k^0\right)\left(E_n^0 - E_m^0\right)} - \frac{H'_{nn} H'_{kn}}{\left(E_n^0 - E_k^0\right)^2} \right] \left|\varphi_k^0\right\rangle$$

$$+ \sum_k{}' \frac{H''_{kn}}{(E_n^0 - E_k^0)} \left|\varphi_k^0\right\rangle + \cdots$$

Example: x^3 and x^4 perturbation of the Harmonic Oscillator



Vibrational potential of molecules not harmonic.

Approximately harmonic near potential minimum.

Expand potential in power series.

First additional terms in potential after x^2 term are x^3 and x^4.

$$\underline{H} = \frac{\underline{p}^2}{2m} + \frac{1}{2}k\underline{x}^2 + c\underline{x}^3 + q\underline{x}^4$$

quartic "force constant"

cubic "force constant"

$$\underline{H}^0 = \frac{\underline{p}^2}{2m} + \frac{1}{2}k\underline{x}^2$$

harmonic oscillator – know solutions

$$\underline{H}^0 = \frac{1}{2}\hbar\omega\left(\underline{a}\underline{a}^+ + \underline{a}^+\underline{a}\right)$$

$$E^0 = \left(n + \frac{1}{2}\right)\hbar\omega_0$$

zeroth order eigenvalues

$$|n\rangle$$

zeroth order eigenkets

$$\underline{H}' = c\underline{x}^3 + q\underline{x}^4$$

perturbation

c and q are expansion coefficients like λ.

When c and $q \to 0$, $\underline{H} \to \underline{H}_0$

$$H'_{nn} = \langle n | \underline{H}' | n \rangle$$

$$= \langle n | c\,\underline{x}^3 + q\,\underline{x}^4 | n \rangle$$

$$= c\langle n | \underline{x}^3 | n \rangle + q\langle n | \underline{x}^4 | n \rangle$$

In Dirac representation

$$\underline{x} = \left(\frac{\hbar\omega_0}{2k} \right)^{\frac{1}{2}} \left(\underline{a} + \underline{a}^+ \right)$$

First consider cubic term.

$$\underline{x}^3 \propto \left(\underline{a} + \underline{a}^+ \right)^3$$

Multiply out. Many terms.

$$\underline{a}^3, \underline{a}^2\underline{a}^+, \underline{a}\underline{a}^+\underline{a}, \cdots \underline{a}^{+3}.$$

None of the terms have the same number of raising and lowering operators.

$\langle n | \underline{x}^3 | n \rangle = 0$ (At second order will not be zero.)

$$\langle n|\underline{x}^4|n\rangle = \frac{\hbar^2\omega_0^2}{4k^2}\langle n|\left(\underline{a}+\underline{a}^+\right)^4|n\rangle$$

$\left(\underline{a}+\underline{a}^+\right)^4$ **has terms with same number of raising and lowering operators.**

Therefore, $\langle n|\underline{x}^4|n\rangle \neq 0$

Using $a|n\rangle = n^{1/2}|n-1\rangle$ **and** $a^+|n\rangle = (n+1)^{1/2}|n+1\rangle$

$$\langle n|\underline{a}\underline{a}\underline{a}^+\underline{a}^+|n\rangle = (n+1)(n+2)$$

$$\langle n|\underline{a}^+\underline{a}^+\underline{a}\underline{a}|n\rangle = n(n-1)$$

$$\langle n|\underline{a}\underline{a}^+\underline{a}\underline{a}^+|n\rangle = (n+1)^2$$

$$\langle n|\underline{a}^+\underline{a}\underline{a}^+\underline{a}|n\rangle = n^2$$

$$\langle n|\underline{a}\underline{a}^+\underline{a}^+\underline{a}|n\rangle = n(n+1)$$

$$\langle n|\underline{a}^+\underline{a}\underline{a}\underline{a}^+|n\rangle = (n+1)n$$

Only terms with the same number of raising and lowering operators are non-zero.
There are six terms.

Sum of the six terms

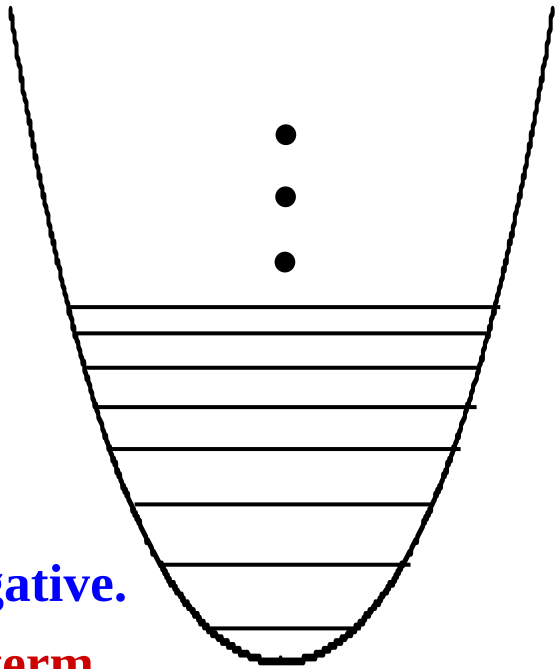
$$\langle n | \left(\underline{a} + \underline{a}^{+} \right)^{4} | n \rangle = 6(n^{2} + n + 1/2)$$

Therefore

$$H'_{nn} = \frac{q\hbar^{2}\omega_{0}^{2}}{k^{2}} \frac{3}{2} \left(n^{2} + n + \frac{1}{2} \right)$$

With $\omega_{0} = \sqrt{k/m}$ $k^{2} = \omega_{0}^{4} m^{2}$

$$E_{n} = \left(n + \frac{1}{2} \right) \hbar\omega_{0} + q \frac{3}{2} \left(n^{2} + n + \frac{1}{2} \right) \frac{\hbar^{2}}{m^{2}\omega_{0}^{2}}$$



Energy levels not equally spaced.

Real molecules, levels get closer together – q is negative.

Correction grows with *n* faster than zeroth order term

→ decrease in level spacing.

Perturbation Theory for Degenerate States

$$\underline{H}\left|\varphi_1\right\rangle = E\left|\varphi_1\right\rangle$$

$$\underline{H}\left|\varphi_2\right\rangle = E\left|\varphi_2\right\rangle$$

$\left|\varphi_1\right\rangle$ **and** $\left|\varphi_2\right\rangle$

normalize and orthogonal

$\left|\varphi_1\right\rangle$ **and** $\left|\varphi_2\right\rangle$ **Degenerate, same eigenvalue,** ***E*****.**

If $\left|\psi\right\rangle = c_1\left|\varphi_1\right\rangle + c_2\left|\varphi_2\right\rangle$

with $\bar{c}_1 c_1 + \bar{c}_2 c_2 = 1$

$$\underline{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$$

Any superposition of degenerate eigenstates is also an eigenstate with the same eigenvalue.

n **linearly independent states with same eigenvalue**

→ **system *n*-fold degenerate**

Can form *n* orthonormal $\left|\psi_i\right\rangle$ **from the *n* degerate** $\left|\varphi_n\right\rangle$**.**

Can form an infinite number of sets of $\left|\psi_i\right\rangle$**.**

Nothing unique about any one set of *n* degenerate eigenkets.

Want approximate solution to

$$\left(\underline{H}^0 + \lambda \underline{H}'\right)\left|\varphi_j\right\rangle = E_j\left|\varphi_j\right\rangle$$

zeroth order Hamiltonian

perturbation

$$\lambda \to 0 \qquad \underline{H}^0\left|\varphi_j^0\right\rangle = E_j^0\left|\varphi_j^0\right\rangle$$

zeroth order eigenket

zeroth order energy

But E_i^0 is *m*-fold degenerate.
Call these *m* eigenkets belonging to the *m*-fold degenerate E_1^0

$$\left|\varphi_1^0\right\rangle, \left|\varphi_2^0\right\rangle \cdots \left|\varphi_m^0\right\rangle$$

orthonormal

With $E_1^0 = E_2^0 = \cdots = E_m^0 \equiv E_1^0$

Here is the difficulty

$\lambda \rightarrow 0$

$$|\varphi_i\rangle \rightarrow |\psi_i^0\rangle$$

perturbed ket **zeroth order ket having eigenvalue,** E_1^0

But, $|\psi_i^0\rangle$ **is a linear combination of the** $|\varphi_i^0\rangle$**.**

$$|\psi_i^0\rangle = c_1|\varphi_1^0\rangle + c_2|\varphi_2^0\rangle + \cdots + c_m|\varphi_m^0\rangle$$

We don't know which particular linear combination it is.

$|\psi_i^0\rangle$ **is the correct zeroth order ket, but we don't know the** c_i**.**

The correct zero order ket depends on the nature of the perturbation.
p states of the H atom in external
magnetic field – p_1, p_0, p_{-1}
electric field – p_x, p_z, p_y

To solve problem

Expand E and $|\varphi_i\rangle$

$$E = E_1^0 + \lambda E' + \cdots$$

$$|\varphi_i\rangle = \sum_{j=1}^{m} c_j |\varphi_j^0\rangle + \lambda |\varphi_i'\rangle + \cdots$$

Some superposition, but we don't know the c_j.

→ **Don't know correct zeroth order function.**

Substituting the expansions for E and $|\varphi_i\rangle$ into

$$\left(\underline{H}^0 + \lambda \underline{H}'\right)|\varphi_i\rangle = E_i |\varphi_i\rangle$$

and obtaining the coefficients of powers of λ, gives

zeroth order

$$\underline{H}^0 \sum_{j=1}^{m} c_j |\varphi_j^0\rangle = E_1^0 \sum_{j=1}^{m} c_j |\varphi_j^0\rangle$$

first order

$$\left(\underline{H}^0 - E_1^0\right)|\varphi_i'\rangle = \sum_{j=1}^{m} c_j \left(E' - \underline{H}'\right)|\varphi_j^0\rangle$$

want these

$$\left(\underline{H}^0 - E_1^0\right)\left|\varphi_i'\right\rangle = \sum_{j=1}^{m} c_j \left(E' - \underline{H}'\right)\left|\varphi_j^0\right\rangle$$ To solve

substitute $$\left|\varphi_i'\right\rangle = \sum_k A_k \left|\varphi_k^0\right\rangle$$

Need $\underline{H}'\left|\varphi_j^0\right\rangle$

Use projection operator $\left|\varphi_k^0\right\rangle\left\langle\varphi_k^0\right|$

$$\underline{H}'\left|\varphi_j^0\right\rangle = \sum_k \left|\varphi_k^0\right\rangle\left\langle\varphi_k^0\right|\underline{H}'\left|\varphi_j^0\right\rangle$$

The projection operator gives the piece of $\underline{H}'\left|\varphi_j^0\right\rangle$ that is $\left|\varphi_k^0\right\rangle$.

Then the sum over all *k* gives the expansion of $\underline{H}'\left|\varphi_j^0\right\rangle$ in terms of the $\left|\varphi_i^0\right\rangle$.

Defining $\underline{H}'_{kj} = \left\langle\varphi_k^0\right|\underline{H}'\left|\varphi_j^0\right\rangle$

Known – know perturbation piece of the Hamiltonian and the zeroth order kets.

$$\underline{H}'\left|\varphi_j^0\right\rangle = \sum_k H'_{kj}\left|\varphi_k^0\right\rangle$$

$$\left(\underline{H}^0 - E_1^0\right)\left|\varphi_i'\right\rangle = \sum_{j=1}^{m} c_j \left(E' - \underline{H}'\right)\left|\varphi_j^0\right\rangle \qquad \underline{H}'\left|\varphi_j^0\right\rangle = \sum_k H'_{kj}\left|\varphi_k^0\right\rangle$$

this piece becomes

$$\sum_{j=1}^{m} c_j H'\left|\varphi_j^0\right\rangle = \sum_{j=1}^{m}\sum_k c_j H'_{kj}\left|\varphi_k^0\right\rangle$$

Substituting this and $\left|\varphi_i'\right\rangle = \sum_k A_k \left|\varphi_k^0\right\rangle$ gives

$$\sum_k \left(E_k^0 - E_1^0\right) A_k \left|\varphi_k^0\right\rangle = \sum_{j=1}^{m} E' c_j \left|\varphi_j^0\right\rangle - \sum_k \left(\sum_{j=1}^{m} c_j H'_{kj}\right)\left|\varphi_k^0\right\rangle$$

Result of operating $\underline{H}^0$ on the zeroth order kets.

Left multiplying by $\left\langle\varphi_i^0\right|$

$$\sum_k \left(E_k^0 - E_1^0\right) A_k \left\langle\varphi_i^0\middle|\varphi_k^0\right\rangle = \sum_{j=1}^{m} E' c_j \left\langle\varphi_i^0\middle|\varphi_j^0\right\rangle - \sum_k \left(\sum_{j=1}^{m} c_j H'_{kj}\right)\left\langle\varphi_i^0\middle|\varphi_k^0\right\rangle$$

$$\sum_k \left(E_k^0 - E_1^0\right) A_k \left\langle \varphi_i^0 \middle| \varphi_k^0 \right\rangle = \sum_{j=1}^{m} E' c_j \left\langle \varphi_i^0 \middle| \varphi_j^0 \right\rangle - \sum_k \left(\sum_{j=1}^{m} c_j H'_{kj} \right) \left\langle \varphi_i^0 \middle| \varphi_k^0 \right\rangle$$

Correction to the Energies

Two cases: $i \le m$ (the degenerate states) and $i > m$.

$i \le m$

Left hand side – sum over k equals zero unless $k = i$.
But with $i \le m$,

$E_i^0 = E_1^0$ **Therefore,** $E_i^0 - E_1^0 = 0$

The left hand side of the equation = 0.

Right hand side, first term non-zero when $j = i$. Bracket = 1, normalization.
Second term non-zero when $k = i$. Bracket = 1, normalization.

The result is

$$\sum_{j=1}^{m} H'_{ij} c_j - E' c_i = 0$$

We don't know the c's and the E's .

$$\sum_{j=1}^{m} H'_{ij} c_j - E' c_i = 0$$ **is a system of *m* of equations for the c_j's.**

$$\left(H'_{11} - E'\right) c_1 + H'_{12} c_2 + \cdots + H'_{1m} c_m = 0$$

$$H'_{21} c_1 + \left(H'_{22} - E'\right) c_2 + \cdots + H'_{2m} c_m = 0$$

One equation for each index *i* of c_i.

$$\vdots$$

$$H'_{m1} c_1 + H'_{m2} c_2 + \cdots + \left(H'_{mm} - E'\right) c_m = 0$$

Besides trivial solution of $c_1 = c_2 = \cdots = c_m = 0$
only get solution if the determinant of the coefficients vanish.

$$\begin{vmatrix} \left(H'_{11} - E'\right) & H'_{12} & \cdots & H'_{1m} \\ \vdots & \left(H'_{22} - E'\right) & \cdots & H'_{2m} \\ & \vdots & & \vdots \\ H'_{m1} & H'_{m2} & \cdots & \left(H'_{mm} - E'\right) \end{vmatrix} = 0$$

We know the $H'_{jk} = \left\langle \varphi_j^0 \middle| H' \middle| \varphi_k^0 \right\rangle$

Have m^{th} degree equation for the E's.

Solve m^{th} degree equation – get the E_i' s . Now have the corrections to energies.

To find the correct zeroth order eigenvectors, one for each E_i', substitute E_i' (one at a time) into system of equations.

Get system of equations for the coefficients, c_j's.

$$\left(H'_{11} - E'_i\right)c_1 + H'_{12}c_2 + \cdots + H'_{1m}c_m = 0$$

Know the H'_{ij} .

$$H'_{21}c_1 + \left(H'_{22} - E'_i\right)c_2 + \cdots + H'_{2m}c_m = 0$$

$$\vdots$$

$$H'_{m1}c_1 + H'_{m2}c_2 + \cdots + \left(H'_{mm} - E'_i\right)c_m = 0$$

There are only m – 1 conditions because can multiply everything by constant. Use normalization for m^{th} condition.

$$c_1^*c_1, + c_2^*c_2, + \cdots + c_m^*c_m = 1$$

Now we have the correct zeroth order functions.

The solutions to the m^{th} degree equation (expanding determinant) are

$$E'_{1},\ E'_{2},\ \cdots\ E'_{m}$$

Therefore, to first order, the energies of the perturbed initially degenerate states are

$$E_i = E_1^0 + E'_i \qquad\qquad 1 \le i \le m$$

Have m different $E'_i s$ (unless some still degenerate).

With $\quad E_i \to E_1^0$

as $\quad \lambda \to 0$

Correction to wavefunctions

Again using equation found substituting the expansions into the first order equation

$$\sum_k \left(E_k^0 - E_1^0\right) A_k \left|\varphi_k^0\right\rangle = \sum_{j=1}^{m} E' c_j \left|\varphi_j^0\right\rangle - \sum_k \left(\sum_{j=1}^{m} c_j H'_{kj}\right) \left|\varphi_k^0\right\rangle$$

Left multiply by

$$\left\langle \varphi_i^0 \right| \qquad i = k > m$$

gives 1 **gives 0**

Orthogonality makes other terms zero.
Normalization gives 1 for non-zero brackets.

$$\left(E_k^0 - E_1^0\right) A_k = -\sum_{j=1}^{m} c_j H'_{kj}$$

Therefore

$$A_k = \frac{\sum_{j=1}^{m} c_j H'_{kj}}{\left(E_1^0 - E_k^0\right)} \qquad k > m$$

Normalization gives $A_j = 0$ for $j \le m$.
Already have part of wavefunction for $j \le m$

First order degenerate perturbation theory results

$$E_i = E_1^0 + \lambda E_i' + \cdots$$

$$\left|\varphi_i\right\rangle = \left|\psi_i^0\right\rangle + \lambda \sum_{k>m} \frac{\sum_{j=1}^{m} c_j H'_{kj}}{\left(E_1^0 - E_k^0\right)} \left|\varphi_k^0\right\rangle + \cdots$$

Correct zeroth order function.
Coefficients c_k determined from
system of equations.

Correction to
zeroth order function.