The Second-order correction

Note Title 4/14/2008

$\psi^{(2)}$ may be expanded as:

$$\psi^{(2)} = \sum_n a_n^{(2)} \psi_n^{(0)} \qquad \psi^{(1)} = \sum_n a_n^{(1)} \psi_n^{(0)}$$

Again we have: $H^{(0)} \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$

For the 2^{nd} order solution we have:

$$(\hat{H}^{(0)} - E_m^{(0)}) \psi^{(2)} = (E^{(1)} - \hat{W}) \psi^{(1)} + E^{(2)} \psi_m^{(0)}$$

$$\hat{H}^{(0)} \sum_n a_n^{(2)} \psi_n^{(0)} - E_m^{(0)} \sum_n a_n^{(2)} \psi_n^{(0)} = E^{(1)} \sum_n a_n^{(1)} \psi_n^{(0)} - \hat{W} \sum_n a_n^{(1)} \psi_n^{(0)} + E^{(2)} \psi_m^{(0)}$$

$$\sum_n a_n^{(2)} \underbrace{\langle \psi_k^{(0)} | \hat{H}^{(0)} | \psi_n^{(0)} \rangle}_{E_n^{(0)} \delta_{kn}} - E_m^{(0)} \sum_n a_n^{(2)} \underbrace{\langle \psi_k^{(0)} | \psi_n^{(0)} \rangle}_{\delta_{kn}} =$$

$$E^{(1)} \sum_n a_n^{(1)} \underbrace{\langle \psi_k^{(0)} | \psi_n^{(0)} \rangle}_{\delta_{kn}} - \sum_n a_n^{(1)} \underbrace{\langle \psi_k^{(0)} | \hat{W} | \psi_n^{(0)} \rangle}_{W_{kn}} + E^{(2)} \underbrace{\langle \psi_k^{(0)} | \psi_m^{(0)} \rangle}_{\delta_{km}}$$

$$\boxed{a_k^{(2)} (E_k^{(0)} - E_m^{(0)}) = a_k^{(1)} E^{(1)} - \sum_n a_n^{(1)} W_{kn} + E^{(2)} \delta_{km}}$$

Second-order correction to eigenvalues $(k=m)$

If $k=m$ $\Rightarrow$ $0 = a_m^{(1)} E^{(1)} - \sum_n a_n^{(1)} W_{mn} + E^{(2)}$ $\rightarrow$

$$E^{(2)} = \sum_n a_n^{(1)} W_{mn} - a_m^{(1)} E^{(1)}$$

$$= \sum_{n \neq m} a_n^{(1)} W_{mn} + a_m^{(1)} W_{mm} - a_m^{(1)} E^{(1)}$$

But from 1st order correction, we had: $E^{(1)} = W_{mm}$ $\Rightarrow$

$$E^{(2)} = \sum_{n \neq m} a_n^{(1)} W_{mn}$$ but we had: $a_n^{(1)} = \dfrac{W_{nm}}{E_m^{(0)} - E_n^{(0)}}$ $\Rightarrow$

$$\boxed{E^{(2)} = \sum_{n \neq m} \frac{|W_{mn}|^2}{E_m^{(0)} - E_n^{(0)}}}$$

$$W_{nm} W_{mn} = W_{mn}^* W_{mn} = |W_{mn}|^2$$

Second-order coefficients $a_k^{(2)}$

There are two cases to consider, $k \neq m$ and $k = m$:

$k \neq m$

we had: $a_n^{(1)} = \dfrac{W_{nm}}{E_m^{(0)} - E_n^{(0)}}$

and $E^{(1)} = W_{mm}$

Substitute into: $a_k^{(2)} (E_k^{(0)} - E_m^{(0)}) = a_k^{(1)} E^{(1)} - \sum a_n^{(1)} W_{kn} + E^{(2)} \overset{0}{\delta_{mk}}$

$$a_k^{(2)} (E_m^{(0)} - E_k^{(0)}) = - a_k^{(1)} E^{(1)} + \sum_n a_n^{(1)} W_{kn}$$

$$= - \frac{E^{(1)} W_{km}}{E_m^{(0)} - E_k^{(0)}} + \sum_n \frac{W_{nm} W_{kn}}{E_m^{(0)} - E_n^{(0)}}$$

$$\boxed{a_k^{(2)} = \sum_n \frac{W_{kn} W_{nm}}{(E_m^{(0)} - E_n^{(0)})(E_m^{(0)} - E_k^{(0)})} - \frac{W_{mm} W_{km}}{(E_m^{(0)} - E_k^{(0)})^2}} \quad k \neq m$$

For the case $k=m$, we find $a_m^{(2)}$ by normalization:

$$\langle \psi | \psi \rangle = \langle \psi_m^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} | \psi_m^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} \rangle = 1$$

$$\sum_n a_n^{(1)*} \langle \psi_n^{(0)} | \psi_m^{(0)} \rangle = a_m^{(1)*}$$

$$1 = \underbrace{\langle \psi_m^{(0)} | \psi_m^{(0)} \rangle}_{1} + \lambda \underbrace{\langle \psi^{(1)}}_{\sum_n \langle a_n^{(1)} \psi_n^{(0)} |} | \psi_m^{(0)} \rangle + \lambda \underbrace{\langle \psi_m^{(0)} | \psi^{(1)} \rangle}_{a_m^{(1)}}$$

$$+ \lambda^2 \underbrace{\langle \psi^{(1)} | \psi^{(1)} \rangle}_{\sum_{n,m} \langle a_n^{(1)} \psi_n^{(0)} | a_m^{(1)} \psi_m^{(0)} \rangle} + \lambda^2 \underbrace{\langle \psi^{(2)} | \psi_m^{(0)} \rangle}_{a_m^{(2)*}} + \lambda^2 \underbrace{\langle \psi_m^{(0)} | \psi^{(2)} \rangle}_{a_m^{(2)}} + \underbrace{\text{higher order terms}}_{\text{ignore}}$$

$$= \sum_{n,m} a_n^{(1)*} a_m^{(1)} \underbrace{\langle \psi_n^{(0)} | \psi_m^{(0)} \rangle}_{\delta_{nm}}$$

$$= \sum_n a_n^{(1)*} a_n^{(1)}$$

$$1 = 1 + \lambda a_m^{(1)*} + \lambda a_m^{(1)} + \lambda^2 \sum_n a_n^{(1)*} a_n^{(1)} + \lambda^2 a_m^{(2)*} + \lambda^2 a_m^{(2)}$$

We had $a_m^{(1)} = 0 \Rightarrow$

$$\lambda^2 \sum_n a_n^{(1)*} a_n^{(1)} + 2\lambda^2 a_m^{(2)} = 0 \quad \Rightarrow$$

$$a_m^{(2)} = -\frac{1}{2} \sum_n |a_n^{(1)}|^2$$

$$= -\frac{1}{2}\underbrace{|a_m^{(1)}|^2}_{=0} - \frac{1}{2}\sum_{n\neq m}|a_n^{(1)}|^2$$

Substitute $a_n^{(1)} = \dfrac{W_{nm}}{E_m^{(0)} - E_n^{(0)}}$, $\Rightarrow$

$$\boxed{a_m^{(2)} = -\frac{1}{2}\sum_{n\neq m}\frac{|W_{mn}|^2}{(E_m^{(0)} - E_n^{(0)})^2} \qquad k=m}$$

We can now write down the 2^{nd} order solutions for the eigenvalues & eigenfunctions of the perturbed system:

$$E = E^{(0)} + E^{(1)} + E^{(2)}$$

$$E = E^{(0)} + W_{mn} + \sum_{n\neq m}\frac{|W_{mn}|^2}{E_m^{(0)} - E_n^{(0)}}$$

$$\psi = \psi^{(0)} + \psi^{(1)} + \psi^{(2)}$$

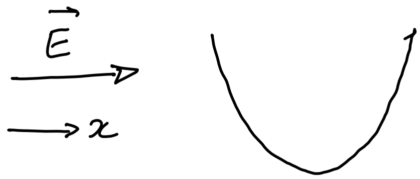
$$\psi = \psi_m^{(0)} + \sum_k a_k^{(1)}\psi_k^{(0)} + \sum_k a_k^{(2)}\psi_k^{(0)}$$

$$\boxed{\begin{aligned}\psi = \psi_m^{(0)} &+ \sum_{k\neq m}\frac{W_{mk}}{E_m^{(0)} - E_k^{(0)}}\psi_k^{(0)} \\ &+ \sum_{k\neq m}\sum_{n\neq m}\left(\frac{W_{kn}W_{mn}}{(E_m^{(0)} - E_n^{(0)})(E_m^{(0)} - E_k^{(0)})} - \frac{W_{mm}W_{km}}{(E_m^{(0)} - E_k^{(0)})^2}\right)\psi_k^{(0)} \\ &- \frac{1}{2}\sum_{n\neq m}\frac{|W_{mn}|^2}{(E_m^{(0)} - E_n^{(0)})^2}\psi_m^{(0)}\end{aligned}}$$

Example 1

Electronic Harmonic Oscillator in Electric Field

$\vec{E} = |E|\,\hat{x}$



$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 + \hat{W} \qquad \hat{W} = e|E|\,\hat{x}$$

$$= \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 + e|E|\,\hat{x} \quad , \quad k = m\omega^2$$

Energy

$$E = E_n^{(0)} + E^{(1)} + E^{(2)}$$

$$E_n^{(0)} = \hbar\omega(n + \tfrac{1}{2})$$

$$E^{(1)} = W_{mm}$$

$$E^{(2)} = \sum_{n \neq m} \frac{|W_{mn}|^2}{E_m - E_n} \qquad x = \left(\frac{\hbar}{2m\omega}\right)^{1/2}(a^{+} + a)$$

$$W_{mn} = \langle m|\hat{W}|n\rangle = \langle m|(-e|E|\hat{x})|n\rangle = -e|E|\langle m|x|n\rangle$$

$$= -e|E|\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left[\langle m|\hat{a}^{+}|n\rangle + \langle m|\hat{a}|n\rangle\right]$$

$$\sqrt{n+1}\,\langle m|n+1\rangle \qquad \sqrt{n}\,\langle m|n-1\rangle$$

$$\sqrt{n+1}\,\delta_{n=m-1} \qquad \sqrt{n}\,\delta_{n=m+1}$$

$$= -e|E|\left(\frac{\hbar}{2m\omega}\right)^{1/2}\left(\sqrt{m}\,\delta_{n,m-1} + \sqrt{m+1}\,\delta_{n,m+1}\right)$$

$E^{(1)} = W_{mm} = 0$ No first order correction

$$E^{(2)} = \sum_{n\neq m} \frac{|W_{mn}|^2}{E_m - E_n} = \frac{e^2|E|^2\hbar}{2m\omega} \sum_{n\neq m} \frac{1}{E_m - E_n}\left(\sqrt{m}\,\delta_{n,m-1} + \sqrt{m+1}\,\delta_{n,m+1}\right)^2$$

$$= \frac{e^2|E|^2\hbar}{2m\omega}\left(\frac{(\sqrt{m})^2}{\underbrace{E_m - E_{m-1}}_{\hbar\omega}} + \frac{(\sqrt{m+1})^2}{\underbrace{E_m - E_{m+1}}_{-\hbar\omega}}\right)$$

$$= \frac{e^2|E|^2}{2m\omega^2}\left(m - m - 1\right)$$

$$= -\frac{e^2|E|^2}{\underbrace{2m\omega^2}_{k}}$$

$$\Rightarrow \quad E = E^{(0)} + E^{(1)} + E^{(2)}$$

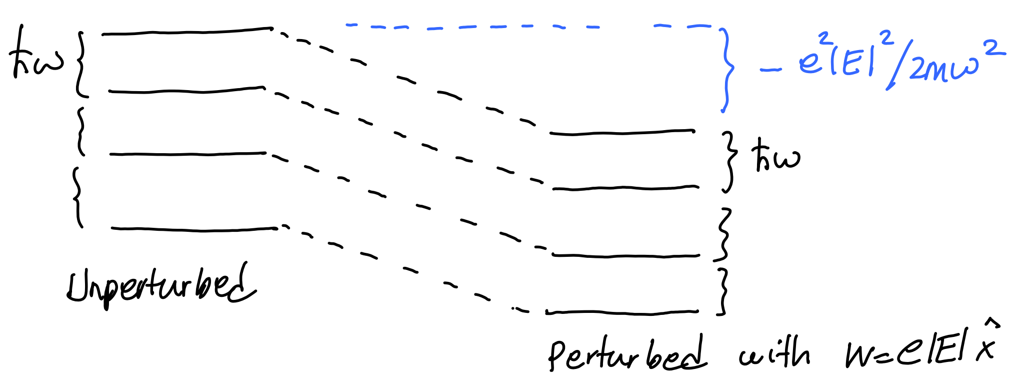
$$\boxed{E = \hbar\omega\left(n + \frac{1}{2}\right) - \frac{e^2|E|^2}{2k}}$$

In chapte 6, the exact solution for this problem is given. Interestingly our second order approximation is equal to the exact answer.

Physically, the particle oscillates at the same frequency ω as the unperturbed case, but it is displaced a distance:

$$kx = e|E| \Rightarrow x = \frac{e|E|}{k} = \frac{e|E|}{m\omega^2}$$

and the new energy levels are shifted by $\frac{-e^2|E|}{2m\omega^2}$.



Example 2 **Harmonic Oscillator in peturbing potential in x^2**

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 + \underbrace{\frac{1}{2}k\xi\,\hat{x}^2}_{\hat{W}}$$

Perturbation is a change in the spring constant.

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 + \frac{1}{2}m\omega^2\xi x^2 = \frac{p^2}{2m} + \frac{1}{2}m\overbrace{\omega^2(1+\xi)}^{\equiv \omega'^2}x^2$$

$$= \frac{p^2}{2m} + \frac{1}{2}m\omega'^2 x^2$$ This is another HO. So:

$$E_n = \hbar\omega'(n+\tfrac{1}{2}) = (n+\tfrac{1}{2})\hbar\omega(1+\xi)^{1/2}$$

Using: $(1+x)^n = 1 + nx + n(n-1)\frac{x^2}{2!} + \cdots \Rightarrow$

$$E_n = (n+\tfrac{1}{2})\hbar\omega\left(1+\frac{\xi}{2} - \frac{\xi^2}{8} + \cdots\right)$$

Let's check the result from the perturbation theory:

$$W = \frac{1}{2}k\xi\hat{x}^2$$

$$= \frac{k}{2}\xi\frac{\hbar}{2m\omega}(\hat{a}^+ + \hat{a})^2 = \frac{m\omega^2}{2}\xi\frac{\hbar}{2m\omega}(a^+ + a)^2$$

$$= \frac{\xi}{4}\hbar\omega(a^{+2} + a^2 + \underbrace{aa^+}_{=a^+a+1} + a^+a) = \frac{\xi}{4}\hbar\omega(\hat{a}^{+2} + \hat{a}^2 + 2\hat{a}^+\hat{a} + 1)$$

$$W_{mn} = \langle m|\hat{w}|n\rangle$$

$$= \frac{\xi}{4}\hbar\omega\left[\langle m|a^{+2}|n\rangle + \langle m|a^2|n\rangle + 2\langle m|a^+a|n\rangle + \langle m|n\rangle\right]$$

$$= \frac{\xi\hbar\omega}{4}\left[\sqrt{n+1}\langle m|a^+|n+1\rangle + \sqrt{n}\langle m|a|n-1\rangle + 2\sqrt{n}\langle m|a^+|n-1\rangle + \delta_{n,m}\right]$$

$$= \frac{\xi\hbar\omega}{4}\left[\sqrt{(n+1)(n+2)}\,\langle m|n+2\rangle + \sqrt{n(n-1)}\,\langle m|n-2\rangle + 2n\,\langle m|n\rangle + \delta_{n,m}\right]$$

$$= \frac{\xi\hbar\omega}{4}\left(\sqrt{(n+1)(n+2)}\,\delta_{n,m-2} + \sqrt{n(n-1)}\,\delta_{n,m+2} + 2n\,\delta_{nm} + \delta_{n,m}\right)$$

$$= \frac{\xi\hbar\omega}{4}\left(\sqrt{m(m-1)}\,\delta_{n,m-2} + \sqrt{(m+1)(m+2)}\,\delta_{n,m+2} + (2m+1)\,\delta_{n,m}\right)$$

$$E = E^{(0)} + E^{(1)} + E^{(2)}$$

$$= \hbar\omega(m+\tfrac{1}{2}) + W_{mm} + \sum_{n\neq m}\frac{|W_{mn}|^2}{E_m - E_n}$$

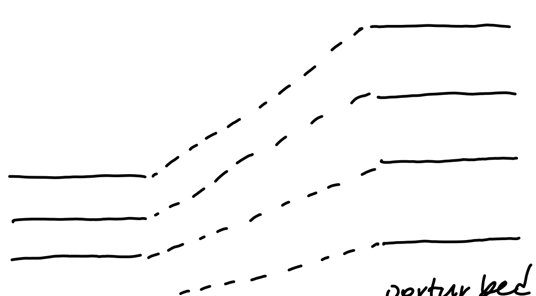
$$= \hbar\omega(m+\tfrac{1}{2}) + \frac{\xi\hbar\omega}{4}(2m+1) + \left(\frac{\xi\hbar\omega}{4}\right)^2\left[\frac{m(m-1)}{\underbrace{E_m - E_{m-2}}_{2\hbar\omega}} + \frac{(m+1)(m+2)}{\underbrace{E_m - E_{m+2}}_{-2\hbar\omega}}\right]$$

$$= \hbar\omega(m+\tfrac{1}{2}) + \hbar\omega\frac{\xi}{2}(m+\tfrac{1}{2}) + \hbar\omega\frac{\xi^2}{32}\Big(\underbrace{m^2 - m - m^2 - 3m - 2}_{= -4m-2 = -4(m+\frac{1}{2})}\Big)$$

$$= \hbar\omega(m+\tfrac{1}{2})\left(1 + \frac{\xi}{2} - \frac{\xi^2}{8}\right)$$

Which agrees with our earlier solution to the 2nd order.

Both energy levels & energy spacings increase in this case:



unperturbed

$E = \hbar\omega(n+\frac{1}{2})$

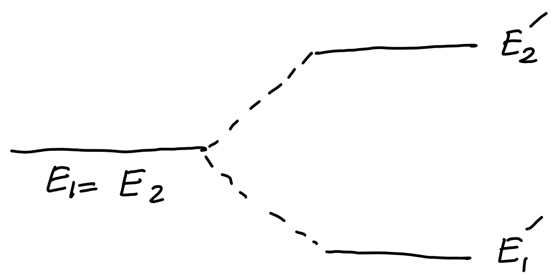
perturbed with $w = \frac{1}{2}k\xi x^2$

$E = \hbar\omega(n+\frac{1}{2})(1 + \frac{\xi}{2} - \frac{\xi^2}{8} + \cdots)$

Time independent degenerate perturbation

Symmetry $\longrightarrow$ degenerate eigenvalues (energy levels)

Perturbation $\longrightarrow$ Break the symmetry $\longrightarrow$ splits the energy levels



Before perturbation After

$\hat{H}^{(0)}$ $\qquad\qquad$ $\hat{H} = \hat{H}^{(0)} + \hat{W}$

$H^{(0)} \psi_m^{(0)} = E_m^{(0)} \psi_m^{(0)}$ $\qquad$ $\hat{H} \psi_n = E_n \psi_n$

Two-fold degeneracy split by time independent perturbation

The first order corrected wave function $\psi_m^{(1)}$ expanded versus the unperturbed $\psi_n^{(0)}$'s is:

$$\psi_m^{(1)} = \sum_n a_{mn}^{(1)} \psi_n^{(0)}$$

$$a_{mn}^{(1)} = \frac{W_{mn}}{E_m^{(0)} - E_n^{(0)}}$$

If we have degeneracy: $E_m^{(0)} = E_n^{(0)}$ at some states $\Rightarrow a_{mn} = \infty$

To get around this problem, we will diagonalize $\hat{H}$.

Matrix method

$$H\Psi^{(1)} = E\,\Psi^{(1)} \rightarrow H\sum_n a_n \Psi_n^{(0)} = E\sum a_n \Psi_n^{(0)}$$

$$H\sum_n a_n |n\rangle^{(0)} = E\sum a_n |n\rangle^{(0)}$$

$$\langle m|H\sum_n a_n |n\rangle = E\sum_n a_n \langle m|n\rangle$$

$$\sum_n \langle m|H|n\rangle a_n = E a_m$$

$$\sum_n^N H_{mn} a_n = E a_m$$

$$\underbrace{\begin{bmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \\ H_{31} & H_{32} & H_{33} & \\ \vdots & & \ddots & \\ & & & H_{NN} \end{bmatrix}}_{\mathbf{H}} \underbrace{\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \\ a_N \end{bmatrix}}_{\mathbf{a}} = E \underbrace{\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \\ a_N \end{bmatrix}}_{\mathbf{a}}$$

Matrix vector

$$H\,a = E\,a$$

$$Ha - Ea = 0 \Rightarrow (H - EI)\,a = 0$$

which has a nontrivial solution if the characteristic determinant is zero:

$$|H - EI| = \begin{vmatrix} H_{11}-E & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22}-E & & \vdots \\ \vdots & \vdots & H_{33}-E & \\ & & & \ddots \\ & & & H_{NN}-E \end{vmatrix} = 0$$

Matrix method for two state :

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

$$(H_{11}-E)(H_{22}-E) - H_{12}H_{21} = 0$$

$$E^2 - EH_{22} - EH_{11} + H_{11}H_{22} - H_{12}H_{21} = 0$$

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

$$E = \frac{(H_{11}+H_{22}) \pm \left[(H_{11}+H_{22})^2 - 4(H_{11}H_{22} - H_{12}H_{21})\right]^{1/2}}{2}$$

$$= \frac{H_{11}+H_{22}}{2} \pm \frac{1}{2}\left[\underbrace{H_{11}^2 + H_{22}^2 + 2H_{11}H_{22} - 4H_{11}H_{22}}_{(H_{11}-H_{22})^2} + 4H_{12}H_{21}\right]^{1/2}$$

$$= \frac{H_{11}+H_{22}}{2} \pm \left[\frac{(H_{11}-H_{22})^2}{4} + H_{12}\underbrace{H_{21}}_{=H_{12}^*}\right]^{1/2}$$

$$\boxed{E_{\pm} = \frac{H_{11}+H_{22}}{2} + \left[\frac{(H_{11}+H_{22})^2}{4} + |H_{12}|^2\right]^{1/2}}$$

Let's now calculate a_1 and a_2. We had:

$$\begin{pmatrix} H_{11}-E & H_{21} \\ H_{21} & H_{22}-E \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = 0 \rightarrow \begin{cases} (H_{11}-E)a_1 + H_{21}a_2 = 0 & \text{(I)} \\ H_{21}a_1 + (H_{22}-E)a_2 = 0 & \text{(II)} \end{cases}$$

ψ must be also normalized: $\psi = a_1 \psi_1^{(0)} + a_2 \psi_2^{(0)}$

$$\int |\psi|^2 = 1 \Rightarrow |a_1|^2 + |a_2|^2 = 1$$

$$(I) \Rightarrow (H_{11} - E) a_1 = -H_{12} a_1 \to (H_{11}-E)^2 |a_1|^2 = H_{12}^2 \underbrace{|a_2|^2}_{=1-|a_1|^2} \to$$

$$(H_{11}-E)^2 |a_1|^2 = H_{12}^2 (1 - |a_1|^2) \to \left[(H_{11}-E)^2 + H_{12}^2\right] |a_1|^2 = H_{12}^2 \to$$

$$|a_1|^2 = \frac{|H_{12}|^2}{\underbrace{(H_{11}-E)^2 + |H_{12}|^2}_{\equiv D^2}} = \frac{|H_{12}|^2}{D^2} \to \boxed{a_1 = \frac{H_{12}}{D}}$$

For a_2, use (I) again:

$$a_2 = \frac{-(H_{11}-E) a_1}{H_{12}} = \frac{-(H_{11}-E)}{H_{12}} \frac{H_{12}}{D} = \frac{E - H_{11}}{D}$$

$$\boxed{a_2 = \frac{E - H_{11}}{D}}$$

So for each E, we find the corresponding a_1, a_2 that gives the corresponding ψ.

<u>Example</u> **2D HO subject to perturbation in xy**

$$\hat{H}^{(0)} = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2} k (x^2 + y^2)$$

$$= \hbar\omega \left(a_x^\dagger a_x + \frac{1}{2} + a_y^\dagger a_y + \frac{1}{2} \right)$$

$$= \hbar\omega \left(a_x^\dagger a_x + a_y^\dagger a_y + 1 \right)$$

where $x = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a_x + a_x^\dagger)$ & $y = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (a_y + a_y^\dagger)$

The eigenstates are of the form:

$$\varphi_{nm} = \varphi_n(x)\,\varphi_m(y) = |n\,m\rangle$$

for x   for y

And the energy:

$$E_{nm} = \hbar\omega(n+m+1)$$

$$E_{00} = \hbar\omega$$

$E_{01} = E_{10} = 2\hbar\omega$ 2-fold degenerate states: $|01\rangle$ and $|10\rangle$

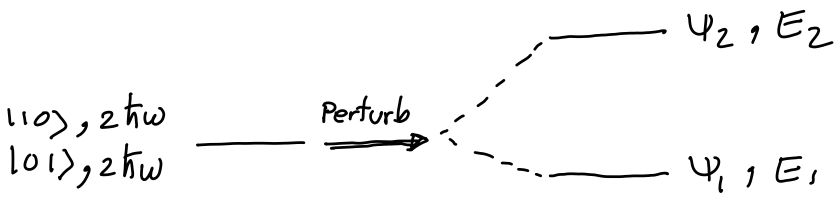
$E_{11} = E_{20} = E_{02} = 3\hbar\omega$ 3-fold degenerate: $|11\rangle, |20\rangle, |02\rangle$

$E_{nm} \longrightarrow$ $(n+m+1)$-fold degenerate.

Let study the effect of the perturbing potential $\hat{W} = k'\hat{x}\hat{y}$;

We will find new wave functions that diagonalize $\hat{W}$.

Let's consider the second energy level that is two-fold degenerate. The perturbed eigenfunction can be expanded versus the degenerate states:



$$\begin{cases} \psi_1 = a_1\varphi_{10} + a_2\varphi_{01} \\ \psi_2 = a_1\varphi_{10} - a_2\varphi_{01} \end{cases}$$

Sub matrix W in the basis of $\{\varphi_{10}, \varphi_{01}\}$ is:

$$W = \begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix} = k' \begin{bmatrix} \langle 10|xy|10\rangle & \langle 10|xy|01\rangle \\ \langle 01|xy|10\rangle & \langle 01|xy|01\rangle \end{bmatrix}$$

$$W_{11} = W_{22} = 0$$

$$W_{12} = k'\frac{\hbar}{2m\omega} \langle 10|(a_x + a_x^\dagger)(a_y + a_y^\dagger)|01\rangle$$

$$= \frac{k'\hbar}{2m\omega} \langle 10|\; \underset{\Rightarrow 0}{a_x a_y} + \underset{\checkmark}{a_x^\dagger a_y} + \underset{\Rightarrow 0}{a_x a_y} + \underset{\text{gives } 0}{a_x a_y^\dagger} \;|01\rangle$$

$$= \frac{k'\hbar}{2m\omega} \langle 10|\underbrace{a_x^\dagger \overbrace{a_y|01\rangle}^{|\cdot 0\rangle}}_{1|1\cdot\rangle} = \frac{k'\hbar}{2m\omega}\langle 10|10\rangle$$

$$= \frac{k'\hbar}{2m\omega}$$

Similarly: $W_{21} = \dfrac{k'\hbar}{2m\omega} \Rightarrow W = \dfrac{\hbar k'}{2m\omega}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$

The secular equation is:

$$\begin{vmatrix} W_{11} - E^{(1)} & W_{12} \\ W_{21} & W_{22} - E^{(1)} \end{vmatrix} = 0 \rightarrow \begin{vmatrix} -E^{(1)} & \frac{\hbar k'}{2m\omega} \\ \frac{\hbar k'}{2m\omega} & -E^{(1)} \end{vmatrix} = 0$$

$$E^{(1)^2} - \left(\frac{\hbar k'}{2m\omega}\right)^2 = 0 \rightarrow E^{(1)} = \pm \frac{\hbar k'}{2m\omega}$$

$E_{10} = 2\hbar\omega$ —— $\xrightarrow{W = k'xy}$ ΔE

$$E_+ = E_{10} + \overbrace{\frac{\hbar k'}{2m\omega}}^{\Delta E/2} = E_{10} + \frac{\Delta E}{2}$$

$$E_- = E_{10} - \frac{\hbar k'}{2m\omega} = E_{10} - \frac{\Delta E}{2}$$

Now let's find the wavefunctions:

Substitute these values into the matrix equation:

$$\begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = E\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \qquad \sum_{m=1,n=1}^{N} [H_{nm} - E\delta_{nm}]\, a_n = 0$$

$$\begin{bmatrix} -E & \frac{\Delta E}{2} \\ \frac{\Delta E}{2} & -E \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0$$

$$\begin{vmatrix} -E & \frac{\Delta E}{2} \\ \frac{\Delta E}{2} & -E \end{vmatrix} = 0 \Rightarrow E^2 = \left(\frac{\Delta E}{2}\right)^2 \rightarrow E = \pm \frac{\Delta E}{2}$$

$$E = \frac{\Delta E}{2} \rightarrow a_1 = a_2 \qquad |a_1|^2 + |a_2|^2 = 1 \rightarrow a_1 = a_2 = \frac{1}{\sqrt{2}}$$

$$E = -\frac{\Delta E}{2} \rightarrow a_1 = -a_2 \rightarrow a_1 = -a_2 = \frac{1}{\sqrt{2}}$$

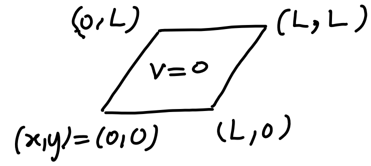
$$\begin{cases} \psi_1 = a_1 \varphi_{10} + a_2 \varphi_{01} = \frac{1}{\sqrt{2}}(\varphi_{10} + \varphi_{01}) \\ E_+ = \frac{\Delta E}{2} \end{cases}$$

Symmetric

$$\begin{cases} \psi_1 = \frac{1}{\sqrt{2}}(\varphi_{10} - \varphi_{01}) \\ E_- = -\frac{\Delta E}{2} \end{cases}$$

Antisymmetric

Perturbation of two-dimensional potential with infinite barrier energy



$$H^{(0)}\psi_n^{(0)}(x,y) = E_n^{(0)}\psi_n^{(0)}(x,y)$$

$$\downarrow$$

$$H^{(0)} = \frac{-\hbar^2}{2m}\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2}\right)$$

$$\psi_n^{(0)}(x,y) = \varphi_{nx}(x)\,\varphi_{ny}(y) = \frac{2}{L}\sin(k_{nx}x)\sin(k_{ny}y)$$

$$E^{(0)}_{n_x,n_y} = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2+n_y^2)$$

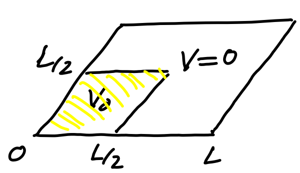
The ground state is not degenerate $\psi_{11}^{(0)}$

The first excited state is degenerate $\psi_{12}^{(0)}$ or $\psi_{21}^{(0)} \rightarrow E_{12}^{(0)} = \frac{5\pi^2\hbar^2}{2mL^2}$

$$\sum_{m=1,n=1}^{N}[H_{nm}^{(0)} - E\delta_{nm}]\,a_n^{(0)} = \begin{bmatrix} H_{11}^{(0)}-E & H_{12}^{(0)} & H_{13}^{(0)} & \vdots \\ H_{21}^{(0)} & H_{22}^{(0)}-E & H_{23}^{(0)} & \vdots \\ \vdots & & & \\ & \cdots & & H_{NN}^{(0)}-E \end{bmatrix}\begin{bmatrix} a_1^{(0)} \\ a_2^{(0)} \\ \vdots \\ a_N^{(0)} \end{bmatrix} = 0$$

$$= \begin{bmatrix} -E & 0 & 0 & \cdots \\ 0 & -E & 0 & \cdots \\ 0 & 0 & -E & \cdots \\ \vdots & & \ddots & -E \end{bmatrix}\begin{bmatrix} a_1^{(0)} \\ a_2^{(0)} \\ \vdots \\ a_N^{(0)} \end{bmatrix} = 0$$

<u>Perturbation</u>:



The correction to ground state energy after the perturbation is applied, to first order is given by the diagonal matrix element of nondegenerate perturbation theory:

$$E_{11}^{(1)} = \langle \psi_{11}^{(0)} | \hat{W} | \psi_{11}^{(0)} \rangle$$

$$= \left(\frac{2}{L}\right)^2 V_0 \int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx \int_0^{L/2} \sin^2\left(\frac{\pi y}{L}\right) dy$$

$$= \left(\frac{2}{L}\right)^2 V_0 \left(\frac{L}{4}\right)^2 = \frac{V_0}{4}$$

The first excited state is degenerate, so we must use degenerate perturbation:

$$\begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix} = \begin{bmatrix} \langle \psi_{12}^{(0)} | \hat{W} | \psi_{12}^{(0)} \rangle & \langle \psi_{12}^{(0)} | \hat{W} | \psi_{21}^{(0)} \rangle \\ \langle \psi_{21}^{(0)} | \hat{W} | \psi_{12}^{(0)} \rangle & \langle \psi_{21}^{(0)} | \hat{W} | \psi_{21}^{(0)} \rangle \end{bmatrix}$$

$$W_{11} = W_{22} = \langle \psi_{12}^{(0)} | \hat{W} | \psi_{12}^{(0)} \rangle$$

$$= \left(\frac{2}{L}\right)^2 V_0 \int_0^{L/2} \sin^2\left(\frac{\pi x}{L}\right) dx \int_0^{L/2} \sin^2\left(\frac{2\pi y}{L}\right) dy$$

$$= \left(\frac{2}{L}\right)^2 V_0 \left(\frac{L}{4}\right)^2 = \frac{V_0}{4}$$

$$W_{12} = W_{21} = \langle \psi_{12}^{(0)} | \hat{W} | \psi_{21}^{(0)} \rangle$$

$$= \left(\frac{2}{L}\right)^2 V_0 \int_0^{L/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi x}{L}\right) dx \int_0^{L/2} \sin\frac{2\pi y}{L} \sin\frac{\pi y}{L}\, dy$$

$$= \frac{V_0}{L^2}\int_0^{L/2}\left[\cos\left(\frac{-\pi x}{L}\right) - \cos\frac{3\pi x}{L}\right]dx \int_0^{L/2}\left[\cos\left(\frac{\pi y}{L}\right) - \cos\frac{3\pi y}{L}\right]dy$$

$$= \frac{V_0}{L^2}\left(\frac{L}{\pi} + \frac{L}{3\pi}\right)\left(\frac{L}{\pi} + \frac{L}{3\pi}\right) = \frac{V_0}{L^2}\left(\frac{4L}{3\pi}\right)\left(\frac{4L}{3\pi}\right) = \frac{16V_0}{9\pi^2}$$

$$\Rightarrow \begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix} = \frac{V_0}{4}\begin{bmatrix} 1 & \frac{64}{9\pi^2} \\ \frac{64}{9\pi^2} & 1 \end{bmatrix}$$

$$\begin{bmatrix} W_{11}-E & W_{12} \\ W_{21} & W_{22}-E \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0 \rightarrow \begin{bmatrix} \frac{V_0}{4}-E & \frac{V_0}{4}\frac{64}{9\pi^2} \\ \frac{V_0}{4}\frac{64}{9\pi^2} & \frac{V_0}{4}-E \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0$$

$$\frac{V_0}{4}\begin{bmatrix} 1-\frac{4}{V_0}E & \frac{64}{9\pi^2} \\ \underbrace{\frac{64}{9\pi^2}}_{\equiv \Delta} & \underbrace{1-\frac{4}{V_0}E}_{E'} \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0$$

$$\det(W-EI) = 0 \rightarrow (1-E')^2 - \Delta^2 = E'^2 - 2E' + (1-\Delta) = 0 \rightarrow$$

$$E' = 1 \pm \sqrt{1-(1-\Delta)} = 1 \pm \Delta \rightarrow E = \frac{V_0}{4}E' = \frac{V_0}{4}\left(1 \pm \frac{64}{9\pi^2}\right)$$

This is the correction term $E^{(1)}$. $\Rightarrow$

$$E = E^{(0)} + E^{(1)} = E_{12}^{(0)} + \frac{V_0}{4}\left(1 \pm \frac{64}{9\pi^2}\right)$$

$$\begin{cases} E_+ = E_{12}^{(0)} + \frac{V_0}{4}\left(1 + \frac{64}{9\pi^2}\right), & \psi_+ = \frac{1}{\sqrt{2}}\left(\psi_{12}^{(0)} + \psi_{21}^{(0)}\right) \\ E_- = E_{12}^{(0)} + \frac{V_0}{4}\left(1 - \frac{64}{9\pi^2}\right), & \psi_- = \frac{1}{\sqrt{2}}\left(\psi_{12}^{(0)} - \psi_{21}^{(0)}\right) \end{cases}$$