Perturbation Theory

We've found that we should be considering the Hamiltonian

$$H = \frac{\underline{p}^2}{2m} - \frac{e^2}{4\pi\varepsilon_0 r} - \frac{1}{2m_e c^2}\left(\frac{\underline{p}^2}{2m_e}\right)^2$$

$$+\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\frac{\underline{S}.\underline{L}}{m_e^2 c^2 r^3}$$

for hydrogen. Now the problem is that the states $|n, l, m\rangle$ are <u>not</u> eigenstates of H; for example it's clear that they are not eigenstates of $\underline{p}^2$ (these are plane waves, and ~~hydrogen~~ are hydrogen wavefunctions are definitely not plane waves!). On the other hand we've estimated the <u>size</u> of these extra effects and its rather small ($\sim 10^{-4}$) by comparison with the gross structure. This suggests that some sort of approximation method might be a good way to proceed.

This method is called perturbation theory. It's not particularly mysterious; it's really just like using Taylor's theorem to approximate a function

ie

$$f(x+\Delta) = f(x) + \Delta f'(x) + \frac{\Delta^2}{2} f''(x\theta).$$

if f'' is not too big then for small Δ we get that $f(x+\Delta) = f(x) + \Delta f'(x)$

to a pretty good approximation. In the physics we've been looking at Δ is about 10^{-4} so higher order terms would be really tiny.

A. Non-degenerate case, Energy shift

Suppose we start with a Hamiltonian whose eigenstates are known, for example the S.H.O,

$$H|n\rangle = E_n|n\rangle$$

and every E_n is different ($(n+\frac{1}{2})\hbar\omega$ for the SHO)

Then we add an extra term, eg $h = \lambda x^4$, so that now $H' = H + h$

$$= \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 + \lambda x^4$$

(which is called an anharmonic oscillator).

We want to find the eigenstates and energies of H' ie

$$H'|n'\rangle = E_n'|n'\rangle$$

Exploit the fact that the original eigenstates of H form a complete set to write

$$|n'\rangle = \sum_k \underset{\uparrow}{C_{nk}} |k\rangle$$

constant coefficients to be determined.

We can write

$$|n'\rangle = C_{nn}|n\rangle + \sum_{k \neq n} C_{nk}|k\rangle$$

when $h \to 0$ we expect ~~so~~ $|n'\rangle \to |n\rangle$

so C_{nn} does not vanish as $h \to 0$

but C_{nk} $k \neq n$ does vanish as $h \to 0$

Altogether of course $|n'\rangle$ is normalized so

$$|C_{nn}|^2 = 1 - \sum_{k \neq n} |C_{nk}|^2$$

Now $|n'\rangle$ is supposed to ~~be~~ satisfy

$$H'|n'\rangle = E_n'|n'\rangle$$

So

$$(H+h)\sum_k c_{nk}|k\rangle = E_n'\sum_k c_{nk}|k\rangle$$

$$E_k|k\rangle$$

or

$$\sum_k c_{nk}\, h|k\rangle = \sum_k c_{nk}(E_n' - E_k)|k\rangle \qquad (1)$$

If we act on the left with $\langle n|$ we get

$$\sum_k c_{nk}\langle n|h|k\rangle = c_{nn}(E_n' - E_n)$$

separate out $k=n$ term

or

$$\langle n|h|n\rangle + \sum_{k\neq n} \underset{\substack{\uparrow\\ \text{also small}}}{\frac{c_{nk}}{c_{nn}}} \underset{\substack{\uparrow\\ \text{small}}}{\langle n|h|k\rangle} = E_n' - E_n$$

so

$$E_n' = E_n + \underset{\substack{\nearrow\\ \text{first order energy shift}}}{\langle n|h|n\rangle} + \text{smaller terms which we'll quantify later}$$

Before we carry on with the formalism let's do the example of the anharmonic oscillator with $h = \lambda x^4$. Then

$$E_n' = \hbar\omega(n+\tfrac{1}{2}) + \overset{\text{"overlap integral"}}{\int_{-\infty}^{\infty}\phi_n^*(x)\,\lambda x^4\,\phi_n(x)\,dx}$$

$n = 0$ case

Here it's easy enough to do the integral

$$\Delta E_0 = \sqrt{\frac{1}{\pi a^2}} \int_{-\infty}^{\infty} \lambda x^4 e^{-x^2/a^2} dx \quad , \; a^2 = \frac{\hbar}{m\omega}$$

$$x = a y .$$

$$= \frac{1}{\sqrt{\pi}} \cdot \frac{1}{a} \lambda a^5 \underbrace{\int_{-\infty}^{\infty} y^4 e^{-y^2} dy}_{\substack{\text{do by parts or} \\ \text{ask Maple/Mathematica} \\ \text{- it's closely related to } \int_{-\infty}^{\infty} e^{-y^2} dy}} = \tfrac{3}{4}\sqrt{\pi}$$

$$= \frac{3}{4} \lambda a^4$$

$n \neq 0$ case

The $\phi_n(x)$ involve Hermite polynomials and the integrals look ghastly. But operator methods actually make it easy! We want

$$\langle n | x^4 | n \rangle$$

Now $x = \sqrt{\dfrac{\hbar}{2m\omega}} (a + a^+)$

so we need

$$\langle n | (a + a^+)^4 | n \rangle$$

Remember that a^+ raises $|n\rangle \to |n+1\rangle$ and

a lowers $|n\rangle \to |n-1\rangle$

So when we expand $(a+a^+)^4$ terms with different numbers of a's and a^+'s will give zero

eg. $\langle n| a^4 |n\rangle \sim \langle n|n-4\rangle = 0$

$$\langle n|a^2 a^+ a|n\rangle \sim \langle n|a^2 a^+|n-1\rangle$$

$$\sim \langle n|a^2|n\rangle$$

$$\sim \langle n|n-2\rangle = 0$$

So

$$\langle n|(a+a^+)^4|n\rangle$$

$$= \langle n|\ a^+a^+aa + a^+aa^+a + a^+aaa^+$$

$$+ aaa^+a^+ + aa^+aa^+ + aa^+a^+a\ |n\rangle$$

We also know $a^+a|n\rangle = n|n\rangle$

and $aa^+ = 1 + a^+a$ (this is $[a,a^+] = 1$).

We get

$$\langle n|(a+a^+)^4|n\rangle = \langle n|\ a^+(aa^+-1)a + n^2 + n(n+1)$$

$$+ a(1+a^+a)a^+ + (n+1)^2 + (n+1)n\ |n\rangle$$

$$= n^2 - n + n^2 + (n+1)^2 + 2n(n+1)$$

$$+ n+1 + (n+1)^2$$

$$= 3 + 6n + 6n^2$$

and $\Delta E_n = \frac{3\lambda}{4}\left(\frac{\hbar}{m\omega}\right)^2(1+2n+2n^2)$ – agrees with ΔE_0 !!

B. The wavefunction shift

We've computed the first order energy shift; what about the states? Return to the formula (1) which we got from setting $H'|n'\rangle = E_n'|n'\rangle$

$$\sum_k c_{nk}\, h|k\rangle = \sum_k c_{nk}(E_n' - E_k)|k\rangle$$

and this time act on the left with an arbitrary state $\langle l|$: Very important formula VIF

$$\boxed{\sum_k c_{nk}\langle l|h|k\rangle = c_{nl}(E_n' - E_l)}$$

separate out $k=n$ term

$$\underbrace{c_{nn}}_{1+O(h^2)}\underbrace{\langle l|h|n\rangle}_{\text{small}} + \sum_{k\neq n}\overset{\text{small}}{c_{nk}}\,\overset{\text{small.}}{\langle l|h|k\rangle}$$

$$= c_{nl}\underbrace{(E_n' - E_l)}_{E_n - E_l + \underbrace{\Delta E_n}_{\text{small.}}}$$

so $c_{nl} = c_{nn}\dfrac{\langle l|h|n\rangle}{E_n - E_l}$ + smaller terms

This gives us two things; firstly the shifted state

$$|n'\rangle = \sum_k c_{nk}|k\rangle = \sum_{k\neq n}\frac{\langle k|h|n\rangle}{E_n - E_k}|k\rangle + \underbrace{c_{nn}}_{\text{get this by requiring } \langle n'|n'\rangle = 1}|n\rangle$$

and secondly the second order energy shift.

By substituting into (2)

$$E_n' - E_n = \langle n|h|n\rangle + \sum_{k\neq n} \frac{\langle k|h|n\rangle \langle n|h|k\rangle}{E_n - E_k}$$

$$= \langle n|h|n\rangle + \sum_{k\neq n} \frac{|\langle k|h|n\rangle|^2}{E_n - E_k}$$

These results show straightaway that if there are degenerate states then our calculations are not valid — we'll return to this problem in the next lecture. The second order energy shift also fixes the regime of validity for our "small quantities" analysis — basically the second order term should be much smaller than the first order term and this in turn means that

$$\frac{\langle k|h|n\rangle}{E_n - E_k} \ll 1$$

Let's calculate the shifted wavefunction for the ground state of the anharmonic oscillator we have

$$|0'\rangle = C_{00}|0\rangle + \sum_{k\neq 0} \frac{\langle k|\lambda x^4|0\rangle\ |k\rangle}{\tfrac{1}{2}\hbar\omega - \hbar\omega(k+\tfrac{1}{2})}.$$

The way to do this quickly is to look at

$$x^4|0\rangle = \left(\frac{\hbar}{2m\omega}\right)^2 (a+a^\dagger)^4\,|0\rangle$$

$$a|n\rangle = \sqrt{n}\,|n-1\rangle$$
$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 (a+a^\dagger)^3\,|1\rangle$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 (a+a^\dagger)^2\,\left(|0\rangle + \sqrt{2}\,|2\rangle\right)$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 (a+a^\dagger)\,\left(|1\rangle + 2\,|1\rangle + \sqrt{2}\sqrt{3}\,|3\rangle\right)$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \left(3\left(|0\rangle + \sqrt{2}\,|2\rangle\right) + \sqrt{2}\sqrt{3}\left(\sqrt{4}\,|4\rangle + \sqrt{3}\,|2\rangle\right)\right).$$

$$= \left(\frac{\hbar}{2m\omega}\right)^2 \left(3\,|0\rangle + 6\sqrt{2}\,|2\rangle + 2\sqrt{6}\,|4\rangle\right)$$

So we can read off the answer straightaway

$$|0'\rangle = C_{00}|0\rangle + \frac{\lambda}{-\hbar\omega}\left(\frac{\hbar}{2m\omega}\right)^2 \left(\frac{6\sqrt{2}}{2}\,|2\rangle + \frac{2\sqrt{6}}{4}\,|4\rangle\right)$$

and normalization fixes

$$|C_{00}|^2 = 1 - \frac{\lambda^2}{\hbar^2\omega^2}\left(\frac{\hbar}{2m\omega}\right)^4 \left(9.2 + \frac{6}{4}\right)$$

Note that C_{00} is therefore $1 + O(\lambda^2)$ – and that its phase is abitrary – we can choose C_{00} to be real and +ve.

It's interesting that the states $|2\rangle$ and $|4\rangle$ get involved but not for example $|1\rangle$ and $|3\rangle$ — this is because of the nature of the perturbing potential. If we'd had λx^3 so $(a+a^\dagger)^3$ then you can see from the calculation that $|1\rangle$ and $|3\rangle$ would have been involved but not $|2\rangle$ and $|4\rangle$. In terms of <u>wavefunctions</u> because λx^4 is even overlap integrals involving

$$\int \phi_{\text{even}}\, \lambda x^4\, \phi_{\text{odd}} = 0 \quad \text{automatically}$$

so even and odd functions don't get mixed. On the other hand λx^3 doesn't mix different even functions.

Degeneracy and Perturbation Theory.

We saw last time that the perturbation theory method gets into difficulties if

a) The unperturbed states are degenerate

b) The matrix element of the perturbation between degenerate states $\langle k|h|n\rangle \neq 0$

In this case our formula for the first order shifted state

$$|n'\rangle = C_{nn}\left(|n\rangle + \sum_{k\neq n} \frac{\langle k|h|n\rangle\, |k\rangle}{E_n - E_k}\right)$$

gives an undefined result. To fix it we have to go back to an earlier stage in the calculation.

A. The formalism

Let's go back to the VIF from the last lecture:

$$\sum_k \langle l|h|k\rangle C_{nk} = (E_n' - E_l)\, C_{nl}$$

This formula is exact. All we have done so far is to expand the eigenstate $|n'\rangle$ of the perturbed

Hamiltonian $H' = H + h$ as a linear superposition of the eigenstates $|k\rangle$ of the unperturbed Hamiltonian H. It's convenient to rearrange the formula a little to

$$\sum_k \left(\langle l | h | k \rangle + E_l \, \delta_{lk} \right) C_{nk} = E_n' \, C_{nl}$$

This can be written in terms of matrices and vectors

$$\begin{pmatrix} h_{11} + E_1 & h_{12} & \cdots \\ h_{21} & h_{22} + E_2 & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} C_{n1} \\ C_{n2} \\ \vdots \end{pmatrix} = E_n' \begin{pmatrix} C_{n1} \\ C_{n2} \\ \vdots \end{pmatrix}$$

Now our problem with PT arises if $h_{12} \neq 0$ when, say, $E_1 = E_2 \equiv E$ The way to deal with it is to make a change of basis to one in which $h_{\tilde{1}\tilde{2}}$ is automatically zero. We can do this by concentrating on the degenerate part of the equation

$$\begin{pmatrix} h_{11}+E & h_{12} \\ h_{21} & h_{22}+E \end{pmatrix}\begin{pmatrix} C_{n1} \\ C_{n2} \end{pmatrix} = E_n'\begin{pmatrix} C_{n1} \\ C_{n2} \end{pmatrix}$$

We want to make a change of basis such that the l.h.s. becomes diagonal. But you know how to do this! Write

$$\begin{pmatrix} C_{n1} \\ C_{n2} \end{pmatrix} = O\begin{pmatrix} \tilde{C}_{n1} \\ \tilde{C}_{n2} \end{pmatrix}$$

where $O^T\left(\qquad \right) O$ = Diagonal matrix

then the entries of the Diagonal matrix are the eigenvalues $D = \begin{pmatrix} E_+ & 0 \\ 0 & E_- \end{pmatrix}$

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

and the matrix $O = \begin{pmatrix} \underline{V}_+ & \underline{V}_- \\ \vdots & \vdots \end{pmatrix}$ $\underline{V}_{\pm}$ = normalized eigenvectors

- If we've actually looking at a two state system we have finished and can conclude that

i) The degeneracy is lifted – the states now have energies E_+ and E_- respectively

ii) An abitrary state is written in the original basis as

$$(c_1, c_2)\begin{pmatrix}|1\rangle\\|2\rangle\end{pmatrix} = (\hat{c}_1, \hat{c}_2)\, O^T \begin{pmatrix}|1\rangle\\|2\rangle\end{pmatrix}$$

$$= (\hat{c}_1, \hat{c}_2)\begin{pmatrix}\underline{V}_+ \dots\\ \underline{V}_- \dots\end{pmatrix}\begin{pmatrix}|1\rangle\\|2\rangle\end{pmatrix}.$$

$$= (\hat{c}_1, \hat{c}_2)\begin{pmatrix}|+\rangle\\|-\rangle\end{pmatrix}$$

where $|+\rangle = (\underline{V}_+ \dots)\begin{pmatrix}|1\rangle\\|2\rangle\end{pmatrix}$ new basis state of energy E_+

$|-\rangle = (\underline{V}_-, \dots)\begin{pmatrix}|1\rangle\\|2\rangle\end{pmatrix}$ new basis state of energy E_-

iii) Note that if $h_{21} = 0$ then we get the usual non-deg 1st order energy shift.

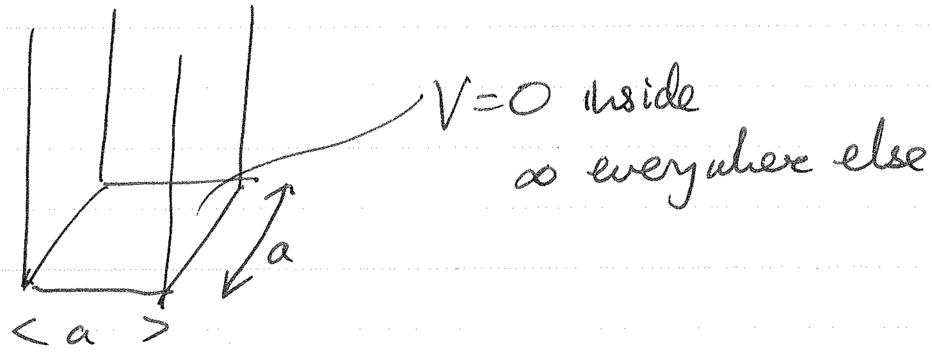
- If we're looking at a more complicated system with many degenerate blocks the procedure is to

i) Deal with each block separately as above; this gives us a new basis in which the degeneracy has been lifted

ii) Then do ordinary perturbation theory in the new basis to get the first order state and the second order energy shift. (We won't ever have to go this far in the present course.)

B. An example

You have probably noticed that none of the one-dimensional QM problems you've studied have a degenerate spectrum; to get an easy example we need to go to 2 dimensions. So let's look at the infinitely deep potential well



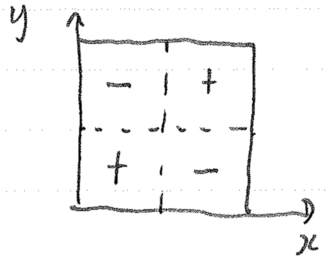
Then the wavefns are

$$\phi_{n,m} = \frac{2}{a} \sin\frac{n\pi x}{a} \sin\frac{m\pi y}{a}$$

with $E_{n,m} = \frac{\hbar^2\pi^2}{2ma^2}(n^2+m^2)$

Now add a perturbation in the well of

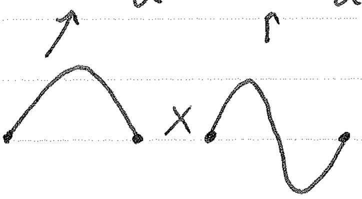
$$h = \lambda \sin\frac{2\pi x}{a} \sin\frac{2\pi y}{a}$$



The groundstate $\phi_{1,1}$ is unique and

$$\Delta E_{1,1} = \int \phi_{1,1}^2\, h \; dx\, dy$$

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



$$= 0$$

and in fact for the same reason

$$\langle n,m \,|\, h \,|\, n,m \rangle = 0 \quad \text{always}$$

The first excited state is degenerate – $\phi_{1,2}$ and $\phi_{2,1}$ have the same energy. Now we need the off-diagonal matrix element

$$\langle 2,1 \,|\, h \,|\, 1,2 \rangle = \int \phi_{1,2}\, \phi_{2,1}\, h \; dx\, dy$$

$$= \left(\frac{2}{a}\right)^2 \lambda \int_0^a dx \, \sin \frac{\pi x}{a} \, \sin^2 \frac{2\pi x}{a} \int_0^a dy \, \sin \frac{\pi y}{a} \, \sin^2 \frac{2\pi y}{a}.$$

$\cancel{x=}\ \pi x/a = \theta$

$$= \left(\frac{2}{a}\right)^2 \lambda \left(\frac{a}{\pi} \int_0^{\pi} d\theta \, \sin\theta \, \sin^2 2\theta \right)^2$$

$$= \left(\frac{2}{a}\right)^2 \lambda \left(\frac{a}{\pi} \cdot \frac{16}{15} \right)^2$$

$$= \frac{2^{10}\, \lambda}{15^2\, \pi^2}$$

So the Hamiltonian matrix for these states is

$$\begin{pmatrix} \frac{\hbar^2\pi^2}{2ma^2}.5 & \frac{2^{10}}{15^2}\frac{\lambda}{\pi^2} \\ \frac{2^{10}\lambda}{15^2\pi^2} & \frac{\hbar^2\pi^2}{2ma^2}.5 \end{pmatrix}$$

We want the eigenvectors and eigenvalues; in this case we can see straightaway without calculation that

$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$ has e-val $E_+ = \frac{5\hbar^2\pi^2}{2ma^2} + \frac{2^{10}\lambda}{15^2\pi^2}$

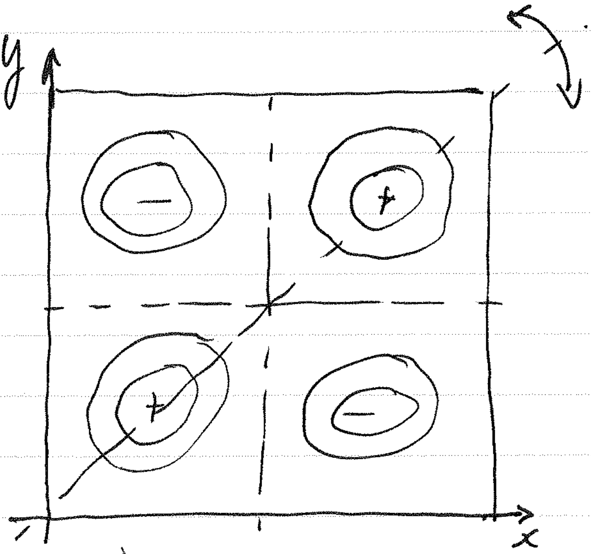
$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$ " " $E_- = \frac{5\hbar^2\pi^2}{2ma^2} - \frac{2^{10}\lambda}{15^2\pi^2}$

So the correct basis for the 1st excited state wavefunctions is

$$\phi_+ = \frac{1}{\sqrt{2}}(1,1)\begin{pmatrix}\phi_{1,2}\\\phi_{2,1}\end{pmatrix} = \frac{1}{\sqrt{2}}(\phi_{1,2}+\phi_{2,1})$$

$$\phi_- = \frac{1}{\sqrt{2}}(1,-1)\begin{pmatrix}\phi_{1,2}\\\phi_{2,1}\end{pmatrix} = \frac{1}{\sqrt{2}}(\phi_{1,2}-\phi_{2,1})$$

It's important to realise that, although the perturbation λ is small, it has a big effect on the wavefunctions. When $\lambda = 0$ ϕ_+ and ϕ_- are degenerate – they are just as good a choice for the first excited state wavefunctions as $\phi_{2,1}$ and $\phi_{1,2}$. Can we understand why ϕ_+ and ϕ_- are better choices when $\lambda \neq 0$?



Potential is symmetric under $x \Leftrightarrow y$

For budding theorists

Let's invent an operator S which swaps $x \Leftrightarrow y$

ie $S\,\phi(x,y) = \phi(y,x)$

Because of the symmetry of the potential

$$[H, S] = 0$$

This means that states can be eigenfunctions of H and S. But $S^2\phi(x,y) = S\phi(y,x) = \phi(x,y)$ so eigenvalues of S^2 are 1, and therefore of S ± 1.

It's easy to see that

$$S\phi_+ = S\frac{1}{\sqrt{2}}\left(\phi_{2,1}(x,y) + \phi_{1,2}(x,y)\right).$$
$$= \frac{1}{\sqrt{2}}\left(\phi_{1,2}(x,y) + \phi_{2,1}(x,y)\right) = \phi_+$$

and

$$S\phi_- = S\frac{1}{\sqrt{2}}\left(\phi_{2,1}(x,y) - \phi_{1,2}(x,y)\right)$$
$$= \frac{1}{\sqrt{2}}\left(\phi_{1,2}(x,y) - \phi_{2,1}(x,y)\right) = -\phi_-$$