Learning Outcomes

You'll be able to:

- Identify nondegenerate and degenerate quantum systems
- Identify conditions for the application of perturbation theory
- Write down
  - 1st order corrections to energy levels and wavefunctions for nondegenerate systems
  - 2nd order corrections to energy levels for nondegenerate systems
- Define "good states" for application in degenerate perturbation theory
- Write down the first order correction to the energy levels in degenerate perturbation theory
- Apply nondegenerate and degenerate perturbation theory to simple one-dimensional quantum mechanical systems

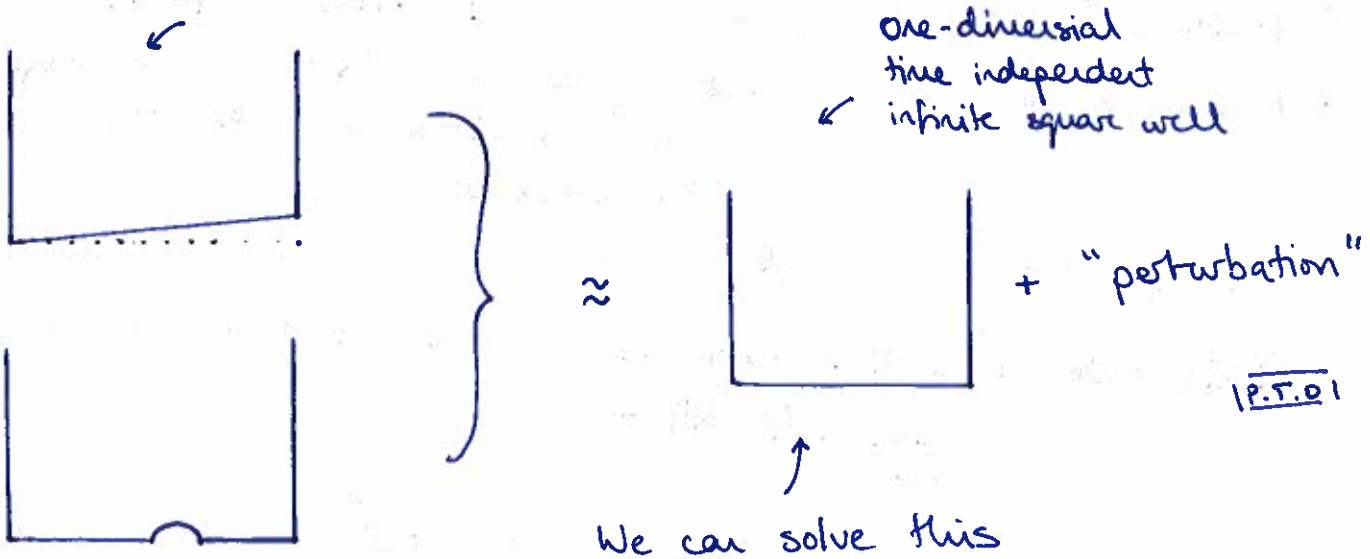
Time-independent Perturbation Theory

Nondegenerate systems

We want to solve the Schrödinger equation for (almost) arbitrary potentials - but, unless we're lucky, this is generally not possible to do exactly. But it is frequently possible to do this approximately, using perturbation theory or variational methods, for example.

We will start with perturbation theory - a systematic procedure for obtaining approximate solutions.

Suppose we have a time-independent potential that is not too dissimilar to one we know how to solve



We can solve this

$H^0 \psi_n^0 = E_n^0 \psi_n^0$ for ψ_n^0 and E_n^0.

superscript "0" indicates unperturbed potential

We start by writing the perturbed Hamiltonian as

$$H = H^0 + \lambda H' \qquad \text{so} \quad H\psi_n = E_n \psi_n$$

H^0: unperturbed; λ: start with $\lambda \ll 1$

small perturbations should only change our state a little

Now we assume we can expand the full solutions in λ

$$\psi_n = \psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots$$
$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots$$

← note, this is a label, not a power

E_n^m is the "m-th order correction" to the n-th eigenvalue

We now plug these solutions into the Schrödinger equation

$$[H^0 + \lambda H'][\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots]$$
$$= [E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \dots][\psi_n^0 + \lambda \psi_n^1 + \lambda^2 \psi_n^2 + \dots]$$

Now let's collect powers of λ

$$H^0\psi_n^0 + \lambda[H'\psi_n^0 + H^0\psi_n^1] + \lambda^2[H^0\psi_n^2 + H'\psi_n^1] + \dots$$
$$= E_n^0\psi_n^0 + \lambda[E_n^1\psi_n^0 + E_n^0\psi_n^1] + \lambda^2[E_n^0\psi_n^2 + E_n^1\psi_n^1 + E_n^2\psi_n^0] + \dots$$

and equate powers of λ:

$O(\lambda^0)$: $H^0\psi_n^0 = E_n^0\psi_n^0$ ← our unperturbed equation!

λ^1: $H^0\psi_n^1 + H'\psi_n^0 = E_n^0\psi_n^1 + E_n^1\psi_n^0$

λ^2: $H^0\psi_n^2 + H'\psi_n^1 = E_n^0\psi_n^2 + E_n^2\psi_n^0 + E_n^1\psi_n^1$

$\vdots$

Now, for ψ_n° to be solutions of our unperturbed equation, they must satisfy $\langle \psi_n^\circ | \psi_m^\circ \rangle = \delta_{nm}$

↑ expresses orthonormality

Let's take inner products of our 1st order equation

$$\langle \psi_n^\circ | H^\circ \psi_n' \rangle + \langle \psi_n^\circ | H' \psi_n^\circ \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n' \rangle + E_n' \langle \psi_n^\circ | \psi_n^\circ \rangle$$

Now

$$\begin{aligned} \langle \psi_n^\circ | H^\circ \psi_n' \rangle &= \langle H^\circ \psi_n^\circ | \psi_n' \rangle \\ &= \langle E_n^\circ \psi_n^\circ | \psi_n' \rangle \\ &= E_n^\circ \langle \psi_n^\circ | \psi_n' \rangle \end{aligned}$$

$$\Rightarrow E_n^\circ \langle \psi_n^\circ | \psi_n' \rangle \quad \langle \psi_n^\circ | H' \psi_n^\circ \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n' \rangle + E_n' \underbrace{\langle \psi_n^\circ | \psi_n^\circ \rangle}_{= \delta_{nn} = 1}$$

↑ these two cancel →

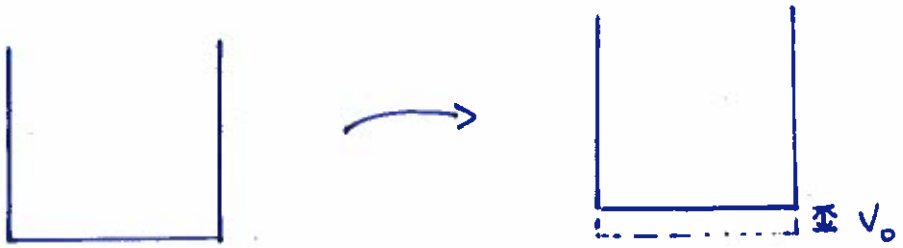
So we have

$$\boxed{E_n' = \langle \psi_n^\circ | H' | \psi_n^\circ \rangle}$$

This is a hugely important equation - the first order correction to the energy is given by the expectation value of the perturbation, in the unperturbed state.

Example 7.1

Suppose we start with an infinite square well and raise the bottom of the potential well by an amount V_0.

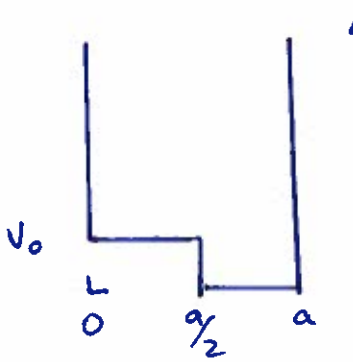


The first order correction to the energy levels is given by

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$
$$= \langle \psi_n^0 | V_0 | \psi_n^0 \rangle$$
$$= V_0 \quad \Rightarrow \text{ each energy level is lifted by } V_0$$

This is an example of a general phenomenon - all higher order corrections vanish for a constant perturbation.

What about the case where only half the floor is raised?



Now we need our square well solutions

$$\psi_n^0 = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right),$$

which we plug into our expectation value

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$
$$= \int_0^{a/2} dx \left[\sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)\right]^2 V_0$$
$$= \frac{V_0}{2}$$

$$\int_0^{a/2} dx \, \sin^2\left(\frac{n\pi}{a}x\right) = \frac{a}{4}\left(1 - \frac{\sin n\pi}{n\pi}\right)$$

$= 0$ if n integer

Having found the correction to the energies, we now want the first-order correction to the wavefunctions.

We first reorganise our first-order equation

$$(H^\circ - E_n^\circ)\,\psi_n^1 = -(H' - E_n^1)\,\psi_n^\circ$$

known — what we want — known — known — just calculated! — known

this side is known

We want to express things in terms of our known unperturbed wavefunctions and energies, so let's write

$$\psi_n^1 = \sum_{m \neq n} c_m^{(n)} \psi_m^\circ$$

↑ complete basis set of wavefunctions

← note we choose $c_{m=n}^{(n)} = 0$ to ensure $\langle \psi_n^\circ | \psi_n^1 \rangle = 0$ and then $\langle \psi_n | \psi_n \rangle = \langle \psi_n^\circ | \psi_n^\circ \rangle + \lambda(\langle \psi_n^\circ | \psi_n^1 \rangle + \langle \psi_n^1 | \psi_n^\circ \rangle)$, $= 1$

and then our job is to find the $c_m^{(n)}$. Let's plug this solution into our equation

$$(H^\circ - E_n^\circ) \sum_{m \neq n} c_m^{(n)} \psi_m^\circ = -(H' - E_n^1)\,\psi_n^\circ$$

↓ $H^\circ \psi_m^\circ = E_m^\circ \psi_m^\circ$

$$\sum_{m \neq n} (E_m^\circ - E_n^\circ)\, c_m^{(n)} \psi_m^\circ = -(H' - E_n^1)\,\psi_n^\circ$$

recall $\langle f | g \rangle \equiv \int f^*(x) g(x)\,dx$ ↓

Now we take the inner product

$$\sum_{m \neq n} (E_m^\circ - E_n^\circ)\, c_m^{(n)} \langle \psi_\ell^\circ | \psi_m^\circ \rangle = -\langle \psi_\ell^\circ | H' | \psi_n^\circ \rangle + E_n^1 \langle \psi_\ell^\circ | \psi_n^\circ \rangle$$

If $\ell = n$ then the left hand side is zero and we find

$$E_n^1 = \langle \psi_n^\circ | H' | \psi_n^\circ \rangle$$

↑ we've seen this before!

Q. Why $\sum_{m \neq n}$ and not $\sum_{m}$ in $\psi_n' = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n \rangle}{E_n^0 - E_m^0} \psi_m^0$?

or, equivalently, $\psi_n' = \sum_{m \neq n} c_m^{(n)} \psi_m^0$

First answer:

If we allow our sum over m to include n, then the denominator $(E_n^0 - E_m^0)$ would vanish for the $m = n$ case. Since the numerator is almost certainly nonzero, this term would diverge and we'd be in trouble.

Second answer:

OK - so we can see that we don't <u>want</u> $m = n$, but this doesn't really justify excluding this term (it just says it's desirable to do so). How do we justify excluding $m = n$? In other words, why can we write

$$\psi_n' = \sum_{m \neq n} c_m^{(n)} \psi_m^0 \quad ?$$

↖ Equation 7.11 of Griffiths and Schroeter. (G+S)

Again there are two answers to this.

a) The more intuitive answer to me is explained in a footnote on page 282 of G+S.

We assumed that we can write

$$\psi_n = \psi_n^0 + \lambda \psi_n' + \lambda \psi_n^2 + \dots$$

This means that the norm of this state is

$$\langle \psi_n | \psi_n \rangle = \langle \psi_n^0 | \psi_n^0 \rangle + \lambda \left(\langle \psi_n^0 | \psi_n' \rangle + \langle \psi_n' | \psi_n^0 \rangle \right) + \dots$$

We know that

$$\langle \psi_n^0 | \psi_n^0 \rangle = 1$$

since these are the unperturbed states, which we know how to obtain.

To ensure that we also have (to 1st order in λ)

$$\langle \psi_n | \psi_n \rangle = 1,$$

we therefore want

$$\lambda\left(\langle \psi_n^0 | \psi_n' \rangle + \langle \psi_n' | \psi_n^0 \rangle\right) = 0$$

If we plug in $\psi_n' = \sum_m c_m^{(n)} \psi_m^0$ we see

$$\begin{aligned}\langle \psi_n^0 | \psi_n' \rangle &= \sum_m c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle \\ &= c_n^{(n)} \underbrace{\langle \psi_n^0 | \psi_n^0 \rangle}_{=1} + \sum_{m \neq n} c_m^{(n)} \langle \psi_n^0 | \psi_m^0 \rangle \\ &= c_n^{(n)} + \sum_{m \neq n} c_m^{(n)} \underbrace{\langle \psi_n^0 | \psi_m^0 \rangle}_{=0} = c_n^{(n)}\end{aligned}$$

This tells us we should choose $c_n^{(n)} = 0$.

$$\Rightarrow \psi_n' = \sum_{m \neq n} c_m^{(n)} \psi_m^0$$

to ensure $\langle \psi_n | \psi_n \rangle = 1$ to 1st order in λ.

b) We have now shown that it is natural to choose $\sum_{m \neq n}$ (or, equivalently, set $c_n^{(n)} = 0$), and we can confirm that this is justified as follows.

We know ψ_n^1 satisfies ← equation 7.11 of G+S.

$$(H^0 - E_n^0)\psi_n^1 = -(H' - E_n^1)\psi_n^0, \qquad (*)$$

but so too does $X_n^1 = \psi_n^1 + \alpha\psi_n^0$ (where α is a constant)

Let's show this:

$$(H^0 - E_n^0)X_n^1 = (H^0 - E_n^0)(\psi_n^1 + \alpha\psi_n^0)$$

$$= (H^0 - E_n^0)\psi_n^1 + \alpha(H^0 - E_n^0)\psi_n^0$$

But $(H^0 - E_n^0)\psi_n^0 = 0$, because this is the <u>unperturbed</u> time-independent Hamiltonian equation. So we have

$$(H^0 - E_n^0)X_n^1 = (H^0 - E_n^0)\psi_n^1$$

$$= -(H' - E_n^1)\psi_n^0 \qquad \leftarrow \text{by } (*)$$

<u>Therefore</u> we can add a constant times ψ_n^0 to our solution ψ_n^1 and it is still a solution of $(*)$. In particular we can add $-c_n^{(n)}\psi_n^0$ to our solution!

To sum up, if we choose

$$\psi_n^1 = \sum_m c_m^{(n)}\psi_m^0$$

as our solution, then

$$\psi_n^1 - c_n^{(n)}\psi_n^0$$

is <u>also</u> a solution. But this equals

$$\psi_n^1 - c_n^{(n)}\psi_n^0 = \sum_m c_m^{(n)}\psi_m^0 - c_n^{(n)}\psi_n^0 = \underbrace{\sum_{m\neq n} c_m^{(n)}\psi_m^0}_{**}$$

So $**$ <u>is</u> a solution of the first order equation $(*)$ and we are justified in dropping $m=n$ from our sum

But if $\ell \neq n$ then

$$\sum_{m \neq n} (E_m^0 - E_n^0) c_m^{(n)} \delta_{\ell m} = - \langle \psi_\ell^0 | H' | \psi_n^0 \rangle + E_n' \cdot 0$$

$$\Rightarrow \quad (E_\ell^0 - E_n^0) c_\ell^{(n)} = - \langle \psi_\ell^0 | H' | \psi_n^0 \rangle$$

So

$$c_\ell^{(n)} = \frac{\langle \psi_\ell^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_\ell^0}$$

Then, relabelling $\ell \to m$ in our sum, we have

$$\boxed{\psi_n' = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{E_n^0 - E_m^0} \psi_m^0}$$

↗ convenient to write $H'_{mn} = \langle \psi_m^0 | H' | \psi_n^0 \rangle$ or $V_{mn} = \langle \psi_m | V | \psi_n \rangle$ more generally

↑ This denominator is why we started by studying nondegenerate perturbation theory - if $E_{n_1}^0 = E_{n_2}^0$ (degenerate energy levels in the unperturbed system) then $E_n^0 - E_m^0$ can be zero, even if $m \neq n_1$ (say).

We've now exhausted the first order corrections in nondegenerate, time-independent perturbation theory. What happens at higher orders?

↑ Really we will only consider the energies at second order (not even the wavefunctions). For more information on references for higher orders, see Griffiths p. 285.

Let's go back to our equation obtained by comparing terms of λ^2 - this was

$$H^\circ \psi_n^2 + H' \psi_n^1 = E_n^\circ \psi_n^2 + E_n^2 \psi_n^\circ + E_n^1 \psi_n^1$$

We can take the inner product again

$$\langle \psi_n^\circ | H^\circ \psi_n^2 \rangle + \langle \psi_n^\circ | H' \psi_n^1 \rangle = E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle + E_n^2 \langle \psi_n^\circ | \psi_n^\circ \rangle + E_n^1 \langle \psi_n^\circ | \psi_n^1 \rangle$$

Using the Hermiticity property of H° again, we have

$$\begin{aligned} \langle \psi_n^\circ | H^\circ \psi_n^2 \rangle &= \langle H^\circ \psi_n^\circ | \psi_n^2 \rangle \\ &= \langle E_n^\circ \psi_n^\circ | \psi_n^2 \rangle \\ &= E_n^\circ \langle \psi_n^\circ | \psi_n^2 \rangle \end{aligned}$$

and, once again, we see that this term will cancel from both sides - so

$$\langle \psi_n^\circ | H' \psi_n^1 \rangle = E_n^2 \underbrace{\langle \psi_n^\circ | \psi_n^\circ \rangle}_{=1} + E_n^1 \underbrace{\langle \psi_n^\circ | \psi_n^1 \rangle}_{=0}$$

$= 0$ since $\langle \psi_n^\circ | \psi_n^1 \rangle = \sum_{m \neq n} c_m^{(n)} \langle \psi_n^\circ | \psi_m^\circ \rangle$

In other words

$$\begin{aligned} E_n^2 &= \langle \psi_n^\circ | H' | \psi_n^1 \rangle \\ &= \sum_{m \neq n} c_m^{(n)} \langle \psi_n^\circ | H' | \psi_m^\circ \rangle \\ &= \sum_{m \neq n} \frac{\langle \psi_m^\circ | H' | \psi_n^\circ \rangle}{E_n^\circ - E_m^\circ} \langle \psi_n^\circ | H' | \psi_m^\circ \rangle \end{aligned}$$

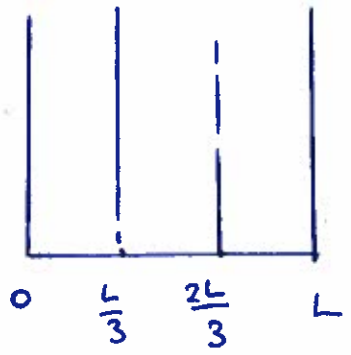
← we just derived this expression for $c_m^{(n)}$

This is usually written as

$$\boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^\circ | H' | \psi_n^\circ \rangle|^2}{E_n - E_m}}$$

Example

Infinite square well with two delta function spikes



In this case the Hamiltonian is

$$H = \begin{cases} \infty & x \le 0,\ x \ge L \\ \delta\left(x - \frac{L}{3}\right) + \delta\left(x - \frac{2L}{3}\right) & 0 < x < L \end{cases}$$

First order correction to the energies is

$$E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle$$

$$= \int_0^L \left[\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)\right]^2 \left[\delta\left(x - \frac{L}{3}\right) + \delta\left(x - \frac{2L}{3}\right)\right] dx$$

$$= \frac{2}{L}\left[\sin^2\left(\frac{n\pi}{3}\right) + \sin^2\left(\frac{2n\pi}{3}\right)\right]$$

This is zero for $n = 3m$ with m an integer, because ↑ that is, for $n = 0, \pm 3, \pm 6, \ldots$ the corresponding wavefunctions have nodes at $\frac{L}{3}$ and $\frac{2L}{3}$, so they don't "feel" the perturbation.

What about the second order correction?

$$E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n - E_m}$$

$$= \sum_{m \neq n} \frac{\left| \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi x}{L}\right) \left[\delta\left(x - \frac{L}{3}\right) + \delta\left(x - \frac{2L}{3}\right)\right] \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \right|^2}{\frac{n^2\pi^2\hbar^2}{2\mu L^2} - \frac{m^2\pi^2\hbar^2}{2\mu L^2}}$$

So

$$E_n^2 = \frac{2\mu}{L} \Big/ \frac{\pi^2\hbar^2}{2L^2} \sum_{m\neq n} \frac{\left[\sin\left(\frac{m\pi}{3}\right)\sin\left(\frac{n\pi}{3}\right) + \sin\left(\frac{2m\pi}{3}\right)\sin\left(\frac{2n\pi}{3}\right)\right]^2}{n^2-m^2}$$

$$= \frac{4L\mu}{\pi^2\hbar^2} \sum_{m\neq n} \frac{1}{n^2-m^2}\left[\sin\left(\frac{m\pi}{3}\right)\sin\left(\frac{n\pi}{3}\right) + \sin\left(\frac{2m\pi}{3}\right)\sin\left(\frac{2n\pi}{3}\right)\right]^2$$

Lets consider the ground state, $n=1$ ← $\sin\frac{\pi}{3} = \sin\frac{2\pi}{3} = \frac{\sqrt{3}}{2}$

$$\Rightarrow E_1^2 = \frac{4L\mu}{\pi^2\hbar^2} \sum_{m\neq 1} \frac{1}{1-m^2} \cdot \left(\frac{\sqrt{3}}{2}\right)^2 \left[\sin\left(\frac{m\pi}{3}\right) + \sin\left(\frac{2m\pi}{3}\right)\right]^2$$

$$= \frac{3L\mu}{\pi^2\hbar^2} \sum_{m\neq 1} \frac{1}{1-m^2}\left[\sin\left(\frac{m\pi}{3}\right) + \sin\left(\frac{2m\pi}{3}\right)\right]^2$$

Note: $m = 2, 3, \ldots$ corrections all vanish.

Q: What is first nonzero correction? PTO

Degenerate systems

So far we have always assumed that the unperturbed system has <u>nondegenerate</u> energy levels, so no two states have the same energy. This is to ensure that, provided $m\neq n$, $E_n - E_m \neq 0$ in our expression for the perturbed wavefunction (or second order correction to the energy). What do we do if our system is degenerate?

↑ Practically every realistic quantum system <u>is</u> degenerate.

Two (unperturbed) states are degenerate if they satisfy

$$H^\circ \psi_a^\circ = E^\circ \psi_a^\circ$$
$$H^\circ \psi_b^\circ = E^\circ \psi_b^\circ$$

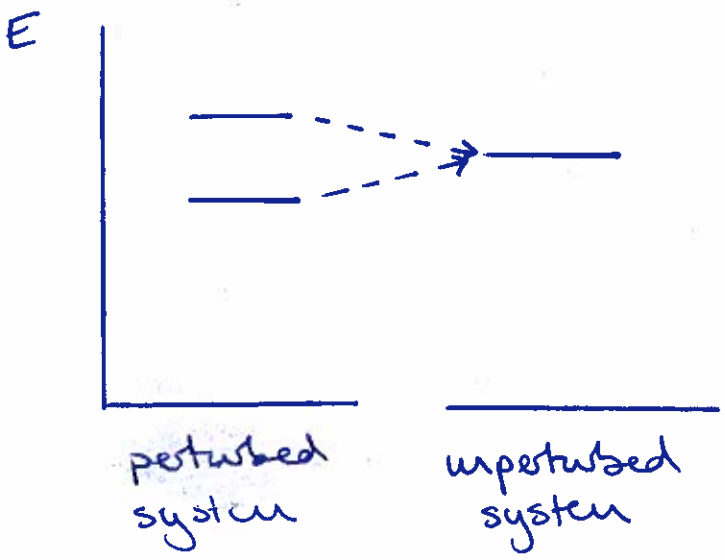
} with $\langle \psi_a^\circ | \psi_a^\circ \rangle = \langle \psi_b^\circ | \psi_b^\circ \rangle = 1$

$\langle \psi_a^\circ | \psi_b^\circ \rangle = 0$

Any linear combination of these states is also an eigenstate of the unperturbed Hamiltonian

$$H^\circ (\alpha \psi_a^\circ + \beta \psi_b^\circ) = E^\circ (\alpha \psi_a^\circ + \beta \psi_b^\circ)$$

In the perturbed system, these degenerate energy levels will generally split apart ("lift the degeneracy")



As we "turn off" the perturbation, the split energy levels reduce to the degenerate energy level. And the perturbed states will reduce to two orthogonal combinations of the degenerate states.

say $(\alpha \psi_a^\circ + \beta \psi_b^\circ)$ and $(\gamma \psi_a^\circ + \delta \psi_b^\circ)$

We refer to these states as the "<u>good states</u>" - they are so-called because, if we can find them, they lead us to the correct perturbed states (and, it turns out, the correct first order energies in our usual formula).

The good states are defined as the limit of the true eigenstates as we remove the perturbation - but this is not a practical way to actually calculate them.

To do that, let's return to our system:

Recall: $H^\circ \varphi_a^\circ = E^\circ \varphi_a^\circ$, $H^\circ \varphi_b^\circ = E^\circ \varphi_b^\circ$, $\langle \varphi_a^\circ | \varphi_b^\circ \rangle = 0$

$$H\varphi_n = E_n \varphi_n$$

and define $\varphi^\circ \equiv \chi_1^\circ = \alpha_1 \varphi_a^\circ + \beta_1 \varphi_b^\circ$ to be one of the good states (the other can be $\chi_2^\circ = \alpha_2 \varphi_a^\circ + \beta_2 \varphi_b^\circ$)

When we expanded this at first order in λ, we obtained

$$H^\circ \varphi_n' + H' \chi_1^\circ = E_n^\circ \varphi_n' + E_n' \chi_1^\circ$$

($\chi_1^\circ = \varphi_1^\circ$!)

(last time it was with φ_n°)

Now we take the inner product with φ_a°

$$\langle \varphi_a^\circ | H^\circ \varphi_n' \rangle + \langle \varphi_a^\circ | H' \chi_1^\circ \rangle = E_n^\circ \langle \varphi_a^\circ | \varphi_n' \rangle + E_n' \langle \varphi_a^\circ | \chi_1^\circ \rangle$$

$\uparrow = \langle H^\circ \varphi_a^\circ | \varphi_n' \rangle = E_n^\circ \langle \varphi_a^\circ | \varphi_n' \rangle$ (these two cancel)

$$\langle \varphi_a^\circ | \chi_1^\circ \rangle = \langle \varphi_a^\circ | \alpha \varphi_a^\circ \rangle + \langle \varphi_a^\circ | \beta \varphi_b^\circ \rangle$$
$$= \alpha \underbrace{\langle \varphi_a^\circ | \varphi_a^\circ \rangle}_{=1} + \beta \underbrace{\langle \varphi_a^\circ | \varphi_b^\circ \rangle}_{=0}$$
$$= \alpha$$

$$\Rightarrow \langle \varphi_a^\circ | H' \chi_1^\circ \rangle = \alpha E_n'$$

or

$$\alpha \langle \varphi_a^\circ | H' | \varphi_a^\circ \rangle + \beta \langle \varphi_a^\circ | H' | \varphi_b^\circ \rangle = \alpha E_n'$$

If we repeat the trick, but with φ_b° instead, we find

$$\alpha \langle \varphi_b^\circ | H' | \varphi_a^\circ \rangle + \beta \langle \varphi_b^\circ | H' | \varphi_b^\circ \rangle = \beta E_n'$$

The first thing we notice about these equations is that we can simplify them, if we can find states that diagonalise the perturbing Hamiltonian, then our life is much easier!

↑ i.e. $\langle \psi_a^\circ | H' | \psi_b^\circ \rangle = \langle \psi_b^\circ | H' | \psi_a^\circ \rangle = 0$

In this case our equations reduce to

$$E_+^1 = \langle \psi_a^\circ | H' | \psi_a^\circ \rangle$$
$$E_-^1 = \langle \psi_b^\circ | H' | \psi_b^\circ \rangle$$

} these are exactly our expressions from nondegenerate perturbation theory!

But we (hopefully) know how to diagonalise our system - this is just diagonalising a 2x2 matrix (i.e. finding the eigenvalues and eigenvectors).

We'll tidy things up by defining

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \equiv \begin{pmatrix} \langle \psi_a^\circ | H' | \psi_a^\circ \rangle & \langle \psi_a^\circ | H' | \psi_b^\circ \rangle \\ \langle \psi_b^\circ | H' | \psi_a^\circ \rangle & \langle \psi_b^\circ | H' | \psi_b^\circ \rangle \end{pmatrix}$$

Then our two equations can be written as

$$\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_n^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

To find the eigenvalues we need to solve

$$\begin{vmatrix} W_{aa} - E_n^1 & W_{ab} \\ W_{ba} & W_{bb} - E_n^1 \end{vmatrix} = (W_{aa} - E_n^1)(W_{bb} - E_n^1) - |W_{ab}|^2 = 0$$

↑ $W_{ba} = W_{ab}^*$

or $(E_n^1)^2 - (W_{aa} + W_{bb}) E_n^1 + W_{aa} W_{bb} - |W_{ab}|^2 = 0$

The solutions are

$$E_{\pm}^{1} = \frac{1}{2}\left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4|W_{ab}|^2}\right]$$

N.B. $W_{ij} = \langle \psi_i^0 | H' | \psi_j^0 \rangle$

This is the central result of degenerate perturbation theory — the two energies E_+ and E_- are the split energy levels at first order in λ.

Earlier we pointed out that we can use nondegenerate perturbation theory, if we can find the good states straight off the bat. (or we can solve the matrix equation for α, β.)

It turns out there is a way to do this.

Proof is on page 292 of Griffiths and Schroeter

- Find a Hermitian operator A that commutes with both H^0 and H'.
- If ψ_a^0 and ψ_b^0 are degenerate eigenfunctions of H^0, but nondegenerate eigenfunctions of A, then they are the "good states" to use in perturbation theory.

$H^0 \psi_{a,b}^0 = E_n^0 \psi_{a,b}^0$ but $A\psi_a^0 = \mu\psi_a^0$, $A\psi_b^0 = \nu\psi_b^0$ $\}$ $\mu \neq \nu$

where $[H^0, A] = [H', A] = 0$

Finding such an operator often relies on symmetry arguments, or some physics intuition. We will explore this more later on.