Perturbation theory

Standard approach to QM problems so far (time - independent case)

1. Write hamiltonian $\hat{H}$
2. Solve ~~Solve~~ Schrodinger equation $\hat{H}\psi = E\psi$
3. Use boundary conditions to determine energy eigen values E_n and eigenfunction $\{\psi_n\}$
4. done

Since $\{\psi_n\}$ form a complete orthonormal set

$$\langle \psi_n | \psi_m \rangle = \delta_{nm} \quad \text{for any } n, m$$

any wavefunction $|\psi\rangle$ can be represented as a combination of these eigenfunctions:

$$|\psi\rangle = \sum_{n=1}^{\infty} c_n \psi_n$$

What if we have a different hamiltonian? So far we had to repeat the same steps from the beginning, and get a new set of eigenvalues and eigenfunctions. However, technically, each of ~~no~~ the eigenfunctions of a new hamiltonian could be written as a superposition of the wave functions of the old hamiltonian.

So what if a new hamiltonian is quite similar to the old one? Well, then we'd expect that the eigenenergies and eigenfunctions would be similar to those of the original hamiltonian, with some small correction.

$$\hat{H}^{(0)} \longrightarrow E_n^{(0)}, \psi_n^{(0)}$$

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

λ — obviously small parameter $\lambda \ll 1$

This will remind us that the added hamiltonian component is small compare ~~to~~ to the main one. In this case we expect that ~~when~~ if we solve $\hat{H}\psi = E\psi$ and obtain the new set of E_n, $\{\psi_n\}$, then

$$E_n = E_n^{(0)} + \langle \text{small correction} \rangle \; \Delta E_n^{(\sim\lambda)}$$

$$\psi_n = \psi_n^{(0)} + \langle \text{small correction} \rangle \; \cancel{\text{combinat}} \; \underset{(\sim\lambda)}{\Delta\psi_n}$$

$$\hat{H}\psi_n = E_n\psi_n \Rightarrow (\hat{H}^{(0)} + \lambda\hat{H}')(\psi_n^{(0)} + \Delta\psi_n) = (E_n^{(0)} + \Delta E_n)(\psi_n^{(0)} + \Delta\psi_n)$$

$$\cancel{\hat{H}^{(0)}\psi_n^{(0)}} + \underbrace{\hat{H}^{(0)}\Delta\psi_n}_{\text{first-order}} + \underbrace{\lambda\hat{H}'\psi_n^{(0)}}_{\text{first order}} + \underbrace{\lambda\hat{H}'\Delta\psi_n}_{2^{nd}\text{ order}} = \cancel{E_n^{(0)}\psi_n^{(0)}} + E_n^{(0)}\Delta\psi_n + \Delta E_n\psi_n^{(0)} + \Delta E_n\Delta\psi_n$$

One can see that we can now search for corrections as a power series of our small parameter

$$\psi_n = \psi_n^{(0)} + \underbrace{\lambda\psi_n^{(1)} + \lambda^2\psi_n^{(2)} + \ldots}_{\Delta\psi_n}$$

note for the future: $\Delta\psi_n$ can be decomposed into $\{\psi_i^{(0)}\}$, but this decomposition will not include $i = n$

$$E_n = E_n^{(0)} + \underbrace{\lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots}_{\Delta E_n}$$

first order correction

second-order correction

You use as many orders as you need to achieve desired accuracy. Often, the first order is good enough.

$\hat{H}\psi_n = E_n \psi$ $\qquad \hat{H} = \hat{H}^{(0)} + \lambda \hat{H}'$

$$\hat{E}_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots$$

"0th" order (no λ) $\qquad \hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$ ✓

"1st" order : $\sim\lambda$ $\qquad \hat{H}'\psi_n^{(0)} + \hat{H}_0^{(0)}\psi_n^{(1)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$

2nd order : $\sim\lambda^2$ $\qquad \hat{H}_0^{(0)}\psi_n^{(2)} + \hat{H}'\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}$

~~Lets~~ Before we go on why bother?
There are only ~~a~~ few simple problems that allow analytical solution (square well, SHO, 1/r potential, to name a few). So we ~~ar~~ are going to use these known sets of eigenfunctions to approximate as many more complicated situations, ~~as~~ whenever possible.

The first-order energy correction

$$\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}'\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)}$$

Take inner product $\langle\psi_n^{(0)}| \dots$

$$\underbrace{\langle\psi_n^{(0)}|\hat{H}^{(0)}\psi_n^{(1)}\rangle}_{\langle\hat{H}^{(0)}\psi_n^{(0)}|\psi_n^{(1)}\rangle = \cancel{E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle}} + \langle\psi_n^{(0)}|\hat{H}'\psi_n^{(0)}\rangle = \cancel{E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle} + E_n^{(1)}\underbrace{\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle}_{=1}$$

$$E_n^{(1)} = \langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle$$

expectation value of the perturbation over the original states

First-order wave-function correction

$$\psi_n^{(1)} = \sum_{k\neq n} c_{kn}^{(1)} \psi_k^{(0)}$$

(it does not make sense to include $\psi_n^{(0)}$ into the mix, since it is already in the zeroth approximation)

Back to the first-order equation

$$\hat{H}^{(0)} \underline{\psi_n^{(1)}} + \hat{H}' \psi_n^{(0)} = E_n^{(0)} \underline{\psi_n^{(1)}} + E_n^{(1)} \psi_n^{(0)}$$

$$(\hat{H}^{(0)} - E_n^{(0)}) \psi_n^{(1)} = -(\hat{H}' - E_n^{(1)}) \psi_n^{(0)}$$

$$\langle \psi_m^{(0)} | (\hat{H}_0^{(0)} - E_n^{(0)}) \psi_n^{(1)} \rangle = -\langle \psi_m^{(0)} | \hat{H}' - E_n^{(1)} | \psi_n^{(0)} \rangle$$

$$* \ \langle \psi_m^{(0)} | \hat{H}^{(0)} \psi_n^{(1)} \rangle = \langle \hat{H}^{(0)} \psi_m^{(0)} | \psi_n^{(1)} \rangle = E_m^{(0)} \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle$$

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

$$(E_m^{(0)} - E_n^{(0)}) \langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

$$\langle \psi_m^{(0)} | \psi_n^{(1)} \rangle = \langle \psi_m^{(0)} | \sum_{k\neq n} c_{kn}^{(1)} \psi_k^{(0)} \rangle =$$

$$= \sum_{k\neq n} c_{kn}^{(1)} \underbrace{\langle \psi_m^{(0)} | \psi_k^{(0)} \rangle}_{\delta_{mk}} = c_{mn}^{(1)}$$

$$(E_m^{(0)} - E_n^{(0)}) c_{mn}^{(1)} = -\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle$$

$$c_{mn}^{(1)} = -\frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_m^{(0)} - E_n^{(0)}} = \frac{\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}$$

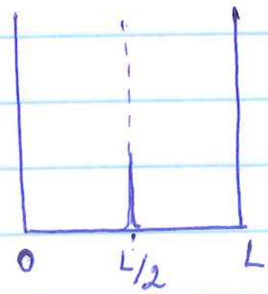
Convenient notation: $\langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \equiv H'_{mn}$ or V_{mn}

$\langle \psi_n^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle \equiv H'_{nn}$ or V_{nn}

Then $E_n^{(1)} = H'_{nn}$

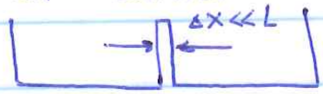
$$c_{mn}^{(1)} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}}$$ more compact

Example



$$\hat{H} = \begin{cases} \infty & x<0,\ x>L \\ \alpha\,\delta(x-\frac{L}{2}) & 0<x<L \end{cases}$$

(this is a simplified version of a small barrier with width $\ll L$)



$$\psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\frac{\pi n x}{L} \qquad E_n^{(0)} = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$$

Physically, that means that a particle gets a shake-up at $x = L/2$

However, for even n a particle never exist ~~is~~ at $x = L/2$! So we would expect these states are not affected by the perturbation

For n-odd state such ~~ch st~~ violent shake can move particle b/w different states; for example, if it is in the ground state, it can be propelled in some higher-order (n-odd) state.

Relevant expectation values

$$H'_{nn} = \langle \psi_n^{(0)} | H' | \psi_n^{(0)} \rangle = \frac{2}{L}\int_0^L \sin^2\frac{\pi n x}{L} \cdot \alpha\, \delta(x-\frac{L}{2})\,dx =$$

$$= \frac{2\alpha}{L}\sin^2\frac{\pi n}{2} = \begin{cases} 2\alpha/L & n = 1, 3 \ldots \\ 0 & n = 2, 4 \ldots \end{cases}$$

As we predicted, only n-odd states are shifted by the δ-perturbation

$$H'_{mn} = \langle \psi_m^{(0)} | \hat{H}' | \psi_n^{(0)} \rangle = \frac{2}{L} \int_0^L \sin\frac{\pi n x}{L} \sin\frac{\pi m x}{L} \cdot \alpha\, \delta(x - \tfrac{L}{2})\, dx =$$

$$= \frac{2\alpha}{L} \sin\frac{\pi n}{2} \sin\frac{\pi m}{2}$$

only if both n and m are odd, $H'_{mn} \neq 0$

Thus

$$c_{mn}^{(1)} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} = \frac{\frac{2\alpha}{L} \overbrace{\sin\frac{\pi n}{2} \sin\frac{\pi m}{2}}^{\pm 1}}{\frac{\pi^2 \hbar^2}{2mL^2}(n^2 - m^2)} = \frac{4\alpha m L}{\pi^2 \hbar^2} \frac{\sin^2\frac{\pi n}{2} \sin^2\frac{\pi m}{2}}{n^2 - m^2}$$

for n, m - odd

otherwise - zero

$$P_{mn}^{(1)} = |c_{mn}^{(1)}|^2 = \frac{16\alpha^2 m^2 L^2}{\pi^2 \hbar^2} \frac{1}{(n^2 - m^2)^2}$$

probability to find a particle in the state $\psi_m^{(0)}$

To ensure the validity of our approach (i.e. that the perturbation is small), we must have $P_{mn}^{(1)} \ll 1$ $\quad \frac{\alpha^2 m^2 L^2}{\pi^2 \hbar^2} \ll 1 \quad \alpha \ll \frac{\pi \hbar}{mL}$

Second - order correction to the energy

$$\hat{H}^{(0)}\psi_n^{(2)} + \hat{H}'\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + \underline{E_n^{(2)}}\psi_n^{(0)}$$

We use the same trick as before

$$\cancel{\langle\psi_n^{(0)}|\hat{H}^{(0)}\psi_n^{(2)}\rangle} + \langle\psi_n^{(0)}|\hat{H}'\psi_n^{(1)}\rangle = \cancel{E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle} + \cancel{E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle}^{=0} + $$
$$+ E_n^{(2)}\underbrace{\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle}_{=1}$$

$$E_n^{(2)} = \langle\psi_n^{(0)}|\hat{H}'\psi_n^{(1)}\rangle = \langle\psi_n^{(0)}|\hat{H}'\sum_{m\neq n} c_{mn}^{(1)}\psi_m^{(0)}\rangle =$$
$$= \sum_{m\neq n} c_{mn}^{(1)}\langle\psi_n^{(0)}|\hat{H}'|\psi_m^{(0)}\rangle$$

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

Because typically $E_n^{(1)} \gg E_n^{(2)}$, often only the first-order correction is considered. However, sometimes $\langle\psi_n^{(0)}|\hat{H}'|\psi_n^{(0)}\rangle = 0$, making the second-order correction the first non-vanishing term. Then we obviously need it!

Fun fact: the second-order correction to the ground state is always <u>negative</u> since $E_{(ground)}^{(0)} < E_m^{(0)}$ for any m, and the numerator is always positive.

Should we be worried about normalization? not until we calculate $\psi_n^{(2)}$!

Indeed

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)}$$ – technically, it is not normalized

However

$$\langle \psi_n | \psi_n \rangle = \langle \psi_n^{(0)} + \lambda \psi_n^{(1)} + \ldots | \psi_n^{(0)} + \lambda \psi_n^{(1)} + \ldots \rangle = \langle \psi_n^{(0)} | \psi_n^{(0)} \rangle +$$
$$+ \lambda \underbrace{\langle \psi_n^{(0)} | \psi_n^{(1)} \rangle}_{=0} + \lambda \underbrace{\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle}_{=0} + \lambda^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \ldots =$$

$$= 1 + \lambda^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle + \{\text{higher-order corrections}\}$$

· The normalization factor $\mathcal{N} = \dfrac{1}{\sqrt{1+\lambda^2 \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle}} \approx 1 - \dfrac{\lambda^2}{2} \langle \psi_n^{(1)} | \psi_n^{(1)} \rangle$

Thus, if we do the exact normalization, it will only contributes to the <u>second order</u> correction of the wave function (and higher orders), which we are not going to use any way.