Lec 4: Time independent perturbation theory

A systematic way of doing approximations in Q.M.
Begin with time independent theory.

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$$

- $\hat{H}_0$ has exact, known solutions
- $\hat{H}_1$ time independent.
- λ small bookkeeping parameter

For example, relativistic KE correction to Hydrogen

$$\lambda \hat{H}_1 = -\frac{1}{8}\frac{\hat{p}^4}{m^3 c^2}$$

no obvious λ but correction is proportional to α^4.

Expand wave function and energies as

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \lambda^2|\psi_n^2\rangle + \cdots$$

$$E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots$$

$$\hat{H}|\psi_n\rangle = (\hat{H}_0 + \lambda \hat{H}_1)\left[|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \cdots\right]$$

$$= (E_n^0 + \lambda E_n^1 + \cdots)\left[|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \cdots\right]$$

Compare order by order in λ

$\mathcal{O}(\lambda^0)$ $\quad (\hat{H}_0 - E_n^0)|\psi_n^0\rangle = 0$

$\mathcal{O}(\lambda^1)$ $\quad (\hat{H}_0 - E_n^0)|\psi_n^1\rangle = (E_n^1 - \hat{H}_1)|\psi_n^0\rangle$

$\mathcal{O}(\lambda^2)$ $\quad (\hat{H}_0 - E_n^0)|\psi_n^2\rangle = (E_n^1 - \hat{H}_1)|\psi_n^1\rangle + E_n^2|\psi_n^0\rangle$

$\mathcal{O}(\lambda^3)$ $\quad (\hat{H}_0 - E_n^0)|\psi_n^3\rangle = (E_n^1 - \hat{H}_1)|\psi_n^2\rangle + E_n^2|\psi_n^1\rangle + E_n^3|\psi_n^0\rangle$

We see we can take $|\psi_n^k\rangle \longrightarrow |\psi_n^k\rangle + c|\psi_n^0\rangle$ and not change left side, thus not effecting result to order k. We are free to choose

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

This ensures $|\psi_n\rangle$ is normalized to first order in λ:

$$\langle \psi_n | \psi_n \rangle = \left(\langle \psi_n^0| + \langle \psi_n^1|\lambda + \cdots\right)\left(|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \cdots\right)$$

$$= 1 + \lambda\left(\langle \psi_n^1|\psi_n^0\rangle + \langle \psi_n^0|\psi_n^1\rangle\right) + \mathcal{O}(\lambda^2)$$

actually, we only need real part of $\langle \psi_n^1|\psi_0\rangle$ to be zero. let $\langle \psi_n^1|\psi_0\rangle = ia$

$$|\psi_n\rangle = |\psi_n^0\rangle + \lambda\left(|\psi_n^1\rangle + ia|\psi_n^0\rangle\right) + \mathcal{O}(\lambda^2)$$

$$= (1 + ia\lambda)|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \mathcal{O}(\lambda^2)$$

$$= e^{ia\lambda}|\psi_n^0\rangle + \lambda|\psi_n^1\rangle + \mathcal{O}(\lambda^2)$$

to this order in λ $\qquad$ an irrelevant phase

First order energy correction: $O(\lambda^1)$ equation and apply bra $\langle \psi_n^0|$

$$\langle \psi_n^0 | \hat{H}_0 - E_0 | \psi_n^1 \rangle = \langle \psi_n^0 | (E_n^1 - \hat{H}_1) | \psi_n^0 \rangle$$

E_n^0

$$E_n^1 = \langle \psi_n^0 | \hat{H}_1 | \psi_n^0 \rangle \equiv [\hat{H}_1]_{nn}$$

matrix element

First order wave function:

Expand $|\psi_n^1\rangle$ in terms of zeroth order wave function, with $\langle \psi_n^1 | \psi_n^0 \rangle = 0$

$$|\psi_n^1\rangle = \sum_{k \neq n} C_k |\psi_k^0\rangle$$

$$(\hat{H}^0 - E_n^0) \sum_{k \neq n} C_k |\psi_k^0\rangle = (E_n^1 - \hat{H}_1) |\psi_n^0\rangle$$

take inner product with $\langle \psi_\ell^0 |$ & $\langle \psi_\ell^0 | \hat{H}^0 = \langle \psi_\ell^0 | E_\ell^0$

$$\sum_{k \neq n} C_k (E_\ell^0 - E_n^0) \underbrace{\langle \psi_\ell^0 | \psi_k^0 \rangle}_{\delta_{\ell k}} = \langle \psi_\ell^0 | (E_n^1 - \hat{H}_1) | \psi_n^0 \rangle$$

$$C_\ell (E_\ell^0 - E_n^0) = E_n^1 \langle \psi_\ell^0 | \psi_n^0 \rangle - \langle \psi_\ell^0 | \hat{H}_1 | \psi_n^0 \rangle$$

for $\ell = n$ recover first order energy.
for $\ell \neq n$

$$C_\ell = \frac{\langle \psi_\ell^0 | \hat{H}_1 | \psi_n^0 \rangle}{E_n^0 - E_\ell^0} = \frac{[\hat{H}_1]_{\ell n}}{E_n^0 - E_\ell^0}$$

changing dummy index l back to k,

$$|\psi_n^1\rangle = \sum_{k \neq n} \frac{[\hat{H}_1]_{kn}}{E_n^0 - E_k^0} |\psi_k^0\rangle$$

Only works if unperturbed states are non-degenerate.

<u>2nd order energy</u> : $\mathcal{O}(\lambda^2)$ equation
act with bra $\langle \psi_n^0|$

$$0 = \langle \psi_n^0 | (E_n^1 - \hat{H}_1) | \psi_n^1 \rangle + E_n^2 \langle \psi_n^0 | \psi_n^0 \rangle$$

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

$$E_n^2 = \langle \psi_n^0 | \hat{H}_1 | \psi_n^1 \rangle =$$

$$\sum_{k \neq n} \frac{\langle \psi_k^0 | \hat{H}_1 | \psi_n^0 \rangle \langle \psi_n^0 | \hat{H}_1 | \psi_k^0 \rangle}{E_n^0 - E_k^0}$$

$$= \sum_{k \neq n} \frac{|[\hat{H}_1]_{kn}|^2}{E_n^0 - E_k^0}$$

Some examples

<u>Example 1</u> perturbed 1D harmonic oscillator

$$\hat{H}_0 = \frac{\hat{P}_x^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

$$\lambda \hat{H}_1 = b\hat{x}^4$$

introduce ground state classical turning point

$$x_c = \sqrt{\frac{\hbar}{m\omega}}$$

$$\hat{y} \equiv \sqrt{\frac{m\omega}{\hbar}}\,\hat{x} = \frac{\hat{x}}{x_c} \quad ; \quad \hat{q} \equiv \frac{\hat{p}}{\sqrt{m\omega\hbar}} = \frac{x_c}{\hbar}\hat{p}$$

$$[\hat{y}, \hat{q}] = i \qquad \text{let } \lambda = \frac{b x_c^4}{\hbar\omega} \quad \text{then}$$

$$\boxed{\hat{H} = \frac{\hbar\omega}{2}\left(\hat{y}^2 + \hat{q}^2\right) + \lambda\hbar\omega\,\hat{y}^4}$$

define $\hat{a} \equiv \frac{1}{\sqrt{2}}(\hat{y} + i\hat{q})$; $[\hat{a}, \hat{a}^+] = 1$

$$\hat{y} = \frac{1}{\sqrt{2}}(\hat{a} + \hat{a}^+)$$

then

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

1st order energy correction

$$\lambda E_n' = \lambda \hbar\omega \langle n|\hat{y}^4|n\rangle$$

$$\hat{y}^2 = \frac{1}{2}(\hat{a}^2 + \hat{a}^{+2} + \hat{a}\hat{a}^+ + \hat{a}^+\hat{a}) = \frac{1}{2}(\hat{a}^2 + \hat{a}^{+2} + 2\hat{a}^+\hat{a} + 1)$$

$$\hat{y}^2|n\rangle = \frac{1}{2}\Big\{\sqrt{n(n-1)}\,|n-2\rangle + \sqrt{(n+1)(n+2)}\,|n+2\rangle + (2n+1)|n\rangle\Big\}$$

$$\langle n|\hat{y}^2\hat{y}^2|n\rangle = \frac{1}{4}\Big[n(n-1) + (n+1)(n+2) + (2n+1)^2\Big]$$

$$= \frac{3}{4}(2n^2 + 2n + 1)$$

for perturbation theory to be valid $\lambda E_n' \ll E_n^0$

$$\lambda E_n' = \lambda\hbar\omega\left(\frac{3}{4}\right)(2n^2+2n+1) \overset{?}{\ll} \hbar\omega(n+\tfrac{1}{2})$$

$$b\,x_c^4\left(\frac{3}{4}\right)(2n^2+2n+1) \overset{?}{\ll} \hbar\omega(n+\tfrac{1}{2})$$

Since $\lambda E_n' \xrightarrow[n\to\infty]{} b\,x_c^4 \frac{3}{2} n^2$ & $E_n^0 \xrightarrow[n\to\infty]{} \hbar\omega n$ eventually perturbation theory breaks down:

$$n > \frac{\hbar\omega}{b\,x_c^4}\left(\frac{2}{3}\right)$$

harmonic oscillator is a special case because $E_{n+1} - E_n = \hbar\omega$ independent of n.

<u>Problem with degeneracy</u>:

Look at $O(\lambda^1)$ equation

$$(\hat{H}_0 - E_n^0)|\psi_n^{(1)}\rangle = (E_n^1 - \hat{H}_1)|\psi_n^{(0)}\rangle$$

which wave function to use in case of degeneracy?

$$|\psi_n^{(1)}\rangle = \sum_{k \neq n} C_n |\psi_k^{(0)}\rangle$$

$$C_k = \frac{\langle \psi_k^0 | \hat{H}_1 | \psi_n^0 \rangle}{E_n^0 - E_k^0}$$

C_k <u>undefined</u> in case of degeneracies.

Variational method

$$E = \langle\psi|H|\psi\rangle \geq E_0 \qquad \langle\psi|\psi\rangle = 1$$

$$E = \sum_n E_n |\langle\psi_n|\psi\rangle|^2 \geq E_0 \sum_n |\langle\psi_n|\psi\rangle|^2 = E_0$$

example $\quad V(x) = \lambda x^4$

take $\quad \psi = \left(\frac{a}{\pi}\right)^{1/2} e^{-ax^2/2} \qquad \int|\psi|^2 dx = 1$

normalized Gaussian

$$\frac{d^2}{dx^2} e^{-ax^2/2} = (-a + a^2x^2)\, e^{-ax^2/2}$$

normalized Gaussian integrals are

$$\langle 1\rangle = 1 \ ; \ \langle x^2\rangle = \frac{1}{2}\frac{1}{a}$$

$$\langle x^4\rangle = \frac{3}{4}\frac{1}{a^2}$$

$$\langle\psi|H|\psi\rangle = \sqrt{\frac{a}{\pi}} \int dx\, e^{-ax^2} \left[\frac{\hbar^2}{2m} a - \frac{\hbar^2}{2m} a^2 x^2 + \lambda x^4\right]$$

$$= \frac{\hbar^2 a}{4m} + \frac{3\lambda}{4a^2}$$

$$\langle H \rangle = \frac{\hbar^2 a}{4M} + \frac{3\lambda}{4a^2}$$

find min

$$\frac{d}{da}\langle H \rangle = \frac{\hbar^2}{4M} - \frac{3}{2}\frac{\lambda}{a^3} = 0$$

$$a_{min} = \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}$$

then

$$E_0 \leq \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{1/3}$$

check dimensions:

$[\lambda]$ energy $\cdot$ (dist)$^{-4}$

$$\frac{\hbar^4 c^4}{m^2 c^4} = \frac{(\text{energy} \cdot \text{dist})^4}{(\text{energy})^2}$$

$(\text{energy})^3$ ✓

Degenerate Perturbation Theory

Consider n^{th} eigenstate of $\hat{H}_0$ to be d-fold degenerate. We want to use as zeroth order states, linear combinations that diagonalize perturbation $\hat{H}_1$:

$$\hat{H}_0 |\psi^0_{n,i}\rangle = E^0_n |\psi^0_{n,i}\rangle \qquad i = 1, \ldots, d$$

Expand wave function as

$$|\psi_n\rangle = \sum_i c_i |\psi^0_{n,i}\rangle + \lambda |\psi'_n\rangle + \cdots$$

Actually, there are d first order wave function corrections $|\psi_n'\rangle$, but we will not derive them. See Sakurai.

To first order in λ:

$$(\hat{H}_0 + \lambda \hat{H}_1) |\psi_n\rangle = (E^0_n + \lambda E'_n) |\psi_n\rangle$$

becomes

$$\overset{\checkmark}{\hat{H}_0 \sum_i c_i |\psi^0_{n,i}\rangle} + \lambda \hat{H}_0 |\psi'_n\rangle + \lambda \hat{H}_1 \sum_i c_i |\psi^0_{n,i}\rangle$$

$$= \overset{\checkmark}{E^0_n \sum_i c_i |\psi^0_{n,i}\rangle} + \lambda E^0_n |\psi'_n\rangle + \lambda E'_n \sum_i c_i |\psi^0_{n,i}\rangle$$

cancel ✓ term

$$\lambda \hat{H}_0 |\psi'_n\rangle + \lambda \hat{H}_1 \sum_i c_i |\psi^0_{n,i}\rangle = \lambda E^0_n |\psi'_n\rangle + \lambda E'_n \sum_i c_i |\psi^0_{n,i}\rangle$$

again we can choose corrections

$$\langle \psi_n^1 | \psi_n^0 \rangle = 0 \quad \text{and use} \quad \langle \psi_{n_i}^0 | \psi_{n_j}^0 \rangle = \delta_{ij}$$

then

$$\sum_i C_i \langle \psi_{n_j} | \hat{H}_1 | \psi_{n_i} \rangle = E_n^{(1)} C_j$$

This is eigenvalue equation for the energy corrections E'_{n_i}. In matrix notation,

with $[\hat{H}_1]_{ij} \equiv \langle \psi_{n_j} | \hat{H}_1 | \psi_{n_i} \rangle$

$$[\hat{H}_1] \cdot \vec{C} = E_n^{(1)} \vec{C}$$

Solution gives first order corrections and zeroth order wave functions that diagonalize $\hat{H}_1$. Again, we will not derive (and do not need) first order wave function corrections

Simple example from 521 final,
spin-1 particle with

$$\hat{H}_0 = \frac{a}{\hbar^2} S_z^2 \quad ; \quad \hat{H}_1 = \frac{b}{\hbar^2}\left[\hat{S}_x^2 - \hat{S}_y^2\right]$$

Eigenstate of $\hat{H}_0$ are $|1,m\rangle$ $m = -1, 0, +1$

and $\hat{H}_0 |1,m\rangle = a m^2 |1,m\rangle$ $m = \pm 1$ degenerate

In $m = \pm 1$ subspace

$$\left[\hat{H}_0\right] = a \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\hat{S}_x = \frac{1}{2}\left(\hat{S}_+ + \hat{S}_-\right) \qquad \hat{S}_y = \frac{1}{2}\left(\hat{S}_+ - \hat{S}_-\right)$$

$$\hat{S}_x^2 - \hat{S}_y^2 = \frac{1}{2}\left(S_+^2 + S_-^2\right)$$

$$\hat{S}_\pm |1,m\rangle = \sqrt{2 \pm m(m \pm 1)}\ |1,m\rangle$$

$$\left.\begin{array}{l} S_+ |1,-1\rangle = \sqrt{2}\, |1,0\rangle \\ S_+ |1,0\rangle = \sqrt{2}\, |1,+1\rangle \end{array}\right\} \quad S_+^2 |1,-1\rangle = 2 |1,+1\rangle$$

so $\left[\hat{H}_1\right] = b \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$

$$b \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E^{(1)} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

gives $E^1 = \pm b$

diagonal zeroth order wave functions:

$$|\pm b\rangle = \frac{1}{\sqrt{2}}\left(|1,1\rangle \pm |1,-1\rangle \right)$$

Exact energies easily found from

$$[\hat{H}] = \begin{pmatrix} a & b \\ b & a \end{pmatrix} \Rightarrow E_{\pm} = a \pm b$$