PHY 456 Lecture 8
Non-Degenerate, Time Independent Perturbation Theory

Motivation:

- Only a handful of problems solvable in physics, can simplify difficult problems into ones that we're actually able to solve.

ex. pendulum $\ddot{\theta} = -\frac{g}{L}\sin\theta$; $\omega = \sqrt{\frac{g}{L}}$

Taking $\sin\theta \simeq \theta$ is a linear ODE, very easy to solve.

But what if $\sin\theta \simeq \theta - \frac{1}{3!}\theta^3 + O(\theta^5)$ is more important?

Consider harmonic oscillator potential $V_0 = \frac{1}{2}\omega^2 x^2$ with a small anharmonic term $V_1 = \frac{1}{4}\lambda x^4$:

$$m\ddot{x} = -\frac{dV}{dx} = -\omega^2 x - \lambda x^3.$$

How to solve? Take $x(t)$ as an expansion in λ:

$$x(t) = x_0(t) + \lambda x_1(t) + \lambda^2 x_2(t) + \ldots$$

which implies

$$m\ddot{x}_0 + m\lambda\ddot{x}_1 + m\lambda^2\ddot{x}_2 = -\omega^2 x_0 - \omega^2\lambda x_1 - \omega^2\lambda^2 x_2 - \dots$$
$$- \lambda(x_0 + \lambda x_1 + \lambda^2 x_2 + \dots)^3$$

$$= -\omega^2 x_0 - \lambda(\omega^2 x_1 + x_0^3)$$
$$- \lambda^2(\omega^2 x_2 + 3x_0^3 x_1)$$
$$+ O(\lambda^3)$$

Equating powers of λ imply

$$m\ddot{x}_0 = -\omega^2 x_0$$

Solve for x_0, plug in

solve for x_1, plug in

$$m\ddot{x}_1 = -\omega^2 x_1 - x_0^3$$

$$m\ddot{x}_2 = -\omega^2 x_2 - 3x_0^3 x_1$$

Solve for x_2, etc.

$$\vdots$$

However note that each solution for each $x_i(t)$ requires 2 necessary boundary conditions for an exact solution; hence n^{th} order of perturbation $\Rightarrow$ 2^{n+1} arbitrary constants.

FIRST ORDER NON-DEGENERATE

$$H = H_0 + \lambda H_1$$

$$H_0 = \frac{\hat{p}^2}{2m} + \frac{m\omega^2}{2}\hat{x}^2$$

$$H_1 = \hat{x}^4$$ (no explicit time dependence in the H_1 perturbation)

Goal: Find eigenvalues / States of $i\hbar \frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$.

Since Stationary states are discretely valued, label $|\psi\rangle = |n\rangle e^{-i\frac{E_n t}{\hbar}}$

thus we want $H|n\rangle = E_n|n\rangle$ as the stationary state equation that we want to solve.

Let's expand $(H_0 + \lambda H_1)|n\rangle = E_n|n\rangle$ into expansions of orders of λ:

$$|n\rangle \longrightarrow |n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \ldots$$

$$E_n \longrightarrow E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \ldots$$

Such that $H_0|n^0\rangle = E_n^0|n^0\rangle$ eg. $E_n^0 = \hbar\omega(n + \frac{1}{2})$ $n \in \mathbb{N}$.

We have

$$(H_0 + \lambda H_1)(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \ldots) = (E_n^0 + \lambda E_n^1 + \ldots)(|n^0\rangle + \lambda|n^1\rangle + \ldots)$$

Expanding & equating powers of λ give

(0) $H_0|n^0\rangle = E_n^0|n^0\rangle$ (trivial)

(1) $H_0|n^1\rangle + H_1|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle$

(2) $H_0|n^2\rangle + H_1|n^2\rangle = E_n^0|n^2\rangle + E_n^1|n^2\rangle + E_n^2|n^2\rangle$

Observe that (1) implies

$$|n^0\rangle E_n^1 = H_0|n^1\rangle + H_1|n^0\rangle - |n^1\rangle E_n^0$$

$$\Rightarrow \quad \underbrace{\langle m^0|n^0\rangle}_{\delta_{mn}} E_n^1 = \underbrace{\langle m^0|H_0|n^1\rangle}_{E_m^0 \langle m^0|n^1\rangle} - \langle m^0|H_1|n^0\rangle - \langle m^0|n^1\rangle E_n^0$$

m=n: $E_n^1 = \langle n^0 | H^1 | n^0\rangle$ 1st order correction to n^{th} energy level; expectation value of perturbation in unpertubed state

m≠n: $0 = (E_m^0 - E_n^0)\langle m^0|n^1\rangle + \langle m^0|H^1|n^0\rangle$

or $\langle m^0|n^1\rangle = \dfrac{\langle m^0|H_1|n^0\rangle}{E_m^0 - E_n^0}$ Expansion of first correction to the n^{th} eigenstate in terms of unpertubed states

In general, since $\{|m^0\rangle\}$ is a complete set,

$$|n^1\rangle = \sum_{m^0} |m^0\rangle\langle m^0|n^1\rangle$$

$$= \sum_{m_0 \neq n_0} |m^0\rangle \underbrace{\langle m^0|n^1\rangle}_{\text{Known}} + |n^0\rangle \underbrace{\langle n^0|n^1\rangle}_{\text{Must be 0 by normalization:}}$$

$|n\rangle = |n^0\rangle + \lambda|n^1\rangle + \dots$

and $\langle n^0|n^0\rangle = 1$ (from unpertubed harmonic oscillator states)

$$\langle n|n\rangle = \left(\langle n^0| + \lambda\langle n^1| + \dots\right)\left(|n^0\rangle + \lambda|n^1\rangle + \lambda^2|n^2\rangle + \dots\right)$$

$$= \langle n^0|n^0\rangle + \lambda\left(\langle n^1|n^0\rangle + \langle n^0|n^1\rangle\right) + \lambda^2\left(\langle n^2|n^0\rangle + \langle n^1|n^1\rangle + \dots\right) + \dots$$

$\underset{(\text{demand})}{=} 1 + \mathcal{O}(\lambda^2)$ if working to order λ, so

$\Rightarrow \langle n^0 | n' \rangle = i\alpha$ (take $\alpha = 0$ for now).

Therefore

$$E_n = E_n^0 + \lambda \langle n^0 | H_1 | n^0 \rangle + \mathcal{O}(\lambda^2)$$

$$|n\rangle = |n^0\rangle + \lambda \sum_{m \neq n} \frac{|m^0\rangle \langle m^0 | H_1 | n^0 \rangle}{E_m^0 - E_n^0}$$

$$\langle n | n \rangle = 1 + \mathcal{O}(\lambda^2)$$

1^{st} order, non-degenerate PT.

Enforce criteria $\lambda \ll 1$, and $|\langle m^0 | H_1 | n^0 \rangle| \ll |E_n^0 - E_m^0|$

so second term doesn't blow up.

For our anharmonic oscillator above, we find that

$$E_n = \hbar \omega_0 (n + \tfrac{1}{2}) + \frac{\hbar^2 \lambda}{16 m_p^2 \omega_0^2} (6n^2 + 6n + 3) + \mathcal{O}(\lambda^2)$$

Large if n large,

$\therefore$ we have constraints.

PT. Has limited applicability.

SECOND ORDER NON-DEGENERATE

Same problem: $H = H_0 + \lambda H_1$, $H_0|n^0\rangle = E_n^0|n^0\rangle$.

Recall the powers of λ after expansion:

$\mathcal{O}(\lambda^0)$
$$H_0|n^0\rangle = E_n^0|n^0\rangle$$

$\mathcal{O}(\lambda^1)$
$$H_0|n^1\rangle + H_1|n^0\rangle = E_n^0|n^1\rangle + E_n^1|n^0\rangle \qquad (\text{gives } |n^1\rangle, E_n^1)$$

$\mathcal{O}(\lambda^2)$
$$H_0|n^2\rangle + H_1|n^1\rangle = E_n^0|n^2\rangle + E_n^1|n^1\rangle + E_n^2|n^0\rangle$$

Same procedure: multiply through by $\langle m^0|$ on $\mathcal{O}(\lambda^2)$:

$$\langle m^0|H_0|n^2\rangle + \langle m^0|H_1|n^1\rangle = E_n^0\langle m^0|n^2\rangle + E_n^1\langle m^0|n^1\rangle + E_n^2\delta_{nm}$$

$$\Rightarrow \langle m^0|n^2\rangle(E_m^0 - E_n^0) - E_n^1\langle m^0|n^1\rangle + \langle m^0|H_1|n^1\rangle = E_n^2\delta_{nm}$$

<u>m=n</u>: $E_n^2 = \langle n^0|H_1|n^1\rangle \qquad (\langle m^0|n^1\rangle = i\alpha \to 0)$

$$= \langle n^0|H_1 \sum_{m\neq n}|m^0\rangle \frac{\langle m^0|H_1|n^0\rangle}{E_n^0 - E_m^0} \Bigg\} \quad |m^0\rangle\langle m^0|n^1\rangle$$

known

$$= \sum_{m\neq n} \frac{\langle n^0|H_1|m^0\rangle\langle m^0|H_1|n^0\rangle}{E_m^0 - E_n^0}$$

$$= \sum_{m\neq n} \frac{|\langle n^0|H_1|m^0\rangle|^2}{E_m^0 - E_n^0}$$

Thus

$$E_n = E_n^{\circ} + \lambda \langle n^{\circ} | H_1 | n^{\circ} \rangle + \lambda^2 \sum_{n \neq m} \frac{|\langle n^{\circ} | H_1 | m^{\circ} \rangle|^2}{E_m^{\circ} - E_n^{\circ}}$$

← shift of energy to $\mathcal{O}(\lambda^2)$.

Wavefunction 2nd order correction $|n^2\rangle$ similar, but as order increases series get more complicated.

2nd order important as there may/may not be an energy shift at first order; diagonal matrix element could vanish by symmetry.

Stark Effect for Ground State Hydrogen

Label H states $\psi_{n\ell m} \equiv \langle x | n \, \ell \, m \rangle$.

Take the hydrogen Hamiltonian $H_0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r}$

with perturbative term $H_1 = e \vec{\mathcal{E}} \cdot \vec{r}$ where $\vec{\mathcal{E}}$ is an applied homogeneous external field. What is effect of $\vec{\mathcal{E}}$ on ground state?

First-order energy shift $E^1_{(100)} = \langle 100 | e \vec{\mathcal{E}} \cdot \vec{r} | 100 \rangle$

$= \langle 100 | \vec{r} | 100 \rangle \, e \vec{\mathcal{E}}$

$= 0$ by parity symmetry ...

$\langle 100 | \vec{r} | 100 \rangle = - \langle 100 | \vec{r} | 100 \rangle$

in H ground state.

Second-order energy shift $E^{2}_{(100)} = e^2 \mathcal{E}^2 \sum_{n\ell m \neq 100} \frac{|\langle 100|z|100\rangle|^2}{E^{\circ}_{(100)} - E^{\circ}_{(n\ell m)}}$

Take $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$
No generality loss

$$E^{\circ}_{(n\ell m)} = -R_y \frac{1}{n^2} \quad \text{so}$$

$$E^{\circ}_{(100)} - E^{\circ}_{(n\ell m)} = -R_y\left(1 - \frac{1}{n^2}\right)$$

which all are negative.

$$|E^{2}_{(100)}| \leq e^2 \mathcal{E}^2 \sum_{n\ell m \neq 100} \frac{|\langle n\ell m|z|100\rangle|^2}{E^{\circ}_{(100)} - E^{\circ}_{n\ell m}} \leq \frac{e^2 \mathcal{E}^2}{E^{\circ}_{(100)} - E^{\circ}_{(200)}} \sum_{n\ell m \neq 100} |\langle n\ell m|z|100\rangle|^2$$

$$= \frac{e^2 \mathcal{E}^2}{E^{(\circ)}_{(100)} - E^{\circ}_{(200)}} \left[\sum_{n\ell m} |\langle n\ell m|z|100\rangle|^2 - \underbrace{|\langle 100|z|100\rangle|^2}_{0}\right]$$

$$= \frac{e^2 \mathcal{E}^2}{E^{(\circ)}_{(100)} - E^{(\circ)}_{(200)}} \sum_{n\ell m} \langle 100|z\underbrace{|n\ell m\rangle\langle n\ell m|}_{\mathbb{1}\ \text{(completeness)}}z|100\rangle$$

$$= \frac{e^2 \mathcal{E}^2}{E^{(0)}_{(100)} - E^{(\circ)}_{(200)}} \underbrace{\langle 100|z^2|100\rangle}_{a_0^2}$$

$$\text{or} \quad |E^{(2)}_{(100)}| \leq \frac{e^2 \mathcal{E}^2}{\left(1-\frac{1}{4}\right)\frac{e^2}{2a_0}} a_0^2 = \frac{8}{3} a_0^3 \mathcal{E}^2$$

and the second order correction is $E^{\circ}_{(100)} = \frac{e^2}{2a_0} - \frac{8}{3} a_0^3 \mathcal{E}^2$

occurs because H is electrically neutral, no dipole moment, so $\vec{\mathcal{E}}$ polarizes the atom, generating an electric dipole

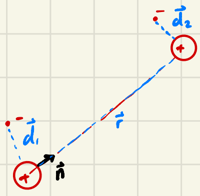
Polarizability is $\alpha \approx 5.2\, a_0^3$ (exact $4.5\, a_0^3$)

Higher-order states require degenerate perturbation theory.

$\boxed{\text{Multiple Atom State}}$

Consider two H-like atoms, far apart $(r \gg a_0)$ both with 0 charge, but with dipole/quadrupole moments.

$$\hat{V} = \frac{-\vec{d}_1 \cdot \vec{d}_2 + 3(\vec{d}_1 \cdot \vec{n})(\vec{d}_2 \cdot \vec{n})}{\hat{r}^3}$$



Let $\hat{H} = \hat{H}_0 + \hat{V}$ where $\hat{H}_0 = \hat{H}_{01} + \hat{H}_{02}$ (individual Hamiltonians)

First order: interaction energy is $\langle \Psi_0 | \hat{V} | \Psi_0 \rangle$ with $\Psi_0 = \Psi_{01}(\vec{r}_1)\Psi_{02}(\vec{r}_2)$

but diagonal dipole matrix elements in Stationary (s)-states vanish, so first-order correction is absent.

(Since the state is symmetric under exchange of states)

Second-order: r-dependence is $\sim |\langle \hat{V} \rangle|^2$ and is < 0 hence

$$E_{\text{interaction}} \sim -\frac{1}{r^6} \Rightarrow \text{Van-Der-Waals attraction}$$

At close distances electrons repel of course.