Approximation Techniques.

Perturbation → Time-indep

- [ ] Non-degenerate
- [ ] Degenerate
- [ ] Examples

Variational Techniques

WKB

Time-independent Perturbation Theory

Problem Setting

We are given a time-indep. Hamiltonian

$$H = H_0 + \lambda W.$$

We know the spectrum of H_0 i.e. $\{E^0_n, |\psi^0_n\rangle \mid H_0|\psi^0_n\rangle = E^0_n|\psi^0\rangle\}$, but we are interested in the spectrum of H.

* Remark If $[H_0, W] = 0$, then $\{E_n^{(0)}, |\psi^{(0)}_n\rangle\}$ would give the eigensystem of H too.

→ What if $[H_0, W] \neq 0$?

We will consider two settings:

① Non-degenerate Spectrum: $\forall_{\substack{n,m \\ n\neq m}}$ $E_n \neq E_m$.

② Degenerate Spectrum

Examples

1 H.O

Consider the following Hamiltonian:

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 + \lambda x \longrightarrow \text{charged H.O. in E field.}$$

or

$$H = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 + \lambda x^4 \longrightarrow \text{Anharmonic Oscillator}$$

Try to find the eigenenergies & eigenstates of these Hamiltonians.

2. Hydrogen atom

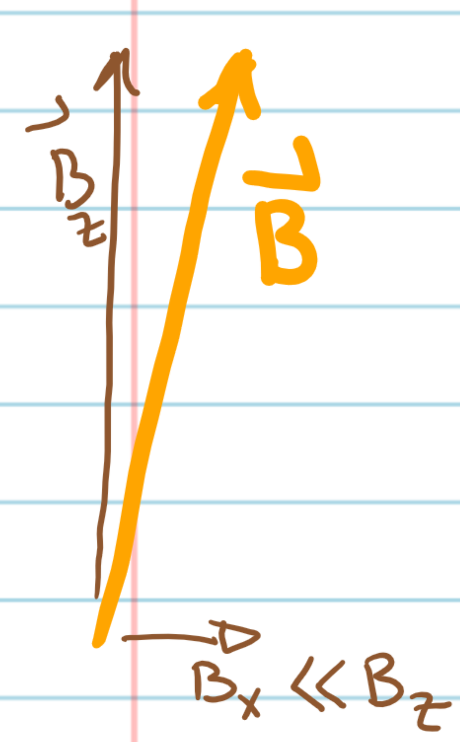
Find the eigenstates & eigenenergies of H with

* Stark effect $\quad H = H_0 + \lambda z \quad \lambda = e\mathcal{E}$
* Zeeman effect $\quad H = H_0 + \lambda(2S_z + L_z) \quad \lambda = \frac{eB}{2m_e c}$
* Spin_Orbit coupling $\quad H = H_0 + \lambda \frac{S.L}{r^3} \quad \lambda = \frac{e^2}{2m^2c^2}$
* Relativistic Corrections $\quad H = H_0 + \lambda p^4 \quad \lambda = \frac{+1}{8m^3c^2}$

3_ Spin in B field

$$H = \frac{e}{mc}(\vec{B}.\vec{S}) = \frac{e\hbar}{2mc}(B_z \sigma_z + B_x \sigma_x)$$

$B_x \ll B_z$



$\longrightarrow$ If $B_x = 0 \longrightarrow |gs\rangle = |z+\rangle, \; |ex\rangle = |z-\rangle$

$$\mathcal{E}_{gs} = \frac{-e\hbar}{2mc} \qquad \mathcal{E}_{ex} = \frac{e\hbar}{2mc}$$

But what if $B_x \neq 0$?

Let's assume that the new eigenbasis is $\{|\phi_n\rangle\}$ and

$$H|\phi_n\rangle = E|\phi_n\rangle \qquad (*)$$

I can take

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots$$

$$|\phi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \cdots$$

This is a <u>perturbative</u> expansion. →

Now we can plug this in eq. (*) above and seperate different orders of λ.

λ^0 $$H_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle$$

λ^1 $$W|\psi_n^{(0)}\rangle + H_0|\psi_n^{(1)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle$$

⋮

λ^k $$W|\psi_n^{(k-1)}\rangle + H_0|\psi_n^{(k)}\rangle = E_n^{(0)}|\psi_n^{(k)}\rangle + E_n^{(1)}|\psi_n^{(k-1)}\rangle + \cdots + E_n^{(k)}|\psi_n^{(0)}\rangle$$

Our goal is to solve these equations and find different orders of correction to the eigen energies & eigenstates.

Non-Degenerate Perturbation Theory (NDPT)

First, we make a simplifying assumption which is $\langle \psi_n^{(l)} | \psi_n^{(0)} \rangle = 0$

in $|\phi_n\rangle = |\phi_n^{(0)}\rangle + \lambda |\phi_n^{(1)}\rangle + \lambda^2 |\phi_n^{(2)}\rangle + \cdots$. (*)

This is b/c for any l: $|\psi_n^{(l)}\rangle = \alpha |\psi_n^{(0)}\rangle + \beta |\psi_{n\perp}^{(0)}\rangle$

and we can always absorb the first part $|\psi_n^{(0)}\rangle$ into the first term in (*) above. and then take the factor of $|\psi_n^{(0)}\rangle$ to be 1 before adding the normalization factor.

For simplicity, we'll reorder the equations from last page.

λ^0

$$H_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle \qquad \text{(eq. P0)}$$

λ^1

$$(H_0 - E_n^{(0)}) |\psi_n^{(1)}\rangle = (E_n^{(1)} - W) |\psi_n^{(0)}\rangle \qquad \text{(eq. P1)}$$

⋮

λ^k

$$(H_0 - E_n^{(0)}) |\psi_n^{(k)}\rangle = (E_n^{(1)} - W) |\psi_n^{(k-1)}\rangle + E_n^{(2)} |\psi_n^{(k-2)}\rangle + \cdots E_n^{(k)} |\psi_n^{(0)}\rangle \qquad \text{(eq. Pk)}$$

Assigment: Show that if $|\psi_n^{(k)}\rangle$ satisfies eq. P_k, then $|\psi_n^{(k)}\rangle + c|\psi_n^{(0)}\rangle$ would " " " too.

Use this to justify the assumption $\langle \psi_n^{(0)} | \psi_n^{(k)} \rangle = 0$

$\lambda^{(0)}$: There's no unknown. To this order

$$\{|\phi_n\rangle, E_n\} = \{|\psi_n^{(0)}\rangle, E_n^{(0)}\}.$$

$\lambda^{(1)}$: First order

$$(H_0 - E_n^{(0)})|\psi_n^{(1)}\rangle = (E_n^{(1)} - W)|\psi_n^{(0)}\rangle$$

Energy: $\langle\psi_n^{(0)}| \times$ — : LHS $\to \underbrace{(E_n^{(0)} - E_n^{(0)})}_{0} \langle\psi_n^{(0)}|\psi_n^{(1)}\rangle = 0$

RHS: $E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle - \langle\psi_n^{(0)}|W|\psi_n^{(0)}\rangle = 0$

→ First order correction to energy.

$$\Rightarrow E_n^{(1)} = \langle\psi_n^{(0)}|W|\psi_n^{(0)}\rangle$$

Eigenstate: $\langle\psi_m^{(0)}| \times$ $m \neq n$: LHS: $\langle\psi_m^{(0)}|H_0 - E_n^{(0)}|\psi_n^{(1)}\rangle = (E_m^{(0)} - E_n^{(0)})|\psi_n^{(1)}\rangle$

RHS: $\underbrace{\langle\psi_m^{(0)}|E_n^{(1)}|\psi_n^{(0)}\rangle}_{0} - \langle\psi_m^{(0)}|W|\psi_n^{(0)}\rangle$ $\quad \langle\psi_m^{0}|\psi_n^{(0)}\rangle = 0$

$$\Rightarrow \langle\psi_m^{(0)}|\psi_n^{(1)}\rangle = \frac{\langle\psi_m^{(0)}|W|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

$$|\psi_n^{(1)}\rangle = \sum_{m\neq n} \langle\psi_m^{(0)}|\psi_n^{(1)}\rangle|\psi_m^{(0)}\rangle = \sum_{m\neq n} \frac{W_{mn}}{E_n^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle$$

First order correction to the eigen states.

Note: Degeneracy of the spectrum:

This is with the assumption that $E_m \neq E_n$ for $m \neq n$.

Later, we'll consider the degenerate case.

Second Order

(eq. P_2): $$\left(H_0 - E_n^{(0)}\right)|\psi_n^{(2)}\rangle = \left(E_n^{(1)} - W\right)|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle$$

* Energy $\langle\psi_n^{(0)}| \times$

LHS: $\left(E_n^{(0)} - E_n^{(0)}\right)\langle\psi_n^{(0)}|\psi_n^{(2)}\rangle = 0$

RHS: $E_n^{(2)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle + E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle - \langle\psi_n^{(0)}|W|\psi_n^{(1)}\rangle$

2^{nd} order perturbation to energy:

$$E_n^{(2)} = \langle\psi_n^{(0)}|W|\psi_n^{(1)}\rangle$$

Assignment: Show that $E_n^{(k)} = \langle\psi_n^{(0)}|W|\psi_n^{(k-1)}\rangle$

Examples:

① $H = \frac{\hbar\omega}{2}\sigma_z + \frac{\hbar\lambda}{2}\sigma_x$, $\boxed{\lambda \ll \omega}$

- This problem can be exactly solved. ⟶ Do it.

- $H_0 = \frac{\hbar\omega}{2}\sigma_z$, $|\psi_\downarrow\rangle = \begin{pmatrix}0\\1\end{pmatrix}$, $|\psi_\uparrow\rangle = \begin{pmatrix}1\\0\end{pmatrix}$

  $\mathcal{E}_\downarrow = -\frac{\hbar\omega}{2}$, $\mathcal{E}_\uparrow = \frac{\hbar\omega}{2}$

- $H|\phi_i\rangle = E|\phi_i\rangle$, $|\phi_i\rangle = |\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle + \lambda^2|\psi_i^{(2)}\rangle + \cdots$

  $E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots$

⟶ $|\psi_\uparrow^{(1)}\rangle$, $E_\uparrow^{(1)} = \langle\psi_\uparrow^{(0)}|W|\psi_\uparrow^{(0)}\rangle = \langle z+|\sigma_x|z+\rangle = 0$

$E_\downarrow^{(1)} = \langle\psi_\downarrow^{(0)}|W|\psi_\downarrow^{(0)}\rangle = \langle z-|\sigma_x|z-\rangle = 0$

$|\psi_\uparrow^{(1)}\rangle = \sum_{i\neq\uparrow} \frac{\langle i|W|z+\rangle}{E_\uparrow - E_i} = \frac{\langle z-|\sigma_x|z+\rangle}{\hbar\omega} =$

$|\phi_\uparrow\rangle \simeq |z+\rangle + \frac{\hbar\lambda}{2\hbar\omega}|z-\rangle$

$E_\uparrow^{(2)} \simeq \langle\psi_\uparrow^{(0)}|W|\psi_\uparrow^{(1)}\rangle$

$= \left(\frac{1}{2}\frac{\lambda}{\omega}\right)\underbrace{\langle z+|\sigma_x|z-\rangle}_{1}$

$|\psi_\downarrow^{(1)}\rangle = \frac{\langle z+|\sigma_x|z-\rangle}{-\hbar\omega} = \frac{-1}{\hbar\omega}$

$E_\uparrow \sim \frac{\hbar\omega}{2} + \frac{1}{2}\left(\frac{\lambda}{\omega}\right)^2$

$|\phi_\downarrow\rangle = |z-\rangle - \frac{\lambda}{2\omega}|z+\rangle$ ⟶

Example 2: H.O. with x^4: Anharmonic Oscillator

$$H = \frac{P^2}{2m} + \frac{1}{2} m\omega^2 x^2 + \tilde{\lambda} x^4 = \hbar\omega\Big(\underbrace{\left(\frac{\hat{P}}{P_0}\right)^2 + \left(\frac{\hat{x}}{x_0}\right)^2}_{a^\dagger a + 1/2} + \lambda\left(\frac{x}{x_0}\right)^4\Big)$$

Reminder: $\frac{x}{x_0} = \frac{a + a^\dagger}{\sqrt{2}}$

$$W = \hbar\omega\left(\frac{x}{x_0}\right)^4 = \hbar\omega\left(\frac{a+a^\dagger}{\sqrt{2}}\right)^4 = \frac{\hbar\omega}{4}\left(a+a^\dagger\right)^4$$

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

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

$$E_n^{(1)} = \langle \psi_n^{(0)} | W | \psi_n^{(0)} \rangle = \frac{\hbar\omega}{4} \langle n | \left(a+a^\dagger\right)^4 | n \rangle$$

$\langle n | R | n \rangle = 0$

$$\left(a+a^\dagger\right)^4 = a^2 a^{\dagger 2} + a a^\dagger a a^\dagger + a a^\dagger a^\dagger a + a^{\dagger 2} a^2 + a^\dagger a a^\dagger a + a^\dagger a^2 a^\dagger + R$$

$$\rightarrow E_n^{(1)} = \frac{\hbar\omega}{4}\Big[(n+1)(n+2) + (n+1)^2 + n(n+1) + n(n-1) + n^2 + (n+1)n\Big] + 0$$

$$(n+1)\underbrace{\Big[n+2+n+1+n\Big]}_{(3n+3)} + n\underbrace{\Big[n-1+n+n+1\Big]}_{3n^2}$$

$$= \frac{3\hbar\omega}{4}\left((n+1)^2 + n^2\right) \rightarrow \text{Double check!}$$

Assignment: Calculate the first order perturbation to the state, i.e. $|\psi_n^{(1)}\rangle$.

Assignment: Calculate the 2^{nd} order perturbation to the energy, i.e. $E_n^{(2)}$.

Example: Stark effect

Electric field $\mathcal{E}$
dipole ez

$$H = H_0 + e\mathcal{E}z \rightarrow$$

Correction to the GS: $\psi_{nlm} \rightarrow \langle \psi_{100} | e\mathcal{E}z | \psi_{100} \rangle =$

$$e\mathcal{E} \langle \psi_{100} | z | \psi_{100} \rangle$$

$$\rightarrow \langle \psi_{100} | \hat{z} | \psi_{100} \rangle = \int_{-\infty}^{+\infty} |\psi_{100}|^2 z \, dr = 0$$

Even function, odd parity $\rightarrow 0$

This is expected considering that for the GS the electron is distributed symmetrically.

$\rightarrow$ For the GS $\rightarrow$ No linear responce.

Now, we need to move to the next order:

$$E_0^{(2)} = \sum_{m \neq 0} \frac{|\langle \psi_{100} | z | \psi_{nlm} \rangle|^2}{E_0 - E_m}$$

$$E_n = -\frac{R}{n^2}$$

$$E_0 - E_m \leq -R\left(1 - \frac{1}{4}\right) = \frac{-3}{4}R$$

$$\sum \langle \psi_{100} | z | \psi_{nlm} \rangle \langle \psi_{nlm} | z | \psi_{100} \rangle = \langle \psi_{100} | z \, \mathbb{1} \, z | \psi_{100} \rangle$$

$$= \langle \psi_{100} | z^2 | \psi_{100} \rangle = \langle \psi_{100} | r\cos\theta | \psi_{100} \rangle = a_0^2$$

$$\Rightarrow |E_0^{(2)}| \leq \langle \psi_{100} | z^2 | \psi_{100} \rangle / \left(\frac{3}{4}R\right) = a_0^2 \left(\frac{4}{3} \frac{2a_0}{e^2}\right) = \frac{8a_0^3}{3e^2}$$

$$R = \frac{e^2}{2a_0}$$

$$E \simeq \frac{R}{n^2} + e^2\mathcal{E}^2\left(\frac{-4}{3R} a_0^2\right)$$

(Quadratic) Polarizability $\leq 2\dfrac{\Delta E}{\mathcal{E}^2} = \dfrac{16}{3} a_0^3$

Some Remarks

- $|\psi_{gs}^{(0)}\rangle$ overestimates the ground state energy.

If $|\psi_{gs}^{(0)}\rangle$ is the ground state of H_0 then

up to the first-order $E_n = E_n^{(0)} + \lambda E_n^{(1)} =$

$$\langle \psi_n^{(0)} | H_0 + \lambda W | \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | H | \psi_n^{(0)} \rangle \geq E_{gs} .$$

The naeive argument is that $E_n^{(2)}$ for $n=gs$ is negative:

$$E_{gs}^{(2)} = \sum_m \frac{|\langle \psi_{gs}^{(0)} | W | \psi_m^{(0)} \rangle|^2}{\underbrace{E_{gs}^{(0)} - E_m^{(0)}}_{\leq 0}} \leq 0 .$$

But remember that there's no garantee that this would converge.

So just b/c $E_n^{(2)} \leq 0$ is not enough to say that $\langle \psi_{gs}^{(0)} | H | \psi_{gs}^{(0)} \rangle \geq E_{gs}$.

Assignment: Prove that $\langle \psi_{gs}^{(0)} | H | \psi_{gs}^{(0)} \rangle \geq E_{gs}$.

Level Repulsion:

To the first order $E_n \simeq \langle \psi_n^{(0)} | H = H_0 + \lambda W | \psi_n^{(0)} \rangle$.

The next order, $E_n^{(2)}$ has two contributions, one from higher energy levels & one from lower energy levels.

$$E_n^{(2)} = \underbrace{\sum_{\substack{m \neq n \\ E_m < E_n}} \frac{|W_{m,n}|^2}{E_n^{(0)} - E_m^{(0)}}}_{C_1} - \underbrace{\sum_{\substack{m \neq n \\ E_m > E_n}} \frac{|W_{m,n}|^2}{E_m^{(0)} - E_n^{(0)}}}_{C_2}$$

C_1, the contribution from lower energy levels increases the energy E_n while C_2 the " " higher " " decreases " ".

It is like the higher levels are pushing the level n down while the lower levels are pushing it up. That's why it is called level repulsion. Note that this is only up to the 2nd order.