Quantum II - Physics 492

Lecture 20: Time Independent Perturbation theory

Few problems in nature allow for exact mathematical solutions. The art in physics is the application of well chose approximation methods.

An important example in quantum mechanics is finding the energy eigenvalues and eigenstates of the Hamiltonian, particularly the bound states.

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle \qquad n \text{ discrete}$$

Rarely can we solve this exactly. We've seen almost all of them:
- Particle in ∞-square well
- SHO
- Hydrogen atom

In principle we can solve the problem numerically, but much more insight can be gain through approximate solutions.

General problem:

- Given discrete spectrum of exactly solvable "zeroth order" Hamiltonian $\hat{H}_0|\phi_n^{(0)}\rangle = E_n^{(0)}|\phi_n^{(0)}\rangle$
- Seek solution ~~to~~ $\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle$ where $\hat{H} = \hat{H}_0 + \hat{H}_1$ with $\hat{H}_1$ a "small" perturbation.

Typically we write $\hat{H} = \hat{H}_0 + \epsilon \hat{H}_1$, $\epsilon << 1$

The parameter "ϵ" is introduced for "bookkeeping", though it has a physical interpretation, as we will see.

The set of zeroth order eigenvectors form an othornormal basis for $\hat{H}_0$, $\{|\phi_n^{(0)}\rangle\}$. In this basis $\hat{H}$ has the matrix representation

$$\hat{H} \doteq \begin{bmatrix} E_1^{(0)} & & 0 \\ & E_2^{(0)} & \\ & & E_3^{(0)} \\ 0 & & & \ddots \end{bmatrix} + \epsilon \begin{bmatrix} \langle\phi_1^{(0)}|\hat{H}_1|\phi_1^{(0)}\rangle & \langle\phi_1^{(0)}|\hat{H}_1|\phi_2^{(0)}\rangle & \langle\phi_1^{(0)}|\hat{H}_1|\phi_3^{(0)}\rangle \\ \langle\phi_2^{(0)}|\hat{H}_1|\phi_1^{(0)}\rangle & \langle\phi_2^{(0)}|\hat{H}|\phi_2^{(0)}\rangle & \langle\phi_2^{(0)}|\hat{H}_1|\phi_3^{(0)}\rangle \\ \langle\phi_3^{(0)}|\hat{H}_1|\phi_1^{(0)}\rangle & \langle\phi_3^{(0)}|H|\phi_2^{(0)}\rangle & \langle\phi_3^{(0)}|\hat{H}_1|\phi_3^{(0)}\rangle \\ \vdots & \vdots & \vdots \end{bmatrix}$$

$\hat{H}$ is thus "almost diagonal" as $\epsilon \to 0$.

We thus write the solution to the T.I.S.E. as

$$|\phi_n\rangle = |\phi_n^{(0)}\rangle + |\delta\phi_n\rangle$$

$$E_n = E_n^{(0)} + \delta E_n$$

Where $|\delta\phi_n\rangle$ and $\delta E_n \to 0$ as $\epsilon \to 0$

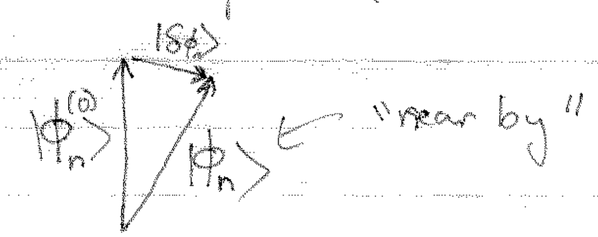
We thus expand both in a power series

$$|\delta\phi_n\rangle = \sum_{k=1}^{\infty} \epsilon^k |\phi_n^{(k)}\rangle$$

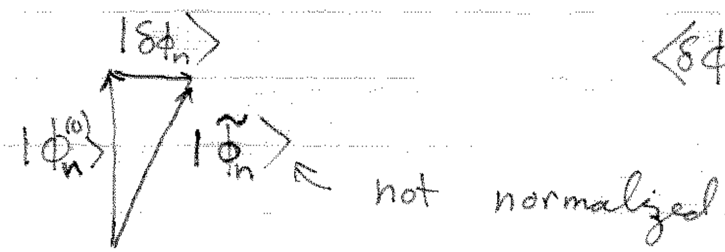
$$E_n = \sum_{k=1}^{\infty} \epsilon^k E_n^{(k)}$$

Perturbed eigenvectors

Consider the eigenvectors in Hilbert space.
Schematic picture



Since all vectors along the ray $|\phi_n\rangle$ are eigenvectors, we can ignore the normalization and choose $|\delta\phi_n\rangle$ orthogonal to $|\phi_n^{(0)}\rangle$



$$\langle \delta\phi_n | \phi_n^{(0)} \rangle = 0$$

With this choice, we can find the corrections to the T.I.S.E. by projecting onto $\langle \phi_n^{(0)}|$

- First Order

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

$$= \langle \phi_n^{(0)} | \underbrace{(E_n^{(0)} - E_n^{(0)})}_{0} | \phi_n^{(0)} \rangle + \langle \phi_n^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle$$

$$\therefore \boxed{E_n^{(1)} = \langle \phi_n^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle}$$

First order correction is the expectation of the perturbation in the zeroth order $\hat{H}_0$.

The TISE can thus we expanded in powers of ϵ

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle \Rightarrow (\hat{H}-E_n)|\phi_n\rangle = 0$$

$$(\hat{H}_0 + \epsilon\hat{H}_1)(|\phi_n^{(0)}\rangle + |\delta\phi_n\rangle) - (E_n^{(0)} + \delta E_n)(|\phi_n^{(0)}\rangle + |\delta\phi_n\rangle) = 0$$

$$\Rightarrow \underbrace{(\hat{H}_0 - E_n^{(0)})|\phi_n^{(0)}\rangle}_{\text{Zeroth order}} + \underbrace{\epsilon\left[(\hat{H}_0 - E_n^{(0)})|\phi_n^{(1)}\rangle + (\hat{H}_1 - E_n^{(1)})|\phi_n^{(0)}\rangle\right]}_{\text{first order}}$$

$$+ \underbrace{\epsilon^2\left[(\hat{H}_0 - E_n^{(0)})|\phi_n^{(2)}\rangle + (\hat{H}_1 - E_n^{(1)})|\phi_n^{(1)}\rangle - E_n^{(2)}|\phi_n^{(0)}\rangle\right]}_{\text{Second order}}$$

$$+ \dots = 0$$

Assuming the power series converges, each term of order k vanishes to order $\mathcal{O}(\epsilon^{k+1})$.

$\Rightarrow$ • Zeroth order: $E_n^{(0)}|\phi_n^{(0)}\rangle = \hat{H}_0|\phi_n^{(0)}\rangle$ (by assumption)

• First order: $E_n^{(1)}|\phi_n^{(0)}\rangle = (\hat{H}_0 - E_n^{(0)})|\phi_n^{(1)}\rangle + \hat{H}_1|\phi_n^{(0)}\rangle$

• Second order: $E_n^{(2)}|\phi_n^{(0)}\rangle = (\hat{H}_0 - E_n^{(0)})|\phi_n^{(2)}\rangle + (\hat{H}_1 - E_n^{(1)})|\phi_n^{(1)}\rangle$

- First order continued

Let us expand $|\phi_n^{(1)}\rangle$ in the basis $\{|\phi_n^{(0)}\rangle\}$

$$\Rightarrow |\phi_n^{(1)}\rangle = \sum_{m=0}^{\infty} C_m^{(1)} |\phi_m^{(0)}\rangle$$

where $C_m^{(1)} = \langle \phi_m^{(0)} | \phi_n^{(1)} \rangle$

Note: $\langle \phi_n^{(0)} | \phi_n^{(1)} \rangle = 0$ by assumption

$\Rightarrow C_m^{(1)} = 0$ if $m = n$

$$\therefore \underbrace{\langle \phi_m^{(0)} | E_n^{(1)} | \phi_n^{(0)} \rangle}_{\substack{\| \\ E_n^{(1)} \langle \phi_m^{(0)} | \phi_n^{(0)} \rangle \\ \| \\ 0}} = \langle \phi_m^{(0)} | (\hat{H}_0 - E_n^{(0)}) | \phi_n^{(1)} \rangle + \langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle$$

$$\Rightarrow E_m^{(0)} - E_n^{(0)} \underbrace{\langle \phi_m^{(0)} | \phi_n^{(1)} \rangle}_{C_m^{(1)}} = - \langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle$$

$$\Rightarrow \boxed{C_m^{(1)} = \frac{\langle \phi_m^{(0)} | \hat{H}_1 | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}} \quad n \neq m$$

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Thus, to first order

$$\boxed{|\phi_n\rangle = |\phi_n^{(0)}\rangle + \sum_{m\neq n} |\phi_m^{(0)}\rangle \frac{\langle\phi_m^{(0)}|\hat{H}_1|\phi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}}$$

<u>Note:</u> the effect of the perturbation is to "mix in" other eigenvectors into the original $|\phi_n^{(0)}\rangle$.

The probability amplitude

$$C_m^{(1)} = \frac{\langle\phi_m^{(0)}|\hat{H}_1|\phi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$$

Should be <u>small</u>

$\Rightarrow$ Perturbation when

$$\underbrace{\left|\langle\phi_m^{(0)}|\hat{H}_1|\phi_n^{(0)}\rangle\right|}_{\text{"transition matrix elements"}} \ll \underbrace{\left|E_n^{(0)} - E_m^{(0)}\right|}_{\text{spacing between energy levels}}$$

<u>Degeneracies?</u>

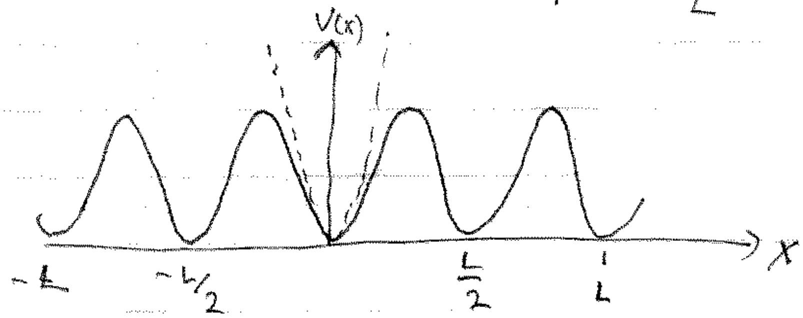
Clearly this procedure breaks down when $E_n^{(0)} = E_m^{(0)}$ for $n \neq m$.

We need to treat degenerate perturbation theory.

Example: An anharmonic oscillator

Consider the potential $V(x) = V_0 \sin^2(Kx)$ $\left(\begin{matrix}\text{From} \\ \text{P.S. \#2}\end{matrix}\right)$

where $K = \frac{2\pi}{L}$



Near an equilibrium point (say the origin) the potential can be approximated by a harmonic potential.

Near origin $V(x) \approx V^{(0)}(x) = \frac{1}{2} m\omega^2 x^2$

where $\omega = \sqrt{\frac{2V_0 K^2}{m}} \Rightarrow \hbar\omega = \sqrt{4V_0 E_K}$

with $E_K = \frac{(\hbar K)^2}{2m} = \frac{h^2}{2mL^2}$

Thus to zeroth order

$$\hat{H} = \hat{H}_0 = \frac{\hat{p}^2}{2m} + \hat{V}^{(0)}(\hat{x}) = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2$$

Solution to TISE

$$|\phi_n^{(0)}\rangle = |n\rangle \qquad n = 0, 1, 2, \ldots$$

$$E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega$$

There are anharmonic corrections

$$V(x) = V_0 \left(Kx - \frac{1}{6}(Kx)^3 + \cdots \right)^2$$

$$= \underbrace{\left(V_0 K^2\right) x^2}_{V^{(0)}(x)} \underbrace{-\left(\frac{1}{3} V_0 K^4\right) x^4}_{V^{(1)}(x)} + \cdots$$

Thus we can treat the x^4 term as a perturbation

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

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 = \hbar\omega\left(\hat{a}^\dagger \hat{a} + \frac{1}{2}\right)$$

$$\hat{H}_1 = -\frac{1}{3} V_0 K \hat{x}^4 = -\frac{1}{3} V_0 \left(\frac{K x_c}{\sqrt{2}}\right)^4 (\hat{a}^\dagger + \hat{a})^4$$

having ~~using~~ used $\begin{cases} \hat{x} = x_c \left(\dfrac{\hat{a} + \hat{a}^\dagger}{2} \right) \\ \hat{p} = p_c \left(\dfrac{\hat{a} - \hat{a}^\dagger}{2i} \right) \end{cases}$

Aside $V_0 \left(\frac{K x_c}{\sqrt{2}}\right)^4 = V_0 \left(K \sqrt{\frac{\hbar}{2m\omega}} \right)^4$

$$= \frac{V_0 \left(\frac{\hbar K}{2m}\right)^2}{(\hbar\omega)^2} = \frac{E_K}{4}$$

Thus, $\hat{H}_1$ is a perturbation if

$$\frac{E_K}{4\hbar\omega} \ll 1 \quad \text{or} \quad \frac{1}{8}\sqrt{\frac{E_K}{V_0}} \ll 1$$

This plays the role of the small parameter ϵ

<u>First order correction to energy</u>

$$E_n^{(1)} = \langle n|\hat{H}_1|n\rangle = -\frac{1}{12} E_K \langle n|(\hat{a}+\hat{a}^\dagger)^4|n\rangle$$

Aside: $\langle n|(\hat{a}+\hat{a}^\dagger)^4|n\rangle = \langle n|(\hat{a}^2+\hat{a}^{\dagger 2}+\hat{a}^\dagger\hat{a}+\hat{a}\hat{a}^\dagger)^2|n\rangle$

$$= \langle n|(\hat{a}^2+\hat{a}^{\dagger 2}+2\hat{N}+1)^2|n\rangle$$

$$= \langle n|\hat{a}^{\dagger 2}\hat{a}^2 + \hat{a}^2\hat{a}^{\dagger 2} + (2\hat{N}+1)^2|n\rangle$$

(note: I have only retained those terms with equal # of $\hat{a}$'s and $\hat{a}^\dagger$'s)

$$\Rightarrow \langle n|(\hat{a}+\hat{a}^\dagger)^4|n\rangle = \|\hat{a}^2|n\rangle\|^2 + \|\hat{a}^{\dagger 2}|n\rangle\|^2 + (2n+1)^2$$

Aside $\hat{a}^2|n\rangle = \sqrt{n(n-1)}\,|n-2\rangle \qquad \hat{a}^{\dagger 2}|n\rangle = \sqrt{(n+1)(n+2)}\,|n+2\rangle$

$$\Rightarrow \|\hat{a}^2|n\rangle\|^2 = n(n-1) \qquad \|\hat{a}^{\dagger 2}|n\rangle\|^2 = (n+1)(n+2)$$

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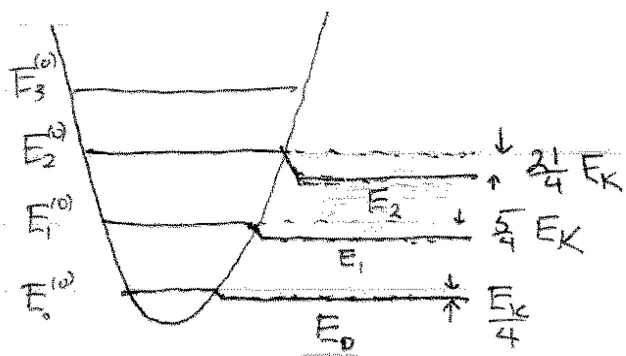
Thus,

$$\langle n | (\hat{a} + \hat{a}^{\dagger})^4 | n \rangle = n(n-1) + (n+1)(n+2) + (2n+1)^2$$
$$= 6(n^2 + n + \tfrac{1}{2})$$

$$\Rightarrow E_n^{(1)} = -\frac{1}{12} E_K \langle n | (\hat{a} + \hat{a}^{\dagger})^4 | n \rangle$$

$$\Rightarrow E_n^{(1)} = -\frac{1}{2} E_K \left(n^2 + n + \tfrac{1}{2}\right)$$



The anharmonic ladder is <u>not</u> evenly spaced

To first order in $\frac{E_K}{\hbar\omega}$, the spacing between neighboring levels

$$\boxed{E_n - E_{n-1} = \hbar\omega - n E_K}$$