PH 451/551 QM

Lecture # 8

Time-independent perturbation theory

Motivation: - Can't solve exactly QM problems beyond particle-in-a box, H.O., & (H)-atom

use known solutions to $\hat{H}_0 |n\rangle = E_n |n\rangle$ & introduce corrections to E_n & $|n\rangle$ due to perturbation $\hat{H}'$

to solve what happens under $\hat{H} = \hat{H}_0 + \hat{H}'$

Typical uses: - corrections to $V(\vec{r})$

- external fields interactions

e.g. (H)-atom in $\vec{E}$-field: $(\vec{E} \parallel Oz)$

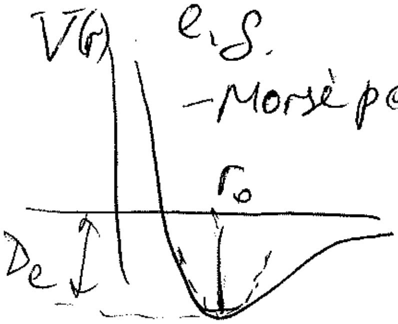
$\hat{H} = \hat{H}_0 \underbrace{- eEz}_{= \hat{H}'}$

or $\vec{B}$-field:

$\hat{H} = \hat{H}_0 \underbrace{- \vec{\mu} \cdot \vec{B}}_{= \hat{H}'}$

magnetic moment (e.g. $\vec{\mu} = \frac{e}{mc} \vec{S}$)

e.g. - Morse potential



$V(r) \simeq -D_e + \frac{\mu\omega^2 (r-r_0)^2}{2} + \alpha (r-r_0)^3$

H.O.

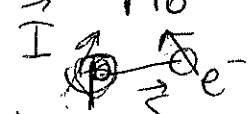
$\hat{H}_0 = \frac{\vec{p}^2}{2\mu} + \frac{\mu\omega^2 (r-r_0)^2}{2}$

account for unharmonicity

$\hat{H}'$

e.g. (H)-atom

$\hat{H}_0 = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{r}$



p-e⁻ Coulomb interact.

$\hat{H}' = A \vec{I} \cdot \vec{S}$

spins of p & e

So, solving $(\hat{H}_0 + \hat{H}')|n'\rangle = E_n|n'\rangle$ (2)
is typically too difficult $\Rightarrow$ need other methods!

approximation methods

One of them is time-independent perturbation theory

Rayleigh-Schrödinger $\overset{\text{a.k.a.}}{\longleftrightarrow}$ perturbation theory

Consider a time-independent Hamiltonian

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{unperturbed Hamiltonian}} + \lambda \hat{H}'$$

$\hat{H}'$ ← perturbation

λ ← real parameter from 0 to 1 ↑ to keep track of perturbation order

We know $\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$ — known

We want: $\hat{H}|n\rangle = E_n|n\rangle$ — ? ?

For now assume that the energy spectrum of $\hat{H}_0$ is <u>non-degenerate</u>

⇑ all $E_n^{(0)}$'s are different, so for each value $E_n^{(0)}$ there is only one $|n^{(0)}\rangle$ state

$\{|n^{(0)}\rangle\}$ is a complete & orthonormal basis

$\langle k^{(0)}|n^{(0)}\rangle = \delta_{kn}$ orthogonality

$\sum_n |n^{(0)}\rangle\langle n^{(0)}| = 1$ completeness

Need to solve $(\hat{H}_0 + \lambda \hat{H}')|n\rangle_\lambda = E_n^{(\lambda)}|n\rangle_\lambda$ 3

The method is based on the assumption that $E_n^{(\lambda)}$ & $|n\rangle_\lambda$ can be expanded in powers of λ:

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

? ?

$$|n\rangle_\lambda = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle + \ldots$$

? ?

Plug these in the Schrödinger equation & collect terms with equal powers of λ:

λ^0: $\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$ ← unperturbed problem

λ^1: $\hat{H}_0|n^{(1)}\rangle + \hat{H}'|n^{(0)}\rangle = E_n^{(0)}|n^{(1)}\rangle + E_n^{(1)}|n^{(0)}\rangle$

⇓ rewrite

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

multiply by $\langle n^{(0)}|$:

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

$\langle n^{(0)}|\hat{H}_0 = \langle n^{(0)}|E_n^{(0)}$ ⇒ so L.H.S. = 0

$$0 = E_n^{(1)} \underbrace{\langle n^{(0)} | n^{(0)} \rangle}_{=1} - \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle$$

$$\Downarrow$$

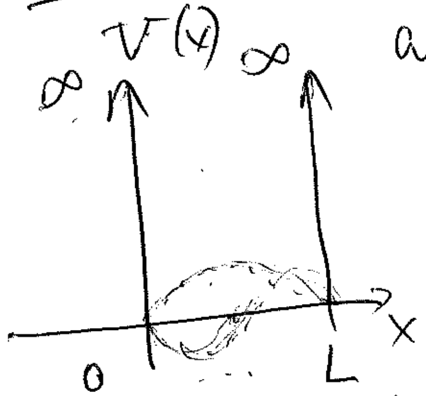
$$\underbrace{E_n^{(1)} = \langle n^{(0)} | \hat{H}' | n^{(0)} \rangle} = H'_{nn}$$

1st-order energy correction is the expectation value of the perturbation with respect to unperturbed state!

In wave function notation,

$$E_n^{(1)} = H'_{nn} = \int \varphi_n^{(0)*}(\vec{r})\, \hat{H}'\, \varphi_n^{(0)}(\vec{r})\, dV$$

<u>Example</u>: An infinite square well is perturbed by an additional potential energy term as follows:



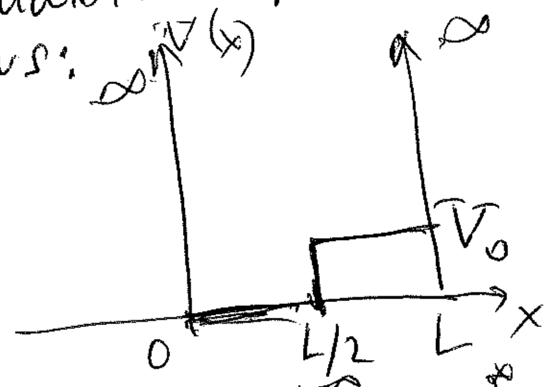
unperturbed problem

$$\Downarrow$$

$$E_n^{(0)} = \frac{\pi^2 \hbar^2 n^2}{2mL^2}$$

$$|n^{(0)}\rangle \doteq \varphi_n^{(0)}(x) = \sqrt{\frac{2}{L}} \sin\frac{\pi n x}{L}$$

$\Rightarrow$



Find $\underline{E_n^{(1)}}$

$$\Downarrow$$

$$E_n^{(1)} = \int_{-\infty}^{+\infty} \varphi_n^{(0)*}(x)\, \underbrace{V(x)}\, \varphi_n^{(0)}(x)\, dx$$

0 @ $[0, \frac{L}{2}]$
V_0 $[\frac{L}{2}, L]$

$$= \int_{L/2}^{L} V_0 |\varphi_n^{(0)}(x)|^2 dx = \underbrace{\frac{V_0}{2}}$$

for all states!