Quantum Mechanics I :-

(LECTURE NOTES OF PROF. ASHOKE SEN)

12.10.2011

Approximation methods

1. Time-independent perturbation theory

$$H\psi = E\psi$$

Suppose, $H = H_0 + \lambda H_1$. For H_0, one knows the solutions exactly. (For both bound & scattering states.)

$\lambda \to$ small parameter

Problem : Find the eigenvalues and eigenfunctions in a Taylor series expansion in λ. (It may happen that this series doesn't converge)

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

$$\psi_n = \sum_m C_{mn} \psi_m^{(0)}$$

$\psi_m^{(0)}$: { form a complete set of basis states }

$$\begin{bmatrix} H\psi_n = E_n \psi_n \\ H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \end{bmatrix}$$

$$C_{mn} = \delta_{mn} + \lambda C_{mn}^{(1)} + \lambda^2 C_{mn}^{(2)} + \cdots$$

$$\therefore \psi_n = \psi_n^{(0)} + \lambda \underbrace{\sum_m C_{mn}^{(1)} \psi_m^{(0)}}_{\psi_n^{(1)}} + \lambda^2 \underbrace{\sum_m C_{mn}^{(2)} \psi_m^{(0)}}_{\psi_n^{(2)}} + \cdots$$

$$(H_0 + \lambda H_1)\left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots\right)$$

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

$$\left(\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots\right)$$

(This is valid for all small λ)

⊛ Match coefficients of λ^n on both sides for each n.

$$\lambda^0 : \underbrace{H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)}}_{\text{automatic !}}$$

$$\lambda^1 : H_0 \psi_n^{(1)} + H_1 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)}$$

$$\psi_n^{(0)} \longrightarrow |n\rangle$$

$$\psi_n^{(k)} = \sum_m C_{mn}^{(k)} |m\rangle \quad \text{in this notation.}$$

$$\boxed{H_0 \sum_m C_{mn}^{(1)} |m\rangle + H_1 |n\rangle = E_n^{(0)} \sum_m C_{mn}^{(1)} |m\rangle + E_n^{(1)} |n\rangle .}$$

(For $O(\lambda)$, i.e. equating coefficients of λ on both sides)

$$\Rightarrow \langle p| \left(\sum_m C_{mn}^{(1)} E_m^{(0)} |m\rangle + H_1 |n\rangle \right)$$

$$= \langle p| \left(E_n^{(0)} \sum_m C_{mn}^{(1)} |m\rangle + E_n^{(1)} |n\rangle \right)$$

unknowns

Take inner product with $|p\rangle$ on both sides

Assume there are bound states (discrete spectrum)

$$\Rightarrow C^{(1)}_{pn} \cancel{E^{(0)}_p} + \langle p | H_1 | n \rangle = E_n^{(0)} C^{(1)}_{pn} + E_n^{(1)} \delta_{np}.$$

$$\therefore \langle p | H_1 | n \rangle = \left(E_n^{(0)} - E_p^{(0)} \right) C^{(1)}_{pn} + E_n^{(1)} \delta_{np}.$$

Cases

① $p = n$

$$E_n^{(1)} = \langle n | H_1 | n \rangle$$

② $p \neq n$ $\longrightarrow$ fails for degenerate eigenvalues of H_0.

$$C^{(1)}_{pn} = \frac{\langle p | H_1 | n \rangle}{E_n^{(0)} - E_p^{(0)}}$$

Degenerate case :- Choose the eigenstates of H_0 such that $\langle p | H_1 | n \rangle = 0$ for $n \neq p$, $E_n^{(0)} = E_p^{(0)}$. (Take appropriate linear combinations)

Example Suppose $E_1^{(0)} = E_2^{(0)}$ & $\langle 1 | H_1 | 2 \rangle \neq 0$.

Take $|\tilde{1}\rangle = a_{11} |1\rangle + a_{21} |2\rangle$

$$|\tilde{2}\rangle = a_{12} |1\rangle + a_{22} |2\rangle$$

$$\boxed{|\tilde{i}\rangle = \sum_k a_{ki} |k\rangle \quad i, k = 1, 2}$$

$$\langle \tilde{i} | H_1 | \tilde{j} \rangle = \sum_k a^*_{ki} \langle k | H_1 \sum_l a_{lj} | l \rangle$$

$$= \sum_k \sum_l a^*_{ki} \underbrace{\langle k | H_1 | l \rangle}_{M_{kl} \text{ (matrix)}} a_{lj}$$

$$= \left(a^\dagger M a \right)_{ij}$$

a diagonalizes $\underbrace{M}_{\text{Hermitian matrix}}$.

$$\psi_n^{(1)} = \sum_m C_{mn}^{(1)} |m\rangle$$

$$\psi = \psi_n^{(0)} + \lambda \psi_n^{(1)} + O(\lambda^2) + \cdots$$

$$= |n\rangle + \lambda \sum_m C_{mn}^{(1)} \quad |m\rangle + O(\lambda^2)$$

We want $\langle\psi|\psi\rangle = 1$.

$$\Rightarrow 1 = \langle n|n\rangle + \lambda \sum_m C_{mn}^{(1)} \langle n/m\rangle + \lambda \sum_m C_{mn}^{(1)*} \langle m|$$

$$\underbrace{C_{nn}^{(1)} + C_{nn}^{(1)*}}_{} = 0. \quad \left(\text{Determines } C_{nn}^{(1)}.\right)$$

imaginary part of $C_{nn}^{(1)}$ is not determined. phase)

(There may be an arbitrary

$$e^{i(\phi_1 \lambda + \phi_2 \lambda^2 + \cdots)} \left(|n\rangle + \lambda \sum_m C_{mn}^{(1)} |m\rangle + \cdots\right)$$

$$(1 + i\phi_1 \lambda + \cdots\cdots)\left(|n\rangle + \lambda \sum_m C_{mn}^{(1)} |m\rangle + \cdots\right)$$

$$= |n\rangle + i\lambda \phi_1 |n\rangle + \lambda \sum_m C_{mn}^{(1)} |m\rangle + \cdots$$

$$C_{nn}^{(1)} \longrightarrow C_{nn}^{(1)} + i\phi_1$$

Can choose $C_{nn}^{(1)} = 0$.

$$\lambda^2 : \quad H_0 \psi_n^{(2)} + H_1 \psi_n^{(1)} = E_n^{(0)} \psi_n^{(2)} + E_n^{(1)} \psi_n^{(1)} + E_n^{(2)} \psi_n^{(0)}$$

$$H_0 \sum_m C_{mn}^{(2)} |m\rangle + H_1 \sum_m C_{mn}^{(1)} |m\rangle$$

$$= E_n^{(0)} \sum_m C_{mn}^{(2)} |m\rangle + E_n^{(1)} \sum_m C_{mn}^{(1)} |m\rangle + E_n^{(2)} |n\rangle$$

Now, we take inner product wrt $\langle p| \ldots$

$$C_{pn}^{(2)} E_p^{(0)} + \sum_{m \neq n} C_{mn}^{(1)} \langle p | H_1 | m \rangle$$

$C_{nn}^{(1)} = 0.$

$$= E_n^{(0)} C_{pn}^{(2)} + E_n^{(1)} C_{pn}^{(1)} + E_p^{(2)} \delta_{np}$$

Case 1 $\quad p = n$

$$E_n^{(2)} = \sum_{m \neq n} C_{mn}^{(1)} \langle n | H_1 | m \rangle$$

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

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

Case 2

$p \neq n$

$$C_{pn}^{(2)} \left(E_p^{(0)} - E_n^{(0)} \right) = - \sum_{m \neq n} C_{mn}^{(1)} \langle p | H_1 | m \rangle + E_n^{(1)} C_{pn}^{(1)} .$$

13. 10. 2011

Scattering problem :-

$$H = H_0 + \lambda H_1$$

$H_0 \Downarrow -\frac{\hbar^2}{2m} \nabla^2$; $\quad \lambda H_1$: potential

(Think in this way !)

(expand in powers of λ)

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \lambda v\right)\psi = E\psi$$

$E = \dfrac{\hbar^2 k^2}{2m} \longrightarrow$ Definition of k (we'll use k instead of E)

$v(r) \longrightarrow 0$ for $r \to \infty$. (assumption)

$$k = \sqrt{\frac{2mE}{\hbar^2}}.$$

[Remember $V = \lambda v$]

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

$\psi^{(0)} = e^{ikz}$ (Take $\psi^{(0)}$ as plane wave).

$$\therefore \left(-\frac{\hbar^2}{2m}\nabla^2 + \lambda v\right)\left(e^{ikz} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \cdots\right)$$
$$= \frac{\hbar^2 k^2}{2m}\left(e^{ikz} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \cdots\right)$$

First $\to$ λ^0 term

$$-\frac{\hbar^2\nabla^2}{2m}e^{ikz} = \frac{\hbar^2 k^2}{2m}e^{ikz} \quad \text{(Obviously true!)}$$

Second $\to$ λ^1 term (upto which we shall discuss)

$$-\frac{\hbar^2\nabla^2}{2m}\psi^{(1)} + v(\vec{r})\psi^{(0)} = \frac{\hbar^2 k^2}{2m}\psi^{(1)}.$$

not neccessarily spherically symmetric

$$\Rightarrow \boxed{\left(\nabla^2 + k^2\right)\psi^{(1)}(\vec{r}) = \frac{2m}{\hbar^2}v(\vec{r})\,e^{ikz}}$$

We have to solve this differential equation.

(Use Green's function technique)

$G(\vec{r}-\vec{r}\,')$ satisfies

$$(\nabla^2 + k^2)\, G(\vec{r}-\vec{r}\,') = \delta^{(3)}(\vec{r}-\vec{r}\,')$$

$$\psi^{(1)}(\vec{r}) = \frac{2m}{\hbar^2}\int G(\vec{r}-\vec{r}\,')\, v(\vec{r}\,')\, e^{ikz'}\, d^3r'$$

k^2 is present $\longrightarrow$ <u>Difference from electrostatics</u>

$$\psi^{(1)}(\vec{r}) \xrightarrow[\vec{r}\to\infty]{} \frac{e^{ikr}}{r} \text{ or } \cancel{\frac{e^{-ikr}}{r}}$$

✓ (radial part).

Actually, for $V(\vec{r}) \not\equiv V(r)$,

$$\psi^{(1)}(\vec{r}) \xrightarrow[\vec{r}\to\infty]{} \frac{e^{ikr}}{r} f(\theta,\phi) \text{ or } \cancel{\frac{e^{-ikr}}{r} f(\theta,\phi)}$$

$$G(\vec{r}-\vec{r}\,') = \int \frac{d^3k'}{\cancel{2m}(2\pi)^3}\, e^{i\vec{k}'\cdot(\vec{r}-\vec{r}\,')}\, \tilde{G}(\vec{k}')$$

$$\therefore (\nabla^2 + k^2)\, G(\vec{r}-\vec{r}\,')$$

$$= \int \frac{d^3k'}{(2\pi)^3}\, e^{i\vec{k}'\cdot(\vec{r}-\vec{r}\,')}\, (-k'^2 + k^2)\, \tilde{G}(\vec{k}')$$

$$\delta^3(\vec{r}-\vec{r}\,') = \int \frac{d^3k'}{(2\pi)^3}\, e^{i\vec{k}'\cdot(\vec{r}-\vec{r}\,')}$$

$$\Rightarrow \tilde{G}(\vec{k}') = \frac{1}{-k'^2 + k^2}.$$

$$\text{So, } G(\vec{r}-\vec{r}\,') = \int \frac{d^3k'}{(2\pi)^3}\, e^{i\vec{k}'\cdot(\vec{r}-\vec{r}\,')}\, \frac{1}{(-k'^2 + k^2)}$$

$$\underbrace{(\nabla^2 + k^2)\, G(\vec{r}-\vec{r}\,') = \delta^3(\vec{r}-\vec{r}\,')}_{\text{This equation should be rotationally invariant}}$$

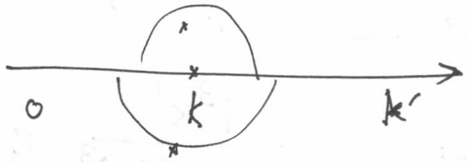
Use spherical polar coordinates (k', θ', ϕ') for $\vec{k}'$ with $\vec{r} - \vec{r}'$ as z-axis.

$$\therefore \; G(\vec{r} - \vec{r}') = \int \frac{1}{(2\pi)^3} k'^2 \sin\theta' \, dk' \, d\theta' \, d\phi' \times e^{i|\vec{r} - \vec{r}'| k' \cos\theta'} \cdot \frac{1}{(-k'^2 + k^2)}$$

$$= \frac{1}{(2\pi)^2} \int_0^\infty \frac{k'^2 \, dk'}{(k^2 - k'^2)} \frac{1}{i k' |\vec{r} - \vec{r}'|} \left(e^{i k' |\vec{r} - \vec{r}'|} - e^{-ik'|\vec{r} - \vec{r}'|} \right)$$

(Integrating and putting limits $\theta = 0$ and $\theta = \pi$).

$$\frac{-1}{(k'-k)(k'+k)}$$



$$\frac{1}{(k'-k)} \Rightarrow \boxed{\frac{1}{(k'-k+i\epsilon)} \quad \text{or} \quad \frac{1}{(k'-k-i\epsilon)}}.$$

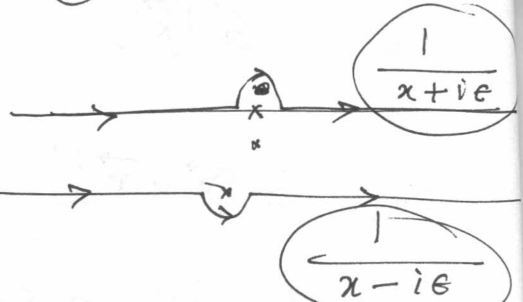
Bypass the poles or any linear combination

(all of these work as the differential equation remains unaltered).

$$\frac{1}{x+i\epsilon} - \frac{1}{x-i\epsilon} = (2\pi i) \, \delta(x) \quad ?$$

$$\int f(x) \, \delta(x) = f(0)$$

$$\int f(x) \left(\frac{1}{x+i\epsilon} - \frac{1}{x-i\epsilon} \right)$$



$$\int f(x) \frac{dx}{x} = 2\pi i f(0)$$

Take the difference between $\left(\dfrac{1}{k'-k+i\epsilon}\right)$ and $\left(\dfrac{1}{k'-k-i\epsilon}\right)$.

You have a solution for the ~~in~~ homogeneous equation.

$$G(\vec{r}-\vec{r}\,') = \frac{1}{(2\pi)^2}\int_0^\infty k'^2\,dk'\,\frac{1}{ik'|\vec{r}-\vec{r}\,'|}\,\frac{(-1)}{k'^2-k^2}\left(e^{ik'|\vec{r}-\vec{r}\,'|} - e^{-ik'|\vec{r}-\vec{r}\,'|}\right)$$

$$\left\{\begin{array}{l}\text{pole at } k' = k + i\epsilon \\ \quad \epsilon : +ve \text{ or } -ve\end{array}\right\}$$

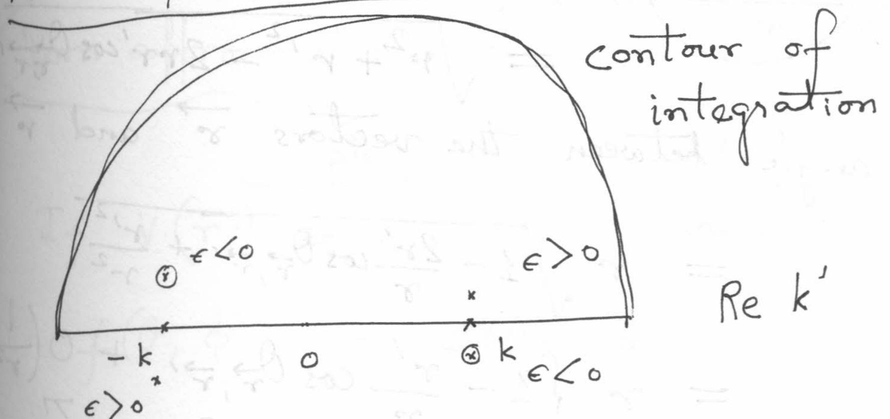
Change variable $k' \to -k'$ in the second integral.

$$= \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} k'^2\,dk'\,\frac{1}{ik'|\vec{r}-\vec{r}\,'|}\,\frac{(-1)}{k'^2-k^2}\,e^{ik'|\vec{r}-\vec{r}\,'|}$$

For $k' \to$ imaginary part $\Rightarrow$ (this damps out)

(pole at $k' = k + i\epsilon$).

Another pole at $k' = -k - i\epsilon$.



$\epsilon > 0$: Use residue theorem.

Pole at $k + i\epsilon$ $(\epsilon > 0)$

$$\therefore\; G(\vec{r}-\vec{r}\,') = (2\pi i)\,\frac{1}{(2\pi)^2}\,\frac{1}{i|\vec{r}-\vec{r}\,'|}\,k\,\frac{(-1)}{2k}\,e^{ik|\vec{r}-\vec{r}\,'|}$$

$$G(\vec{r}-\vec{r}') = (-)\frac{1}{4\pi} \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}.$$

If we had chosen $\epsilon < 0$, we would have had

$$G(\vec{r}-\vec{r}') = - - - - \cdot \frac{e^{-ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}$$

{ not wanted. }

So, we get ~~an~~ a unique, unambiguous Green's function.

$$\psi_\theta^{(1)}(\vec{r}) = \frac{2m}{\hbar^2} \int d^3r' \, G(\vec{r}-\vec{r}') \, v(\vec{r}') e^{ikz'}$$

$$= \frac{2m}{\hbar^2}\left(-\frac{1}{4\pi}\right) \int d^3r' \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} v(\vec{r}') e^{ikz'}$$

For scattering problem

$r \to \infty$ $\quad \frac{e^{ikr}}{r}$ $\quad |\vec{r}-\vec{r}'| = (r^2 + r'^2 - 2\vec{r}\cdot\vec{r}')^{1/2}$

$$= \sqrt{r^2 + r'^2 - 2rr'\cos\theta_{\vec{r},\vec{r}'}}$$

$\theta_{\vec{r},\vec{r}'} \to$ angle between the vectors $\vec{r}$ and $\vec{r}'$.

$$= r\sqrt{1 - \frac{2r'}{r}\cos\theta_{\vec{r},\vec{r}'} + \frac{r'^2}{r^2}}$$

$$= r\left\{1 - \frac{r'}{r}\cos\theta_{\vec{r},\vec{r}'} + O\left(\frac{1}{r^2}\right)\right\}$$

not significant

$$\therefore |\vec{r}-\vec{r}'| \approx r - r'\cos\theta_{\vec{r},\vec{r}'}$$

(Dropping $O\left(\frac{1}{r}\right)$ terms)

For large r, $\psi^{(1)}(\vec{r}) = \frac{e^{ikr}}{r}(-)\frac{m}{2\pi\hbar^2} \times I$ where

$$\underbrace{I = \int d^3r' \, e^{-ikr'\cos\theta_{\vec{r},\vec{r}\,'} + ikz} \, v(\vec{r}\,')}$$

$$\psi = e^{ikz} + f(\theta,\phi)\frac{e^{ikr}}{r} \quad \text{for large } r.$$

$$f(\theta,\phi) = -\frac{m}{2\pi\hbar^2}\int d^3r' \, e^{-ikr'\cos\theta_{\vec{r},\vec{r}\,'} + ikz} \, \lambda v(\vec{r}\,')$$

$\lambda v(\vec{r}\,') \leftarrow V(\vec{r}\,')$

<u>Spherical polar coordinates</u>

$$\vec{r} = (r\sin\theta\cos\phi, \; r\sin\theta\sin\phi, \; r\cos\theta)$$

$$\vec{r}\,' = (r'\sin\theta'\cos\phi', \; r'\sin\theta'\sin\phi', \; r'\cos\theta')$$

$$\vec{r}\cdot\vec{r}\,' = rr'\underbrace{\left(\sin\theta\sin\theta'\cos(\phi-\phi') + \cos\theta\cos\theta'\right)}_{\cos\theta_{\vec{r},\vec{r}\,'}}.$$

$$f(\theta,\phi) = -\frac{m}{2\pi\hbar^2}\int r'^2\sin\theta'\,d\theta'\,d\phi' \times \cancel{e^{-ikr'}}$$
$$e^{-ikr'\{\sin\theta\sin\theta'\cos(\phi-\phi') + \cos\theta\cos\theta'\}} \times$$

Born approximation $\quad e^{+ikr'\cos\theta'} \quad V(\vec{r}\,')$

<u>Upto $O(\lambda)$.</u>

If $V(\vec{r}\,') \equiv V(r')$, (spherically symmetric)

$$f(\theta,\phi) \equiv f(\theta) \text{ only}.$$

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<u>14. 10. 2011</u>

We treat some problems as applications of time-independent perturbation theory.

Simple Harmonic Oscillator

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2$$

Add $\lambda H_1 = \frac{1}{2} \lambda q^2$

Let the corrected 'ω' be $\omega' \Rightarrow$ <u>connect</u>

$$\frac{1}{2} m \omega'^2 = \frac{1}{2} m \omega^2 + \frac{\lambda}{2}$$

$$\Rightarrow \quad \omega'^2 = \omega^2 + \frac{\lambda}{m}$$

$$\Rightarrow \quad \omega' = \sqrt{\omega^2 + \frac{\lambda}{m}}.$$

$$E_0 = \frac{1}{2} \hbar \omega = \frac{1}{2} \hbar \sqrt{\omega^2 + \frac{\lambda}{m}}.$$

(This is exact.)

Now, find the ground state energy to order λ using first order perturbation theory.

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

$$\Rightarrow \quad E_0 = E_0^{(0)} + \lambda \langle 0 | H_1 | 0 \rangle$$

$$|0\rangle = N e^{-m\omega q^2/2\hbar}$$

$$\langle 0 | 0 \rangle = \int_{-\infty}^{\infty} |N|^2 \left(e^{-\frac{m\omega q^2}{2\hbar}}\right)^* \left(e^{-\frac{m\omega q^2}{2\hbar}}\right) dq$$

$$= 1.$$

$$\Rightarrow \quad |N|^2 \int_{-\infty}^{\infty} e^{-\frac{m\omega q^2}{\hbar}} dq = 1$$

$$\Rightarrow |N|^2 \sqrt{\frac{\pi\hbar}{m\omega}} = 1$$

$$\therefore |0\rangle = \sqrt[4]{\left(\frac{\pi\hbar}{m\omega}\right)^{-1}} e^{-\frac{m\omega q^2}{2\hbar}}$$

$$\langle 0|H_1|0\rangle = \int_{-\infty}^{\infty} \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \left(e^{-\frac{m\omega q^2}{2\hbar}}\right)^* \left(\frac{1}{2}\lambda q^2\right) \times \left(e^{\frac{m\omega q^2}{2\hbar}}\right) dq$$

$$= \frac{1}{2}\lambda \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \int_{-\infty}^{\infty} q^2 e^{-\frac{m\omega q^2}{\hbar}} dq$$

$$= \frac{1}{2}\lambda \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} \frac{\sqrt{\pi}}{2\left(\frac{m\omega}{\hbar}\right)^{3/2}}$$

$$\therefore E_0 = \text{- - - -} \quad \text{(after some calculation)}$$

$$= \frac{1}{2}\hbar\omega + \frac{\hbar\lambda}{4m\omega}$$

But, you can do the problem using ladder operators

$$\left.\begin{aligned} a &= \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(q + \frac{i}{m\omega} p\right) \\ a^\dagger &= \left(\frac{m\omega}{2\hbar}\right)^{1/2} \left(q - \frac{i}{m\omega} p\right) \end{aligned}\right\}$$

Take $\lambda H_1 = \lambda q^4$.

Use perturbation theory.

$$E_0^{(1)} = \lambda \langle 0| q^4 |0\rangle$$

$$= \lambda \langle 0| q^2 q^2 |0\rangle$$

$$q = \sqrt{\frac{\hbar}{2m\omega}} \left(a + a^\dagger\right)$$

$$\langle n, l, s=\tfrac{1}{2}, j, m_j' \,|\, H_1 \,|\, n, l, s=\tfrac{1}{2}, j, m_j \rangle$$

$\longrightarrow$ Are these matrix elements diagonal ?

(J_z commutes with H_1. So, the matrix is already diagonal.)

Calculate this(!)

$$\langle n, l, s=\tfrac{1}{2}, j, m_j | \, H_1 \left(\sum_{m_l, m_s} C^{j \; l \; s}_{m_j \, m_l \, m_s} | n, l, m_l, s=\tfrac{1}{2}, m_s \rangle \right)$$

$$= \sum_{m_l, m_s} \langle n, l, s=\tfrac{1}{2}, j, m_j \,|\, n, l, m_l, s, m_s \rangle \; C^{j \; l \; s}_{m_j \, m_l \, m_s} \times \left(-\mu_B B \left(g_L m_l + g_s m_s\right)\right)$$

$$= \sum_{m_l, m_s} \left| C^{j \; l \; s}_{m_j \, m_l \, m_s} \right|^2 \left(-\mu_B B \left(g_L m_l + g_s m_s\right)\right)$$

$$= -\mu_B B \, g_J \, m_j$$

We define g_J in this manner.

What if dominant contribution comes from magnetic field ? (strong fields)

$$H_0 = \frac{p^2}{2m} - \frac{C}{r} - \frac{\mu_B B}{\hbar} \left(g_L L_z + g_s S_z\right)$$

$$\lambda H_1 = \lambda f(r) \, \vec{L} \cdot \vec{S} .$$

Basis

$$| n, l, m_l, s=\tfrac{1}{2}, m_s \rangle$$

Calculate $E_0^{(1)}$.

- - - - - Finally you'll get

$$E_0^{(1)} = \lambda \sum_{j, m_j} \frac{\left| C^{j \;\; l \;\; s}_{m_j \; m_l \; m_s} \right|^2}{2} \times$$

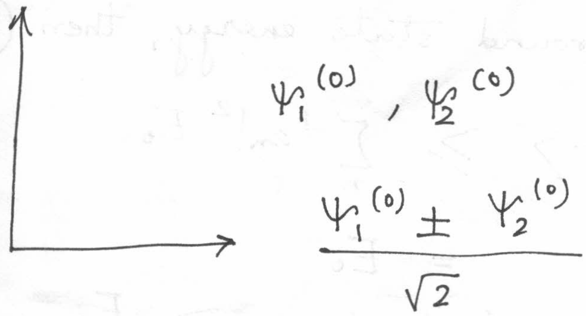
$$\int \left[f_{nl}^*(r) \, f_{nl}(r) \, r^2 \, dr \;\, f(r) \right] \times$$

$$\left(j(j+1) - l(l+1) - s(s+1) \right) \hbar^2$$

02. 11. 2011

$$E_n^{(1)} = \langle n | H_1 | n \rangle$$

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



$$\psi_n^{(1)} = \frac{\langle p | H_1 | n \rangle}{E_p - E_n}$$

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

$$\begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} \Rightarrow \begin{pmatrix} 1 \\ 1 \end{pmatrix} \; \& \; \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\underbrace{\begin{pmatrix} 1 \\ 0 \end{pmatrix} \; \& \; \begin{pmatrix} 0 \\ 1 \end{pmatrix}}$$

(don't go to this) [for small λ]

$$\sum_m \frac{\langle n | H_1 | m \rangle \langle m | H_1 | p \rangle}{E_n^{(0)} - E_m^{(0)}} = M_{np}$$

(2nd order matrix)

Method of variation

- Most useful for ground state energy

$$H\Psi_n = E_n \Psi_n$$

Take a state $|\Psi\rangle = \sum_n a_n \Psi_n$.

$$= \sum_n a_n |n\rangle.$$

$\sum_n |a_n|^2 = 1$. (normalization)

$$\langle m|n\rangle = \delta_{mn}$$

$$\langle\Psi|H|\Psi\rangle = \sum_n |a_n|^2 E_n$$

If E_0 is the ground state energy, then $E_n \geq E_0$.

So, $\langle\Psi|H|\Psi\rangle \geq \sum_n |a_n|^2 E_0$

$$= E_0$$

For any state $|\Psi\rangle$, $\underbrace{\langle\Psi|H|\Psi\rangle \geq E_0}_{\text{(Utilize)}}$. (well known!)

Harmonic Oscillator

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + \frac{1}{2}kq^2$$

Trial wave function

$= Ne^{-\alpha q^2}$ (α is unknown)

$$N^2 \int_{-\infty}^{\infty} e^{-2\alpha q^2}\, dq = 1$$

$$\Rightarrow \quad N^2 \cdot \cancel{2} \times \sqrt{\frac{\pi}{2\alpha}} = 1$$

$$\Rightarrow \quad N^2 = \sqrt{\frac{2\alpha}{\pi}}.$$

$$\langle\psi|H|\psi\rangle = N^2\int_{-\infty}^{\infty} e^{-\alpha q^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dq^2}+\frac{1}{2}kq^2\right)e^{-\alpha q^2}\,dq$$

$$= N^2\int_{-\infty}^{\infty}\left[\frac{\hbar^2}{2m}\left(\frac{d}{dq}e^{-\alpha q^2}\right)^2 + \frac{1}{2}kq^2e^{-2\alpha q^2}\right]dq$$

$$= N^2\int_{-\infty}^{\infty}\left(\frac{\hbar^2}{2m}\left\{4\alpha^2q^2\right\} + \frac{1}{2}kq^2\right)e^{-2\alpha q^2}\,dq$$

$$= N^2\left(\frac{2\hbar^2\alpha^2}{m}+\frac{k}{2}\right)\int_{-\infty}^{\infty} e^{-2\alpha q^2}q^2\,dq$$

$$= N^2\left(\frac{2\hbar^2\alpha^2}{m}+\frac{k}{2}\right)\times\frac{\sqrt{\pi}}{(2\alpha)^{3/2}}\cdot\frac{1}{2}.$$

$$\therefore \langle\psi|H|\psi\rangle = \left(\frac{2\hbar^2\alpha^2}{m}+\frac{k}{2}\right)\frac{1}{2}\cdot\frac{1}{2\alpha}$$

$$= \left(\frac{\hbar^2\alpha}{2m}+\frac{k}{8\alpha}\right)$$

Minimum is at $\dfrac{\hbar^2}{2m} - \dfrac{k}{8\alpha^2} = 0.$

$$\Rightarrow \alpha^2 = \frac{km}{4\hbar^2}$$

$$\Rightarrow \alpha = \frac{\sqrt{mk}}{2\hbar}.$$

$\cancel{k = m\omega^2}$ $$\langle\psi|H|\psi\rangle_{min.} = \frac{\hbar^{\cancel{2}}}{2m}\frac{\sqrt{mk}}{2\cancel{\hbar}} + \frac{k\cdot 2\hbar}{\cancel{8}_4\sqrt{mk}}$$

Our trial wave f^n was too correct!
$$= \frac{\hbar}{4}\left(\sqrt{k/m}+\sqrt{k/m}\right)$$

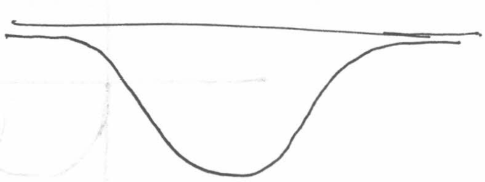
$\sqrt{k/m} = \omega$

$$= \frac{1}{2}\hbar\omega.$$

Exact ground state energy

Try a more non-trivial example

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + V(q)$$



$$V(q) = -V_0\,e^{-aq^2}.$$

$N e^{-\alpha q^2} \longrightarrow$ trial wavefunction

$$N^2 = \sqrt{\frac{2\alpha}{\pi}}.$$

$$\langle \psi | H | \psi \rangle = \frac{2\hbar^2\alpha^2}{m} \times \frac{1}{4\alpha} + \text{2nd term}$$

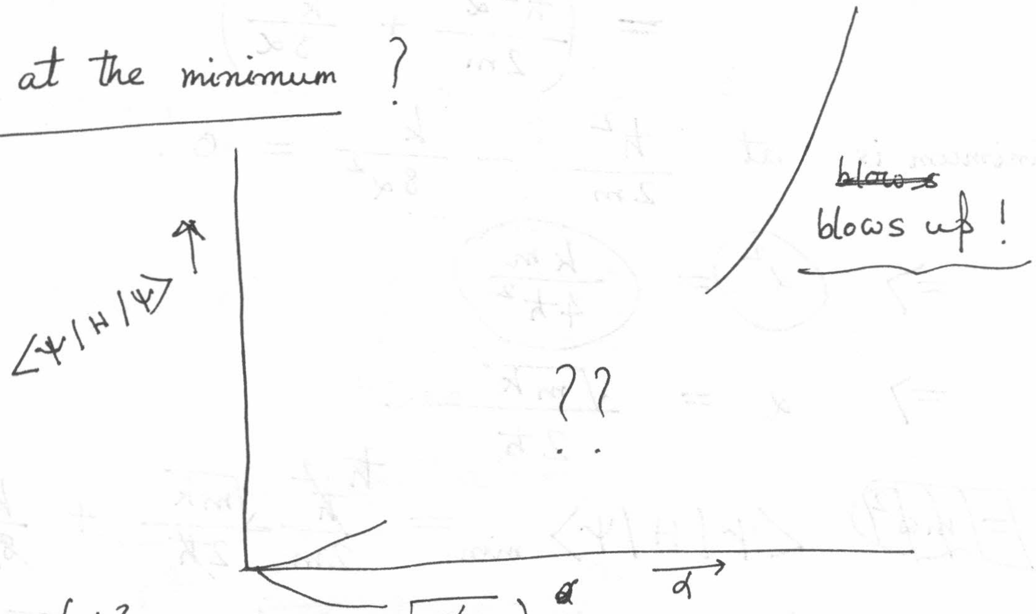
$$- V_0 \int_{-\infty}^{\infty} N^2 e^{-2\alpha q^2 - a q^2}$$

$$= - V_0 \sqrt{\frac{2\alpha}{\pi}} \sqrt{\frac{\pi}{2\alpha + a}}$$

So, $$\langle \psi | H | \psi \rangle = \frac{\hbar^2 \alpha}{2m} - V_0 \sqrt{\frac{2\alpha}{2\alpha + a}}$$

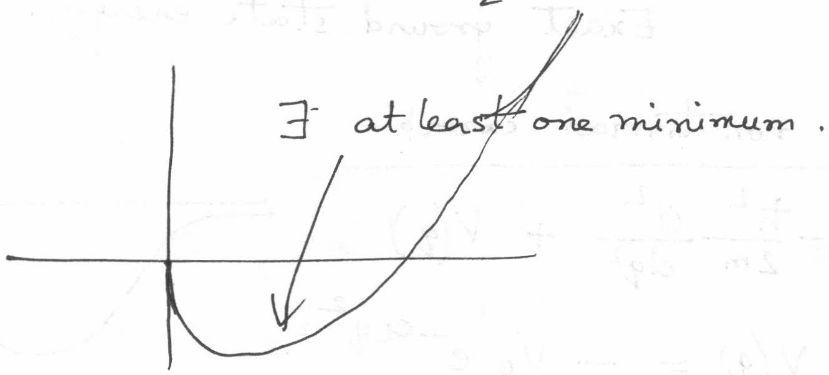
$$= \frac{\hbar^2 \alpha}{2m} - V_0 \sqrt{\frac{\alpha}{\alpha + a/2}}.$$

Look at the minimum ?



$$\frac{d}{d\alpha}\left(\frac{\hbar^2 \alpha}{2m} - V_0 \sqrt{\frac{\alpha}{\alpha + a/2}}\right)$$

$$= \frac{\hbar^2}{2m} - V_0 \sqrt{\frac{\alpha}{\alpha + \frac{a}{2}}} \, \frac{1}{2} \left(\frac{1}{\alpha} - \frac{1}{\alpha + \frac{a}{2}}\right).$$



* We can find α which minimizes $\langle\psi|H|\psi\rangle$.

Try : $\underbrace{N e^{-\alpha q^2}(1+\beta q^2)}$.

(Ground state is even!)

$\longrightarrow$ $(H|\psi\rangle - E|\psi\rangle) \longrightarrow$ calculate the norm and check.

1st excited state :-

$$|\psi\rangle = \sum_n a_n |\psi_n\rangle$$

$$\langle\psi|H|\psi\rangle = \sum_n |a_n|^2 E_n \geqslant E_1 \text{ if } a_0 = 0.$$

* How can we ensure $a_0 = 0$ for trial wavefunction

Method 1 :- (General case)

If we know approximate $|\psi_0\rangle$, then choose

$|\psi\rangle$ such that $\langle\psi|\psi_0\rangle = 0$.

$\longrightarrow$ Errors accumulate !

* But, in some cases, you may be luckly.

Harmonic Oscillator

$\longrightarrow$ odd f^{n} (✓)

For $V = V_0 e^{-aq^2}$, choose

Ex: $\leadsto \psi = N q e^{-\alpha q^2}$ for first excited state.

$\times\ (1+\beta q^2) \longrightarrow$ Further improvement

Suppose, we have a 3d spherically symmetric potential $V(r)$.

Ground State $\longrightarrow$ ✓ (spherically symmetric)

$$|\, l = \cancel{1}, m\rangle = f_l(r)\, Y_{lm}(\theta,\phi)$$

Fix l. Ask which wavefunction has minimum energy?

$$\langle \psi_{lm} | H | \psi_{lm}\rangle$$

$$\psi_{lm} = \sum_n a_n |n, l, m\rangle$$

$$\langle \psi_{lm} | H | \psi_{lm}\rangle = \sum_n |a_n|^2 E_{nl}$$

$$\geqslant E_{0l}$$

03.11.2011

WKB Approximation

- Semiclassical approximation

$\longrightarrow$ $\underbrace{\hbar \text{ is small}}$ (meaning will be clear later!)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dq^2} + V(q)\,\psi(q) = E\psi(q)$$

$$\Rightarrow -\hbar^2 \frac{d^2\psi}{dq^2} = 2m\left(E - V(q)\right)\psi(q) = \{K_1(q)\}^2\psi$$

$$K_1(q) = \sqrt{2m\,(E - V(q))}$$

Introduce $K_2(q) = \sqrt{2m\,(V(q) - E)} = iK_1(q)$

Define $\phi(q)$ via the equation $\psi(q) = e^{i\phi(q)}$

$$\therefore \frac{d\psi}{dq} = i\,\frac{d\phi(q)}{dq}\,e^{i\phi(q)}$$

$$\frac{d^2\psi}{dq^2} = \left\{ i\,\frac{d^2\phi(q)}{dq^2} - \left(\frac{d\phi(q)}{dq}\right)^2 \right\} e^{i\phi(q)}$$

$$\Rightarrow -i\hbar^2 \frac{d^2\phi(q)}{dq^2} + \hbar^2\left\{\frac{d\phi(q)}{dq}\right\}^2 = \underline{\underline{K_1^2(q)}}\ \cancel{\phi(q)}$$

? Try $\phi(q) = \frac{1}{\hbar}\phi_0(q) + \phi_1(q) + \hbar\,\phi_2(q) + \cdots$

and substitute.

We get
$$-i\hbar^2\left(\frac{1}{\hbar}\frac{d^2\phi_0}{dq^2} + \frac{d^2\phi_1}{dq^2} + \hbar\frac{d^2\phi_2}{dq^2} + \cdots\right)$$
$$+\left(\frac{d\phi_0}{dq}(q) + \hbar\frac{d\phi_1(q)}{dq} + \hbar^2\frac{d\phi_2(q)}{dq} + \cdots\right)^2$$
$$= \{K_1(q)\}^2$$

$O(\hbar^0)$:- $\quad \frac{d\phi_0(q)}{dq} = \pm K_1(q)$

$$\Rightarrow \boxed{\phi_0 = \pm\int_{q_0}^{q} K_1(q')\,dq'.}$$

$$\Psi = A e^{i\frac{\phi_0}{\hbar}} + \cdots + B e^{-i\frac{\phi_0}{\hbar}} + \cdots$$
$$= A e^{\frac{i}{\hbar}\int^q K_1(q)\,dq + \cdots} + B e^{-\frac{i}{\hbar}\int^q K_1(q)\,dq + \cdots}$$

Let's go one step further.

$O(\hbar)$:- $\quad -i\cancel{\hbar}\frac{d^2\phi_0}{dq^2} + 2\frac{d\phi_0}{dq}\frac{d\phi_1}{dq} = 0$

$$\Rightarrow \frac{d\phi_1}{dq} = \frac{i}{2}\frac{1}{\left(\frac{d\phi_0}{dq}\right)}\left(\frac{d^2\phi_0}{dq^2}\right)$$
$$= \frac{i}{2}\frac{d}{dq}\left(\ln\frac{d\phi_0}{dq}\right)$$

$$\phi_1 = \frac{i}{2}\ln(\pm K_1) + \text{constant}.$$

$$\therefore \Psi = e^{i\left(\frac{\phi_0}{\hbar} + \phi_1\right) + \cdots}$$

$$= e^{\pm \frac{i}{\hbar} \int_{q_0}^{q} K_1(q')\, dq' - \frac{1}{2} \ln K_1 + \text{const.}}$$

$$= \frac{1}{\sqrt{K_1(q)}}\, e^{\pm \frac{i}{\hbar} \int_{q_0}^{q} K_1(q')\, dq'} + O(\hbar)$$

important term

small in $\hbar \to 0$ limit

WKB approx.

$$\psi(q) = \frac{A}{\sqrt{K_1(q)}}\, e^{\frac{i}{\hbar} \int_{q_0}^{q} K_1(q')\, dq'} + \frac{B}{\sqrt{K_1(q)}}\, e^{-\frac{i}{\hbar} \int_{q_0}^{q} K_1(q')\, dq'}$$

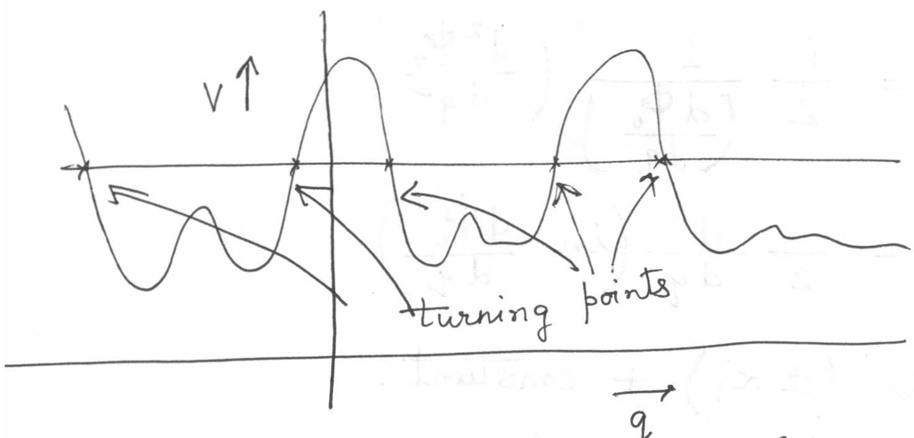
$(E > V(q).)$

If $E < V(q)$,

$$\psi(q) = \frac{\tilde{A}}{\sqrt{K_2(q)}}\, e^{-\frac{1}{\hbar} \int_{q_0}^{q} K_2(q')\, dq'} + \frac{\tilde{B}}{\sqrt{K_2(q)}}\, e^{\frac{1}{\hbar} \int_{q_0}^{q} K_2(q')\, dq'}$$

$$\int_{q_0}^{q_1} K_1(q')\, dq' = \int_{q_0}^{q} \sqrt{2m\,(E - V(q'))}\, dq' = S_{cl} \quad \text{(classical action)}$$

If $S \gg \hbar \longrightarrow$ good approximation



$$- i\hbar^2 \left(\frac{1}{\hbar} \frac{d^2\phi_0}{dq^2} + \frac{d^2\phi_1}{dq^2} + \hbar \frac{d^2\phi_2}{dq^2} + \cdots \right)$$

$$+\left(\frac{d\phi_0}{dq} + \hbar\,\frac{d\phi_1}{dq} + \hbar^2\,\frac{d\phi_2}{dq} + \cdots\right)^2 = \left\{K_1(q)\right\}^2.$$

Let's look at $\hbar^n$ term (!)

$$-i\,\frac{d^2\phi_{n-1}}{dq^2} + 2\,\frac{d\phi_0}{dq}\,\frac{d\phi_n}{dq} + 2\,\frac{d\phi_1}{dq}\,\frac{d\phi_{n-1}}{dq} + \cdots = 0.$$

Determining equation for ϕ_n

$$\frac{d\phi_n}{dq} = \left(\frac{d\phi_0}{dq}\right)^{-1}\left\{\left(\tfrac{1}{2}\right) i\,\frac{d^2\phi_{n-1}}{dq^2} - \frac{d\phi_1}{dq}\,\frac{d\phi_{n-1}}{dq} - \cdots\right\}$$

- Choose units natural to the particle and ensure that ϕ's are of order 1. Then $\hbar$ is small ~~compared~~ in these units and $(\hbar)^n$ becomes smaller and smaller as we increase n.

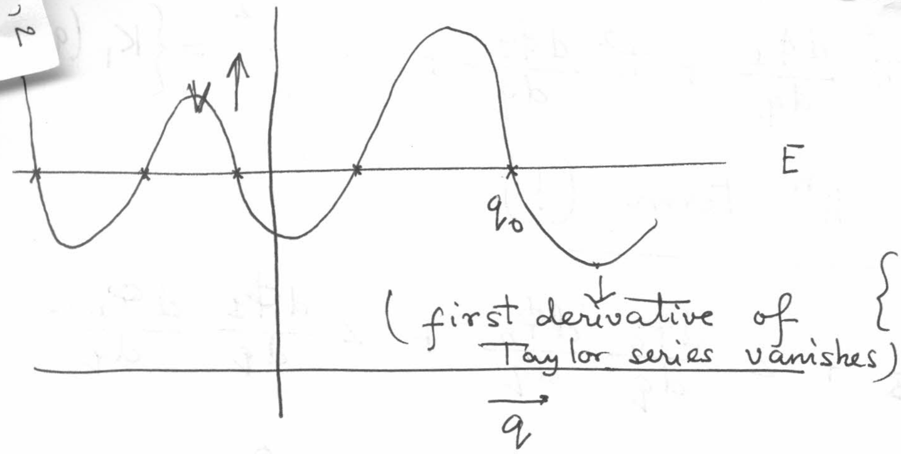
(*) If $\frac{d\psi_0}{dq} \longrightarrow 0$, the approximation is breaking down! How to match?

$$\phi_0 = \int_{q_0}^{q} K_1(q')\,dq'$$

$$\therefore \frac{d\phi_0}{dq} = \pm K_1(q).$$

The WKB approximation breaks down at the turning points. (or $\overset{K_1(q)}{K_2(q)} = 0$.)

- Solve around the turning points using a different approximation. Then match with the WKB solutions at the two ends.



$\{K_1(q)\}^2 = C(q-q_0)^n + \cdots$ (generically)

$$-\hbar^2 \frac{d^2\psi}{dq^2} = \underbrace{\{K_1(q)\}^2}_{2m(E-V(q))} \psi(q)$$

(For most purposes, $n = 1$ is good enough!)

$$= C(q-q_0)^n \psi(q)$$

for $E > V(q)$

$C, D > 0$

$$-\hbar^2 \frac{d^2\psi}{dq^2} = -D\,(q-q_0)^n \,\psi(q)$$

for $E < V(q)$.

$q > q_0$

OR $\quad C > 0$ For $E > V(q)$ and

$\quad C < 0$ " $E < V(q)$.

$q \longrightarrow -q \quad \Rightarrow \quad \tilde{q} - q_0 = q_0 - q$.

Define $$\xi = \int_{q_0}^{q} \sqrt{2m(E - V(q'))}\, dq'$$

$$= \int_{q_0}^{q} \sqrt{C(q'-q_0)^n}\, dq'$$

independent solutions to Bessel's eqn:

Solution :- $$\psi(q) = \frac{\xi(q)^{-1/2}}{K_1(q)^{1/2}} \left\{ A J_\ell\left(\frac{\xi}{\hbar}\right) + B Y_\ell\left(\frac{\xi}{\hbar}\right) \right\}$$

$$\ell = \frac{1}{n+2}$$

$$J_l(x) \xrightarrow[x]{\text{large}} \frac{1}{\sqrt{\xi}} \cos\left(\frac{\xi}{\hbar} - \frac{l\pi}{2} - \frac{\pi}{4}\right)$$

$$Y_l(x) \xrightarrow[x]{\text{large}} -\frac{1}{\sqrt{\xi}} \sin\left(\frac{\xi}{\hbar} - \frac{l\pi}{2} - \frac{\pi}{4}\right)$$

Independent solutions

$$\frac{1}{\sqrt{K_1(q)}} e^{\pm i \frac{\xi(q)}{\hbar}}$$

- We can match now (!)

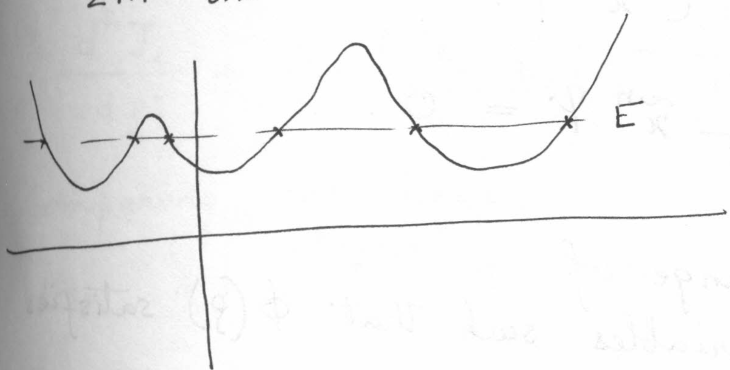
09.11.2011

$$x^+ = A^{(l=1)}_{m=1} \qquad \frac{\langle l, m \mid x^+ \mid l' m' \rangle}{\langle l, m'' \mid z \mid l' m''' \rangle}$$

$$z = A^{(l=1)}_{m=0} \qquad x = \frac{x^+ + x^-}{2}$$

$$\frac{C^{\,l \;\; 1 \;\; l'}_{\,m \;\; 1 \;\; m'}}{C^{\,l \;\; 1 \;\; l'}_{\,m'' \;\; 0 \;\; m'''}} \times \frac{\langle l \| A \| l' \rangle}{\langle l \| A \| l' \rangle}$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$



Away from the turning points, $\psi(x)$ has the form –

$$\psi(x) = \boxed{(K_1(x))^{-1/2} e^{\pm i \int_c^x K_1(x') dx'}} \quad \text{for } E > V(x)$$

$$\left(K_1(x) = \sqrt{2m(E - V(x))} \; . \right)$$

$$= (K_2(x))^{-1/2} e^{\pm \int_c^x K_2(x') dx'} \quad \text{for } E < V(x)$$

$$\left(K_2(x) = \sqrt{2m(V(x) - E)} \; . \right)$$