Quantum Mechanics - I

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[Wave Mechanics in 3D]

Some general properties.

① Discrete & continuous spectra

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

Assume $V(r) \to 0$ as $r \to \infty$.

The spectrum of eigenvalues E may be discrete and/or continuous.

ψ : with a discrete eigenvalue E is normalizable -

$$\int_0^\infty r^2 dr \int |\psi|^2 d\Omega = 1$$

$\Rightarrow$ ψ must diminish to zero more rapidly than $\frac{1}{\sqrt{r^3}}$ as $r \to \infty$

$|\psi|^2 \sim r^{-p}$ $\left(\int_0^\infty dr\, r^{-p+2} = \frac{1}{(3-p)} r^{3-p}\Big|_0^\infty \right)$

$\Rightarrow \psi$ is a bound state ; a stationary state localized in a finite region of space.

if ψ with E in the continuous spectrum is not normalizable $\Rightarrow$ extends to ∞

$E < 0 \Rightarrow$ discrete spectrum.

$\because E = \underbrace{\langle T \rangle}_{>0} + \langle V \rangle \Rightarrow 0 > E > \langle V \rangle$, However $V(r) \to 0$ as $r \to \infty$

$\Rightarrow$ ψ must be a bound state.

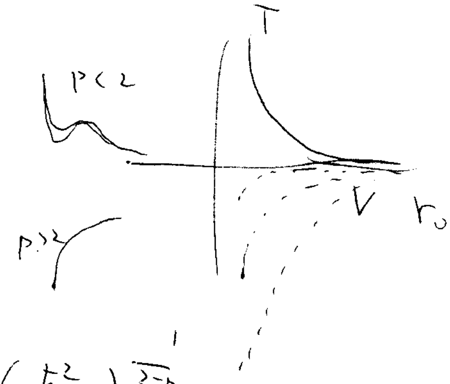
or reversely speaking, the existence of bound states $\Rightarrow$ $V < 0$ in some finite region of space

② Power law potential

$$r \to 0, \quad V(r) \rightsquigarrow \frac{-k}{r^p} \qquad p, k > 0$$

If there is a bound state with WF centered at $r = 0$. and a spatial extent $\sim r_0$. Then $\Delta p \simeq \frac{\hbar}{r_0}$, $\langle T \rangle \simeq \frac{1}{2m}\left(\frac{\hbar}{r_0}\right)^2$

$$[k] = \frac{M L^{2+p}}{T^2}$$



$\langle V \rangle \sim -k r_0^{-p}$

$$\Rightarrow \quad E \sim \frac{\hbar^2}{2m}\frac{1}{r_0^2} - \frac{k}{r_0^p}$$

minimum

$$0 = \frac{\partial E}{\partial r_0} = -\frac{\hbar^2}{m r_0^3} + \frac{pk}{r_0^{p+1}} \quad \Rightarrow \quad r_0 = \left(\frac{\hbar^2}{pmk}\right)^{\frac{1}{2-p}}$$

$$E_{min} \simeq \frac{\hbar^2}{2m}\left(\frac{pmk}{\hbar^2}\right)^{\frac{2}{2-p}} - k\left(\frac{pmk}{\hbar^2}\right)^{\frac{p}{2-p}}$$

$$\frac{\partial^2 E}{\partial r_0^2} = +\frac{3\hbar^2}{m r_0^4} - \frac{p(p+1)k}{r_0^{p+2}} > 0 \quad \Rightarrow \quad r_0^{p-2} > \frac{p(p+1)km}{3\hbar^2} \quad \Rightarrow \boxed{2>p}$$

$p>2$. $r_0 \to 0$, $E \downarrow$, no lower bound.

If $p<2$, there is a r_0 to minimize E.

$\boxed{p=2 \text{ is special}}$

Now consider a potential that $V \to -kr^{-p}$ when $r \to \infty$

If a state (corresponding to a particle) localized in a shell-like region $[r_0, r_0+dr)$ $(dr \ll r_0)$

then $\Delta p \sim \frac{\hbar}{dr}$, $\Rightarrow \langle T \rangle \sim \frac{\hbar^2}{2m(dr)^2}$

and $\langle V \rangle \sim \frac{-k}{r_0^p}$, $E \sim \frac{\hbar^2}{2m r_0^2 \left(\frac{dr}{r_0}\right)^2} - \frac{k}{r_0^p}$

now, increase r_0 but keep $\frac{dr}{r_0}$ fixed.

for $p<2$, E must be negative for sufficiently large r_0.

$\Rightarrow$ bound state with appreciable size in some region arbitrarily far from the origin. $\Rightarrow$ bound state with arbitrarily small negative E $\Rightarrow$ ∞ # of bound states near $E=0$

for $p>2$, there is a last bound state with finite negative E

no bound states for $E \sim 0$.

(3) Feynman-Hellmann theorem,

$$\langle \psi | \psi \rangle = 1$$

$$\frac{\partial E}{\partial \lambda} = \frac{\partial}{\partial \lambda}\langle \psi | H | \psi \rangle = \left(\frac{\partial}{\partial \lambda}\langle \psi|\right) H|\psi\rangle + \langle \psi | H \left(\frac{\partial}{\partial \lambda}|\psi\rangle\right) + \langle\psi|\left(\frac{\partial H}{\partial \lambda}\right)|\psi\rangle = E\underbrace{\left(\left(\frac{\partial}{\partial \lambda}\langle\psi|\right)|\psi\rangle + \langle\psi|\frac{\partial}{\partial\lambda}|\psi\rangle\right)}_{=0} + \langle\psi|\frac{\partial H}{\partial\lambda}|\psi\rangle$$

$$= \langle \psi | \frac{\partial H}{\partial \lambda} | \psi \rangle$$

It holds in 3D problem. Take $\lambda = m$, the mass of a particle bound in a given potential

$$T = \frac{p^2}{2m} \qquad \frac{\partial T}{\partial m} = -\frac{1}{m}\frac{p^2}{2m}$$

$$\frac{\partial E}{\partial m} = \langle \psi | \frac{\partial H}{\partial m} | \psi \rangle = \langle \psi | \frac{\partial T}{\partial m} | \psi \rangle = \frac{-1}{m}\langle \psi | T | \psi \rangle$$

$$= -\frac{1}{m}\langle T \rangle = -\frac{1}{m}\big(\underbrace{E - \langle V \rangle}_{>0}\big)$$

$\Rightarrow$ The energy of a given bound state <u>always</u> decreases as m increases!!

(4). Two particles system

Just like in the classical mechanics.

$\vec{r}_1, \vec{r}_2, \; m_1, m_2 \qquad V(|\vec{r}_1 - \vec{r}_2|) \qquad \vec{R} = \dfrac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2} = X\hat{i} + Y\hat{j} + Z\hat{k}$

relative coordinate $\vec{r} \equiv \vec{r}_1 - \vec{r}_2 = x\hat{i} + y\hat{j} + z\hat{k} \Rightarrow E = \underbrace{E_{cm}}_{\text{center of mass energy}} + E_0 \longrightarrow$ energy of relative motion

$$\Rightarrow -\frac{\hbar^2}{2\mu}\nabla^2\psi + V(r)\psi = E_0\psi$$

$\mu = \dfrac{m_1 + m_2}{m_1+m_2}$ is the reduced mass.

$$\left(-\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(r)\right)\Psi(r_1, r_2) = E\,\Psi(r_1, r_2)$$

$$\frac{\partial}{\partial x_1} = \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} + \frac{\partial X}{\partial X_1}\frac{\partial}{\partial X} = \frac{\partial}{\partial x} + \frac{m_1}{m_1+m_2}\frac{\partial}{\partial X}, \qquad \text{also} \left(\begin{aligned}\vec{r}_1 &= \vec{R} + \frac{m_2}{m_1+m_2}\vec{r} \\ \vec{r}_2 &= \vec{R} - \frac{m_1}{m_1+m_2}\vec{r}\end{aligned}\right)$$

$$\hookrightarrow \left[-\frac{\hbar^2}{2(m_1+m_2)}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(r)\right]\Psi = E\Psi$$

(5) a particle in a fixed central potential.
In spherical polar coordinates.

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\underbrace{\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)}_{= -\frac{\vec{L}^2}{\hbar^2}}$$

$\Rightarrow$ Schrödinger Eq becomes,

$$\frac{-\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\vec{L}^2}{r^2\hbar^2}\right]\psi + V(r)\psi = E\psi$$

~~Let's write~~ Let $\psi = R(r)\, Y_\ell^m(\theta,\phi)$

and $L^2 Y_\ell^m(\theta,\phi) = \hbar^2 \ell(\ell+1) Y_\ell^m(\theta,\phi)$

$$\Rightarrow \quad R'' + \frac{2}{r}R' + \frac{2\mu}{\hbar^2}\left(E - \left(V(r) + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}\right)\right]R = 0$$

It's convenient to make the substitution $\chi = rR$, $R = \frac{\chi}{r}$

$R' = -\frac{\chi}{r^2} + \frac{\chi'}{r}$, $\quad R'' = +\frac{2\chi}{r^3} - \frac{2\chi'}{r^2} + \frac{\chi''}{r}$

$$\frac{\chi''}{r} - \cancel{\frac{2\chi'}{r^2}} \cancel{+\frac{2\chi}{r^3}} + \cancel{\frac{2\chi'}{r^2}} - \frac{2\chi}{r^3} + \frac{2\mu}{\hbar^2}\left[E - V_{eff}\right]\frac{\chi}{r} = 0$$

or $\quad \chi'' + \frac{2\mu}{\hbar^2}\left[E - V_{eff}\right]\chi = 0, \quad V_{eff} = V(r) + \underbrace{\frac{\hbar^2\ell(\ell+1)}{2\mu r^2}}_{\text{centrifugal potential}}$

If $V \xrightarrow{r\to 0}$ goes to ∞ more slowly than r^{-2},
$\Rightarrow$ dominated by the centrifugal potential for small r, $\chi'' \simeq \frac{\ell(\ell+1)}{r^2}\chi$

$\Rightarrow \chi \simeq N_\ell r^{\ell+1} \quad \Rightarrow R \simeq N_\ell r^\ell \quad (r \ll 1)$

since $\ell = 0, 1, 2, \cdots \Rightarrow$ $\boxed{R \text{ must be finite at the origin and } \chi(0) = 0.}$