dinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi \qquad \hat{H} = \frac{\hat{p}^2}{2m} + V \qquad \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

(Hamiltonian operator) (momentum operator

Some probability (age group)

Median : age value T s.t half < T and half population > T.

Deviation : $\Delta j = j - \langle j \rangle$; variance : $\sigma^2 = \langle \Delta j^2 \rangle = \langle j^2 \rangle - \langle j \rangle^2$; stand. dev. σ

Operators $\langle x \rangle = \int \psi^* x \psi \, dx = \langle \psi | x | \psi \rangle$

$\langle p \rangle = \langle \psi | \frac{\hbar}{i}\frac{\partial}{\partial x} | \psi \rangle$

$$\boxed{\langle Q(x,p) \rangle = \langle \psi | Q(x, \tfrac{\hbar}{i}\tfrac{\partial}{\partial x}) | \psi \rangle}$$

ex $T = \frac{p^2}{2m} \rightarrow \langle T \rangle = \langle \psi | \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} | \psi \rangle$

Formalism : $\langle f | g \rangle = \int f^* g \Rightarrow \langle a_n f_n | b_m g_m \rangle = a_n^* b_m \langle f_n | g_m \rangle$

$\langle f | g \rangle \leq |f||g|$ schwartz ineq.

complex inner product

$\langle u | v \rangle = \langle v | u \rangle^*$ $\quad \langle ku | v \rangle = k \langle u | v \rangle$ $\quad \langle u | kv \rangle = k^* \langle u | v \rangle$

Hermitian :

$\langle Q \rangle = \langle \psi | \hat{Q}\psi \rangle = \langle \hat{Q}\psi | \psi \rangle \Rightarrow \hat{Q}^\dagger = \hat{Q}$

observable operator

$\int (\hat{Q}\psi)^\dagger \psi$
$= \int \psi^* \hat{Q}^\dagger \psi$
$= \int \psi^* \hat{Q} \psi$

Determinate state are eigfunc of $\hat{Q}$. ex Stationary state $\langle Q \rangle = q$ time indept

Collection of eig. vals of $\hat{Q}$ is its spectrum.

Hermitian Spectrum
- discrete : in Hilbert space , physical ex Harmonic Oscillator
- continuum : not in Hilbert space , not normalizable ex free particles

ex finite well (Both)

Axiom : Eigenfunc. of observable are complete.

Continuous Spectrum de Broglie $\boxed{\lambda = \frac{2\pi\hbar}{p} = \frac{h}{p}}$ from momentum operator (Solve)

Here Eig. func. of Hermitian are Dirac Orthonormal

$$\langle f_{p'} | f_p \rangle = \delta(p - p')$$

and complete

$$f(x) = \int_{-\infty}^{\infty} c(p) f_p(x) \, dp \quad w/ \quad c(p') = \langle f_{p'} | f \rangle$$

ex position operator : $x g_y = y g_y \Rightarrow g_y = \delta(x - y)$

Generalized Stat. Interpretation

Discrete : $\psi(x,t) = \sum_n c_n f_n(x)$; $|c_n|^2$ — Probability getting eigval q_n of $\hat{Q}$

Continuous : Probability $|c(z)|^2 dz$ and $c(z) = \langle f_z | \psi \rangle$ ex $c(p) = \underbrace{\frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} e^{\frac{ipx}{\hbar}} \psi(x,t) dx}_{\Phi(p,t)}$

momentum space

Generalized uncertainty principle

$$\boxed{\sigma_A \sigma_B \geq \left| \frac{1}{2i} \langle [\hat{A}, \hat{B}] \rangle \right|}$$

$\sigma_A^2 = \langle (\hat{A} - \langle A \rangle)\psi | (\hat{A} - \langle A \rangle)\psi \rangle$

ex $\boxed{[\hat{x}, \hat{p}] = i\hbar \ , \ \sigma_x \sigma_p \geq \frac{\hbar}{2}}$ Heinsenberg's

$\Delta x \Delta p \geq \frac{\hbar}{2}$

$\Delta t \Delta E \geq \frac{\hbar}{2}$ $\quad \Delta t$ — time taken to change $\langle Q \rangle$ by a standard deviation

Q observable not explicitly time dependent, then

$\frac{d\langle Q \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{H}, Q] \rangle$

(i) if $\hat{H}$ & Q commute Q is a constant of motion

(ii) $[Q^2, \hat{H}] = 0$ same idea.

Commutator.

$[A, B] = 0$ iff simultaneous diagonalizable (i.e A, B have common eigfunc) measurement of A won't disturb B.

$[AB, C] = A[B, C] + [A, C]B$

$[A, BC] = \cancel{[A, C]B + B[A, B]}\ [A, B]C + B[A, C]$

Dirac Notation

$|s\rangle$ vector $\quad |s\rangle = \sum_i c_i \overbrace{|x_i\rangle}^{\text{basis}}$ $\quad c_i = \langle x_i | s \rangle = \psi(x,t)$

Wave func. is coeff in expansion of $|s\rangle$ (here is in basis of position eig.func.

ex $\psi(x,t) = \langle x | s \rangle$

$\Phi(p,t) = \langle p | s \rangle$

$c_n(t) = \langle n | s \rangle$ $\quad n$ — n^{th} eig. ~~val~~ state of $\hat{H}$

$$\psi(x,t) = \int \psi(y,t) \underbrace{\delta(x-y)}_{\text{delta function}} dy = \int \Phi(p,t) \underbrace{\frac{1}{\sqrt{2\pi\hbar}} e^{\frac{ipx}{\hbar}}}_{\text{plane wave}} dp = \sum_n c_n e^{-\frac{iE_n t}{\hbar}} \psi_n(x)$$

(seeing thing in different coordinates!)

bra, cat, transformation

$Q_{mn} = \langle e_m | \hat{Q} | e_n \rangle$ $\quad$ from $|\beta\rangle = \hat{Q} |\alpha\rangle$ $\quad$ i.e write $|\alpha\rangle = \sum a_n |e_n\rangle$

bra $\langle \alpha |$ $\quad$ func. space $\quad \langle f | = \int f^*(x) dx$ — shouldn't it more appropriate to define $\langle f | = f^*(x)$ $|f\rangle = f(x)$

finite. space $\quad \langle \alpha | = (a_1^*, a_2^*, \dots, a_n^*)$ $\quad$ cat $|\alpha\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix}$

└ dual space of cat

$|f\rangle = (\int f^* |x\rangle dx)^+$

Projection Operator (outer product)

$\hat{P} \equiv |\alpha\rangle\langle\alpha| \Rightarrow \hat{P}|\beta\rangle = \langle\alpha|\beta\rangle|\alpha\rangle$

$\sum_n |e_n\rangle\langle e_n| = I$, $\cancel{\langle e_n \rangle}$ $\langle e_n | e_m \rangle = \delta_{mn}$

Continuous space

$\langle e_{\acute{z}} | e_z \rangle = \delta(z - \acute{z})$ & $\int |e_z\rangle\langle e_z| dz = 1$

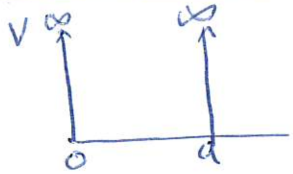
Sol Schrödinger Eq for Special $V(x)$ by sep. var. $\Psi(x,t)=\psi(x)\varphi(t) \Rightarrow$ stationary sta

Delt

$$i\hbar\frac{\partial\Psi}{\partial t}=H\Psi$$

$$\varphi_n(t)=e^{-iE_nt/\hbar} \qquad (\hat{p}+V(x))\psi=E\psi \Longrightarrow E_n$$

1 Infinite Square Well



like standing wave

$$E=\frac{p^2}{2m},\quad p=\frac{2\pi\hbar}{\lambda}\quad \lambda=\frac{2a}{n}$$

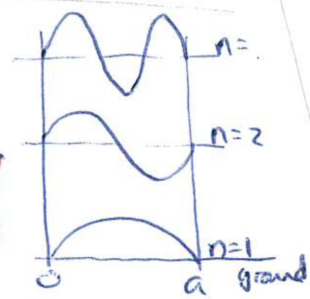
$$\boxed{E_n=\frac{\hbar^2k_n^2}{2m}\quad k_n=\frac{n\pi}{a}}$$

Solve.

$$\psi''=-k^2\psi \quad k=\frac{\sqrt{2mE}}{\hbar}$$

$$\boxed{\psi_n(x)=\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)}$$

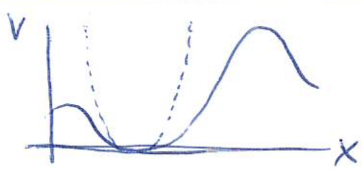
$n=1,2,3,\dots$



Lead to Fourier Series

$$\psi(x,t)=\sum_{n=1}^{\infty}C_n\sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \quad w/\ \frac{2}{a}\int_0^a\sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx=\delta_{mn}$$

2 Harmonic Oscillator



$$V=\frac{1}{2}m\omega^2x^2$$

$\hbar\omega(n+\frac{1}{2})$

rewrite H

$$\frac{1}{2m}[p^2+(m\omega x)^2]\psi=E\psi$$

also

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

$$\boxed{x=\sqrt{\frac{\hbar}{2m\omega}}(a_++a_-) \qquad p=i\sqrt{\frac{\hbar m\omega}{2}}(a_+-a_-)}$$ useful!!

raising / lowering operator

$$\boxed{a_\pm=\frac{1}{\sqrt{2m\hbar\omega}}(\mp ip+m\omega x)}$$

$$[x,p]=i\hbar \longrightarrow \boxed{[a_-,a_+]=1 \quad H=\hbar\omega(a_\pm a_\mp\pm\tfrac{1}{2})}$$

$$\boxed{\begin{aligned}&a_+\psi_n=\sqrt{n+1}\,\psi_{n+1}\\&a_-\psi_n=\sqrt{n}\,\psi_{n-1}\\&H(a_\pm\psi)=(E\pm\hbar\omega)(a_\pm\psi)\end{aligned}}$$

$$\boxed{\begin{aligned}&E_n=(n+\tfrac{1}{2})\hbar\omega\\&E_0=\frac{\hbar\omega}{2}\end{aligned}}$$

$a_-\psi_0=0$

$$\boxed{\begin{aligned}&\psi_n\sim H_n(x)e^{-\frac{V(x)}{\hbar\omega}}\\&\psi_n(x)\propto H_n(x)e^{-\frac{m\omega x^2}{2\hbar}}\end{aligned}}$$

Hermite Poly.

$\frac{\frac{1}{2}m\omega^2x^2}{\hbar\omega}$

$\hbar\omega\sim kT$

3 Free Particle ($V=0$)

Solve $\psi''=-k^2\psi$ $\quad k=\pm\frac{\sqrt{2mE}}{\hbar}$ $\quad$ $k>0$ wave move right, $k<0$ wave move left.

Wave packet (represent true particle)

$$\boxed{\Psi(x,t)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx-\underbrace{\frac{\hbar k^2}{2m}}_{\omega}t)}dk} \Rightarrow \boxed{V_g=V_{class}=2V_p=\sqrt{\frac{2E}{m}}}$$

Quick solve $-\frac{iE_nt}{\hbar}$

$$V_p=\frac{E_n}{k\hbar}=\sqrt{\frac{E}{2m}}$$

$\frac{p^2}{2m}$ free particle only T

$V_p=\frac{\omega}{k}$

$V_g=\frac{d\omega}{dk}$

Faster use $\frac{1}{2}mv^2=E$

I.C

$$\Psi(x,0)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{ikx}dk$$

Fourier Transform

$$\text{IFT}:\ f(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(k)e^{ikx}dk$$

$$\text{FT}:\ f(k)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(x)e^{-ikx}dx$$

why e^{ikx}?

$\psi''=-k^2\psi \Rightarrow \psi(x)=e^{ikx}$

Dirac notation

$f(k)=\langle p|f(x)\rangle$ given

$\langle p|\sim e^{-ikx}$

$f(x)=\langle x|f(k)\rangle$

$\langle x|\sim e^{ikx}$

$p=\hbar k$

$E=\hbar\omega$

$\Rightarrow \omega(k)=\frac{\hbar k^2}{2m}$

dispersion relation

δ-func. Potential: Def Bound State $E < V(-\infty)$ and $V(\infty)$

Scattering State $E > V(-\infty)$ or $V(\infty)$

$V(x) = -\alpha\delta(x)$ $\alpha > 0$

Bound ($E<0$) Solve $\psi'' = k^2\psi$ $k = \frac{\sqrt{-2mE}}{\hbar}$ $\because E<0$

B.C. $\Delta\left(\frac{d\psi}{dx}\right) = -\frac{2m\alpha}{\hbar^2}\psi(0)$

$k = \frac{m\alpha}{\hbar^2}$

$\boxed{E = -\frac{\hbar^2 k^2}{2m}}$ unknown

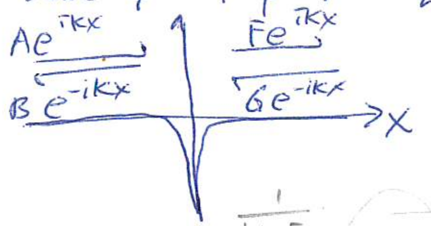
factor $\frac{1}{2}$

dimensional analysis $E \propto \frac{m}{2}\hbar^a\alpha^b \Rightarrow \boxed{E = \frac{-m\alpha^2}{2\hbar^2}} \xrightarrow{\text{solve}} k.$

rem. $\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-\frac{m\alpha|x|}{\hbar^2}}$

delta func only has 1 bound state !!

Scattering ($E>0$) Solve $\psi'' = -k^2\psi$ $k = \frac{\sqrt{2mE}}{\hbar}$



Assume incident from left

A incident

B reflection

F transmission $G = 0$.

Probability

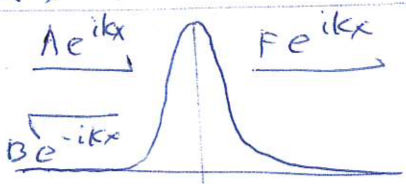
$$R = \frac{|B|^2}{|A|^2} = \frac{1}{1+\left(\frac{2\hbar^2 E}{m\alpha^2}\right)} \quad \frac{1}{1+\frac{E}{|E_b|}}$$

$$T = \frac{|F|^2}{|A|^2} = \frac{1}{1+\left(\frac{m\alpha^2}{2\hbar^2 E}\right)} \quad \frac{1}{1+\frac{|E_b|}{E}}$$

$T + R = 1$ def. $|E_b| = \frac{m\alpha^2}{2\hbar^2}$

Delta Barrier $\alpha < 0$

- No bound state
- Scattering $0 < E < V_{max}$

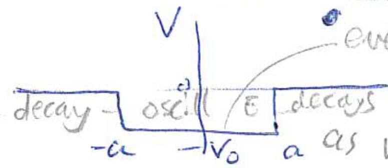


everything the same except now with tunneling effect

$$T = \frac{1}{1+\left(\frac{m\alpha^2}{2\hbar^2 E}\right)}$$

⑤ Finite square well ~~Gives continuity of $\frac{d\psi}{dx}$ except at jump.~~

$$V(x) = \begin{cases} -V_0 & -a \le x \le a \\ 0 & |x| > a \end{cases}$$



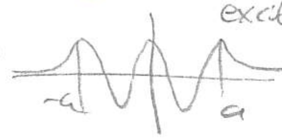
even ⇒ ground state even!

as $V_0 \to 0$ excited state disappear

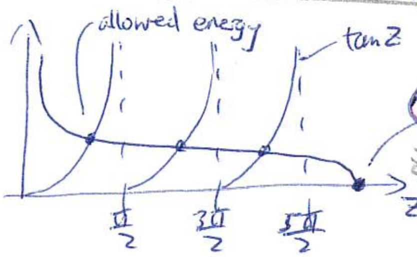
Bound ($E<0$) no oscillation

- $|x| > a$ $\psi'' = k^2\psi$ > 0 gives sinusoidal
- $|x| < a$ $\boxed{-\frac{\hbar^2}{2m}\psi'' = (E+V_0)\psi}$

Solve by transcedental eqn. →



$a\frac{\sqrt{2mV_0}}{\hbar}$ like k rem.



$z_0 = \frac{a}{\hbar}\sqrt{2mV_0}$

size of well determine # of bound state

$z_0 \ll 1$ will always has 1 ground/bound state

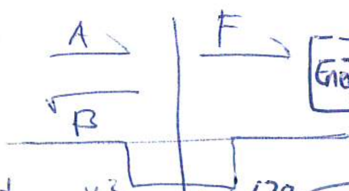
$z_0 \to \infty$ becomes infinite well

$\boxed{E_n + V_0 \simeq \frac{n^2\pi^2\hbar^2}{2m(2a)^2}}$ — $E_n + V_0 \;\; \simeq \;\; \frac{n^2\pi^2\hbar^2}{2m(2a)^2}$ bound

= scatter

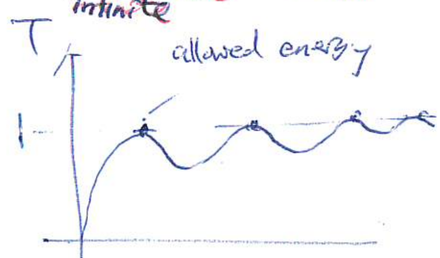
if otherwise infinite

Scattering $E > 0$



$T^{-1} \propto 1 + c\sin^2(x)$

$\boxed{\text{Energy of Perfect transmission } T = 1,\ x = n\pi}$



$$T^{-1} = 1 + \frac{V_0^2}{4E(E+V_0)}\sin^2\left(\frac{2a}{\hbar}\sqrt{2m(E+V_0)}\right)$$

$$\boxed{E_n + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}}$$

$V_0 = 0$ infinite well

3D Schrödinger

$\vec{p} = \frac{\hbar}{i}\nabla \quad p^2 = p_x^2 + p_y^2 + p_z^2 \quad [x_j, p_k] = i\hbar\delta_{jk} \quad \sigma_{x_i}\sigma_{p_i} \geq \frac{\hbar}{2}$

Ang

Sep. var. $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$ Normalization $\int_0^\infty |R|^2 r^2 dr = 1 \quad \int |Y|^2 d\Omega = 1$

Angular eqn: Spherical harmonic soln. (possible due to spherical symmetric potential $V(\vec{r}) = V(r)$ special)

$$Y_\ell^m(\theta,\phi) = \varepsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\, e^{im\phi} P_\ell^m(\cos\theta) \qquad \varepsilon = \begin{cases} 1 & m \leq 0 \\ (-1)^m & m \geq 0 \end{cases}$$

Legendre P: $P_0(x) = 1$, $P_1(x) = x$

Legendre func. $P_0^0 = 1 \quad P_1^1 = \sin\theta$

orthonormality: $\int_0^{2\pi}\int_0^\pi Y_\ell^{m*}(\theta,\phi)\, Y_{\ell'}^{m'}(\theta,\phi)\, d\Omega = \delta_{\ell\ell'}\delta_{mm'}$

$\ell \in \mathbb{Z}^+$ w/ Legendre Polynomial $\boxed{P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell}$

from P_ℓ^m derivative $\Rightarrow |m| \leq \ell$

reflection symm.

ℓ - azimuthal quantum # $\quad \ell = 0, 1, 2, \ldots$

m = magnetic quantum # $\quad m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell-1, \ell$

from periodic $e^{im\phi} \Rightarrow m \in \mathbb{Z}$

m w/ Legendre function $\boxed{P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x)}$

Radial eqn: $u = rR$, $\quad -\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \underbrace{\left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]}_{V_{eff}\ \text{eff. potential}} u = Eu$ centrifugal term ; $\int_0^\infty |u|^2 dr = 1$

$\ell(\ell+1)$ from definition, $\frac{1}{r^2}$ from $\frac{r^2 \partial}{\partial r}$

ex. Infinite spherical well $\quad V(r) = \begin{cases} 0 & r \leq a \\ \infty & r > a \end{cases} \quad \frac{d^2u}{dr^2} = \left[\frac{\ell(\ell+1)}{r^2} - k^2\right]u \Rightarrow k \equiv \frac{\sqrt{2mE}}{\hbar}$

For $\ell = 0$ reduce to 1D infinite well (radial sym.): $E_{n0} = \frac{n^2\pi^2\hbar^2}{2ma^2}$ $\quad \psi_{n00} = \frac{1}{\sqrt{2\pi a}}\frac{\sin\left(\frac{n\pi r}{a}\right)}{r}$ (rem. $\because u = rR$)

note: stationary state $\psi_{n\ell m}(r,\theta,\phi)$ labeled by 3 quantum #

general allowed energy $E_{n\ell} = \frac{\hbar^2}{2ma^2}\underbrace{\beta_{n\ell}}_{n^{th}\text{ zero of }\ell^{th}\ j_\ell(kr)}$ by 2 quantum # $\Rightarrow$ energy degenerate at $2\ell+1$ level per ℓ

$(2\ell+1)$'s m w/ same $E_{n\ell}$

Hydrogen atom $\left(H = \overbrace{\frac{\hbar^2}{2m}\nabla^2}^{KE\text{ of electron}} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)\psi$ (m: e mass) $\quad \boxed{\psi_{n\ell m} = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)}$ $\quad R_{n\ell} = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho)$, $\rho = \frac{r}{an}$

Effect of coulomb $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$

Power series soln truncation $\Rightarrow \boxed{n \equiv j_{max} + \ell + 1} \Rightarrow \boxed{n^2}$ degeneration of E_n for hydrogenic atom

each n has $\ell = 0, \ldots, n-1$ # m = n^2 $\quad \sum_{\ell=0}^{n-1}(2\ell+1)$ $\ell(2\ell+1)$'s m

Bohr formula $\quad a_n = n a_0 \quad$ Bohr radius $\quad$ wave # $\quad$ note w/ ground state wave func.

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10}\,m \quad \text{simply } 0.5\,\text{Å} \qquad k = \frac{1}{an} \qquad \boxed{\psi_{100}(r) \propto e^{-r/a}}$$

like in δ potential $\frac{-m\alpha^2}{2\hbar^2}$

(ground state $E_1 = -13.6\,eV$)

Electron transition $\underline{h\nu = E_i - E_f}$ $\quad$ $i \geq f$

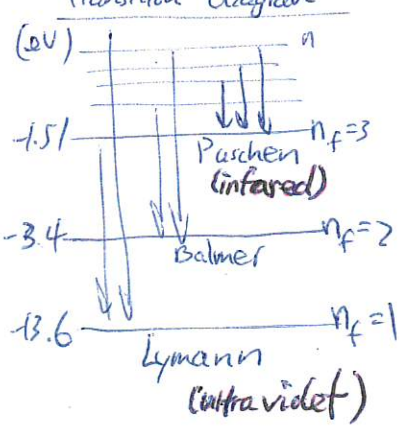
Rydberg formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

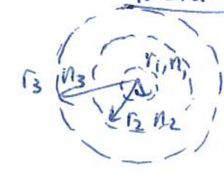
Rydberg constant

$$\frac{m}{4\pi c\hbar^3}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = 1.097 \times 10^7\,m^{-1}$$

Transition diagram



Bohr's Model



- electron in stable orbit unless transition
- Angular momentum $\boxed{mvr = n\hbar}$

ex. hydrogenic atom $\quad e^2 \mapsto Ze^2 \quad$ Z=1 hydrogen, Z=2 helium, Z=3 lithium

- Positronium $\quad m \mapsto \mu = \frac{m_1 m_2}{m_1 + m_2}$ reduced mass

ular Momentum

$\vec{L} = \vec{r} \times \vec{p}$ (ie $L_x = yp_z - zp_y$) uncertainty : $\sigma_{L_x}\sigma_{L_y} \geq \frac{\hbar}{2}|\langle L_z \rangle|$

mmutator (Right hand rule)

$[L_x, L_y] = i\hbar L_z$; $[L_y, L_z] = i\hbar L_x$; $[L_z, L_x] = i\hbar L_y$ incompatible

$\hat{L}_x = \frac{\hat{L}_+ + \hat{L}_-}{2}$ $\hat{L}_y = \frac{\hat{L}_+ - \hat{L}_-}{2i}$

$\hat{L}_\pm |l, m_l\rangle = \hbar\sqrt{l(l+1) - (m_l)(m_l \pm 1)}\, |l, m_l \pm 1\rangle$

$\hbar\sqrt{(l \mp m)(l \pm m + 1)}\, |l, m \pm 1\rangle$

Total angular momentum

$L^2 \equiv L_x^2 + L_y^2 + L_z^2$, $[L^2, \vec{L}] = 0$ commute

$[L^2, L_\pm] = 0$

Ladder operators

$L_\pm \equiv L_x \pm i L_y$, $[L_z, L_\pm] = \pm\hbar L_\pm$, $[L^2, L_\pm] = 0$

see P. 165

$L^2(L_\pm f) = \lambda(L_\pm f)$ (λ eigval of L^2)

$L_z(L_\pm f) = (\mu \pm \hbar)(L_\pm f)$ (μ eigval of L_z)

$\Big\}$ $\lambda \geq \mu^2$ bounded by total λ.

$l = -l + N$

$L^2 Y_l^m = \underbrace{l(l+1)\hbar^2}_{\text{evl}} Y_l^m$ $L_z Y_l^m = \underbrace{m\hbar}_{\text{evl}} Y_l^m$

$m = -l, -l+1, \ldots, 0, l-1, l$ in N steps.

so $l = \frac{N}{2}$ either integer (orbit) or half integer (spin)

means angular momentum

(spherical harmonics are eig.func of L^2, L_z)

Notice that $\sqrt{l(l+1)} > l = m_{max}$ except for $l = 0$

Spherical coordinate $\vec{L} = \frac{\hbar}{i}(\vec{r} \times \nabla)$ $\nabla = \hat{r}\frac{\partial}{\partial r} + \hat{\theta}\frac{1}{r}\frac{\partial}{\partial \theta} + \hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial \phi} = \left(\frac{\partial}{\partial r}, \frac{1}{r}\frac{\partial}{\partial \theta}, \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right)$

$\vec{L} = \frac{\hbar}{i}\left[\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right]$ $L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$ ($-i\hbar\partial\phi$) or $-i\hbar\partial_\phi$ $L^2 = -\hbar^2\nabla^2_{\theta,\phi} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$

For $\vec{J}$; $J^2 = J_x^2 + J_y^2 + J_z^2$; $[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$

$J_\pm = J_x \pm iJ_y$ $J_x = \frac{J_+ + J_-}{2}$ $J_y = \frac{J_+ - J_-}{2i}$

Spin

commutator (Right hand rule)

$[S_x, S_y] = i\hbar S_z$; $[S_y, S_z] = i\hbar S_x$; $[S_z, S_x] = i\hbar S_y$

Eigenval.

$J^2|j,m\rangle = \hbar^2 j(j+1)|j,m\rangle$

$J_z|j,m\rangle = m\hbar|j,m\rangle$

$J_\pm|j,m\rangle = \hbar\sqrt{(j \mp m)(j \pm m + 1)}\,|j, m \pm 1\rangle$

- $S^2|s\,m\rangle = s(s+1)\hbar^2|s\,m\rangle$
- $S_z|s\,m\rangle = m\hbar|s\,m\rangle$

$S_x \leftrightarrow \frac{1}{\sqrt{2}}\binom{1}{1}$ $\frac{1}{\sqrt{2}}\binom{1}{-1}$ $\sim \frac{1}{\sqrt{2}}(|\uparrow\rangle \pm |\downarrow\rangle)$

$S_y \leftrightarrow \frac{1}{\sqrt{2}}\binom{1}{i}$ $\frac{1}{\sqrt{2}}\binom{1}{-i}$ $\sim \frac{1}{\sqrt{2}}(|\uparrow\rangle \pm i|\downarrow\rangle)$

$S_z \leftrightarrow \underset{|\uparrow\rangle}{\binom{1}{0}}$ $\underset{|\downarrow\rangle}{\binom{0}{1}}$

Here a single electron $s = \frac{1}{2} \Rightarrow m = -\frac{1}{2}, \frac{1}{2}$

rising & lowering operator

$S_\pm = S_x \pm iS_y$ $\begin{cases} S_x = \frac{S_+ + S_-}{2} \\ S_y = \frac{S_+ - S_-}{2i} \end{cases}$

$\vec{S}_+\chi_- = \hbar\chi_+$

ie $S_z|\frac{1}{2}\frac{1}{2}\rangle = \frac{1}{2}\hbar|\frac{1}{2}\frac{1}{2}\rangle$

$\vec{S}_-\chi_+ = \hbar\chi_-$

O.T.O.H.

- $S_\pm|s\,m\rangle = \hbar\sqrt{s(s+1) - m(m \pm 1)}\,|s\,(m \pm 1)\rangle$

also $\hbar\sqrt{(s \mp m)(s \pm m + 1)}$

$\vec{S}_+\chi_+ = \vec{S}_-\chi_- = 0$ $S_+|\frac{1}{2}\frac{1}{2}\rangle = 0$

where $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$

$m = -s, -s+1, \ldots, s-1, s$

$\sigma^+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ $\sigma^\pm = \frac{\sigma^1 \pm i\sigma^2}{2}$

$\sigma^- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

Spin $\frac{1}{2}$: State $|s\,m\rangle$ Vector Matrix Representation

spin up $|\frac{1}{2}\frac{1}{2}\rangle$ $\uparrow$ $\chi_+ = \binom{1}{0}$

1234 rule S $\frac{1}{2}\hbar$

$\vec{S} = \underbrace{\frac{\hbar}{2}}_{\text{evl}}\vec{\sigma}$ $\underbrace{\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & \\ 0 & \end{pmatrix}}_{\text{Pauli}}$

spin down $|\frac{1}{2}\,-\frac{1}{2}\rangle$ $\downarrow$ $\chi_- = \binom{0}{1}$

$\vec{S}_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ $\vec{S}_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$

S^2 $\frac{3}{4}\hbar^2$

$\because s = \frac{1}{2}$

$m = \frac{1}{2}, -\frac{1}{2}$

b/c $S^2 = S_x^2 + S_y^2 + S_z^2$ $\leftarrow$ $\vec{S}^2 = \underbrace{\frac{3}{4}\hbar^2}_{\text{evl}}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

$\boxed{\sigma^i\sigma^j = \delta^{ij} + i\epsilon^{ijk}}$

$R =$

Spin Addition (Composite Spin)

Assume atom has two particles with spin $\frac{1}{2}$.
What is the total momentum of the atom? (ie m, the z-component

$$(S_z^{(1)} \otimes S_z^{(2)})(\chi_1 \otimes \chi_2) = (S_z^{(1)}\chi_1) \otimes \chi_2 + \chi_1 \otimes (S_z^{(2)}\chi_2) = m_1\chi_1 \otimes \chi_2 + \chi_1 \cdot$$
$$= (m_1 + m_2)(\chi_1 \otimes \chi_2)$$

so m component adds. And $S = S_1 + S_2,\ (S_1+S_2-1), \dots, |S_1 - S_2|$

possible combination of m:

m_1	m_2	arrow rep.	m
$\frac{1}{2}$	$\frac{1}{2}$	$\uparrow\uparrow$	1
$\frac{1}{2}$	$-\frac{1}{2}$	$\uparrow\downarrow$	0
$-\frac{1}{2}$	$\frac{1}{2}$	$\downarrow\uparrow$	0
$-\frac{1}{2}$	$-\frac{1}{2}$	$\downarrow\downarrow$	-1

notice that w/o $| \rangle$ $\uparrow\uparrow$ implies m_z component with $|\uparrow\downarrow\rangle$ implies $|s\, m\rangle$

we have extra $m=0$!

Check.

$$S_-(\uparrow\uparrow) = (S_-^{(1)}\uparrow)\uparrow + \uparrow(S_-^{(2)}\uparrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow)$$

make use of $S_\pm |s, m\rangle = \hbar\sqrt{(s\mp m)(s\pm m+1)}\,|s, m\pm 1\rangle$ formular for computation.

and

$$S_-(\downarrow\uparrow + \uparrow\downarrow) = 2\hbar(\downarrow\downarrow)$$

thus for $S=1$ we have combination of the "triplet"

$$\begin{cases} |1\,1\rangle \doteq \uparrow\uparrow \\ |1\,0\rangle \doteq \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ |1\,{-1}\rangle \doteq \downarrow\downarrow \end{cases}$$

For $S=0$ the combination of $m_1 + m_2$ must be "0", so ~~ansatz~~

~~Anzats~~
Ansatz $\quad |0\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$ "singlet"

Can check they are indeed eig. vector of S^2

Note that $\quad S^2 = (S^{(1)} + S^{(2)}) \cdot (S^{(1)} + S^{(2)}) = (S^{(1)})^2 + (S^{(2)})^2 + 2S^{(1)} \cdot S^{(2)}$

Ex Net angular momentum of hydrogen atom;

for ψ_{nlm}, $\vec{J}' = $ (spin + orbital) ; $J' = l + \frac{1}{2}$ or $l - \frac{1}{2}$

if throw in proton, total angular momentum ~~$J = J' + l$ or $J' - l$~~

$$J = J' + 1 \text{ or } J' - 1$$

Compute spin of composite particle

Mathematically, the combine state $|s\, m\rangle$

$$|s\, m\rangle = \sum_{m_1+m_2=m} \underbrace{C^{s_1 s_2 s}_{m_1 m_2 m}}_{\text{Clebsch-Gordan coefficients}} |s_1\, m_1\rangle |s_2\, m_2\rangle$$

can also reverse as

$$|s_1\, m_1\rangle |s_2\, m_2\rangle = \sum_{s} C^{s_1 s_2 s}_{m_1 m_2 m} |s\, m\rangle$$

Spin facts ④

S_x, S_y, S_z, S^2 Hermitian, $S_\pm$ Not (nonobservable)

replace by App 1

Eigenspinor of S_z : $\chi_\pm \Longleftrightarrow \pm\frac{\hbar}{2}$; S_x's eigval. $\pm\frac{\hbar}{2}$ (from matrix representation)

Adding Angular Momentum

Composite spin S_1, S_2 :

results from direct product

$$\boxed{\begin{array}{l} S = (S_1+S_2),\ S_1+S_2-1,\ \ldots,\ |S_1-S_2| \\ m = m_1+m_2,\quad m_i = -S_i,\ -S_i+1,\ \ldots,\ S_i \end{array}}$$

$m = -S+1, \ldots, S$

ex Net angular momentum : hydrogen atom (Spin + orbital) $= l+\frac{1}{2}$ or $l-\frac{1}{2}$

arrows in z component

Add proton $= l+1,\ l,\ l-1$

Two spin $\frac{1}{2}$ particles : $\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\uparrow$, $\uparrow\uparrow$ $\quad \vec{S} = \vec{S}^{(1)} + \vec{S}^{(2)}$ $\quad$ (i) acts on i^{th} particle only

$(m_1=\frac{1}{2}\ m_2=\frac{1}{2})$ $(m_1=\frac{1}{2}\ m_2=-\frac{1}{2})$

ex $\quad \uparrow\uparrow : m = 1 \Rightarrow \uparrow\uparrow = |1\,1\rangle$

$S_1, S_2 = \frac{1}{2}$

$|S_1 m_1\rangle\,|S_2 m_2\rangle$ $\quad m_1 = \pm\frac{1}{2} \quad m_2 = \pm\frac{1}{2}$

$S_-(\uparrow\uparrow) = \hbar(\downarrow\uparrow + \uparrow\downarrow)$

possible $m = -1, 0, 1$

$|SM\rangle_{tot} = |1\,1\rangle : m=1 \quad |\frac{1}{2}\frac{1}{2}\rangle|\frac{1}{2}\frac{1}{2}\rangle = \uparrow\uparrow$

$|1, 0\rangle : m=0 \quad |\frac{1}{2}\frac{1}{2}\rangle|\frac{1}{2}\,-\frac{1}{2}\rangle = \uparrow\downarrow \qquad |\frac{1}{2}\,-\frac{1}{2}\rangle|\frac{1}{2}\frac{1}{2}\rangle = \downarrow\uparrow$

$S_\pm|sm\rangle = \hbar\sqrt{s(s+1) - m(m\pm1)}\,|s\,(m\pm1)\rangle$ $\quad |1, -1\rangle : m=-1 \quad |\frac{1}{2}\,-\frac{1}{2}\rangle|\frac{1}{2}\,-\frac{1}{2}\rangle = \downarrow\downarrow$

Gives :

$2s+1$

3

Triplet $(S=1)$	$\lvert 1\,1\rangle = \uparrow\uparrow$ $\lvert 1\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$ $\lvert 1\,-1\rangle = \downarrow\downarrow$	Singlet — $2s+1 = 1$ $(S=0)$ $\quad \lvert 0\,0\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$

Application :

Electron in Magnetic field

gyromagnetic ratio

Magnetic dipole $\vec{\mu}$, spinning charged particle $\vec{\mu} = \gamma\vec{S}$

Torque $\vec{\tau} = \vec{\mu}\times\vec{B}$, energy $H = -\vec{\mu}\cdot\vec{B} \Rightarrow$ Hamiltonian $H = -\gamma\vec{B}\cdot\vec{S}$

matrix

Analog: $\vec{\tau} = \vec{\mu}\times\vec{B}$ $\quad \vec{r}\times\vec{F}$; $H = \vec{\mu}\cdot\vec{B}$ $\quad \vec{r}\cdot\vec{F}$

ex $\quad \vec{B} = B_0\hat{k} \qquad \vec{H} = -\gamma B_0 \vec{S}_z = -\dfrac{\gamma B_0\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$ $\quad$ w/ energy $\mp\frac{\gamma B_0\hbar}{2} \Leftrightarrow \chi_\pm$

γB_0 $\langle \vec{S}\rangle$

time-independent

& electron spin $\frac{1}{2}$ at rest point in $\hat{z}$, the hamiltonian as above ! $\quad$ yield Larmor freq. γB_0

Stern-Gerlach Experiment : Electron deflected under inhomogeneous magnetic field shows existence of spin $\uparrow\downarrow$. (# splitting $2J+1$)

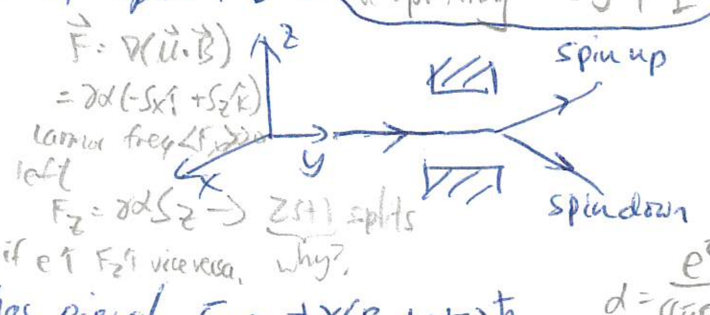
Details :

Under inhomo B-field say

small deviation from homogeneity

$\vec{B}(x,y,z) = -\alpha x\,\hat{i} + (B_0 + \alpha z)\,\hat{k}$

resulting Hamiltonian. $\langle H_x\rangle$ negligible due to Larmor freq.



$$H(t) = \begin{cases} 0 & t<0 \quad \text{off} \\ -\gamma(B_0 + \alpha z)S_z & 0<t<T \quad \text{on} \\ 0 & t>T \quad \text{off} \end{cases}$$

has eig.val $E_\pm = \pm\gamma(B_0 + \alpha z)\frac{\hbar}{2}$ $\qquad \alpha = \frac{e^2}{4\pi\epsilon_0\hbar c}$

acts on $\chi(t) = a\chi_+ + b\chi_-$ $(t\le 0)$ $\rightarrow t>0$, $\chi(t) = a\chi_+ e^{\frac{-iE_+t}{\hbar}} + b\chi_- e^{\frac{-iE_-t}{\hbar}}$

yields momentum $\quad P_{z\pm} = \pm\frac{\hbar}{2}\gamma\alpha T$ given time (From momentum operator : $f_p(x) = \frac{1}{\sqrt{2\pi\hbar}}e^{\frac{ipx}{\hbar}}$)

by $i\hbar\frac{d}{dx}\chi(t) \rightarrow P_{z\pm}\chi(t)$

Two Particle system

State of 2 particles: $\psi(\vec{r}_1, \vec{r}_2, t)$

this explain reduced mass in hydrogenic atom

In schrödinger eqn: $H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$

using reduced mass, center of mass R, relative motion:

$$-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2\psi - \frac{\hbar^2}{2\mu}\nabla_r^2\psi + V(\vec{r})\psi = E\psi$$

$\mu = \frac{m_1 m_2}{m_1+m_2}$

$\vec{r} = \vec{r}_1 - \vec{r}_2$

$E = E_R + E_r$

- Center of mass as free particle
- Reduced mass as single particle subject to V in rel. motion.

Boson & Fermions

distinct particles: $\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$ — state of P_1; particle P_2 in state $\psi_b(\vec{r})$; coord of particle 1

Indistinguishable
Identical particles: (allow position exchange)

mirror
Exchange Operator w/ eigval ± 1

$P\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$ $\Rightarrow$ $\boxed{\psi(\vec{r}_1, \vec{r}_2) = \pm\psi(\vec{r}_2, \vec{r}_1)}$

$[P, H] = 0$

+ sym
− anti sym.

linear comb:

Boson $\psi_+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$

Fermion $\psi_-(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)\right)$

— $\frac{1}{\sqrt{2}}$ for orthonormal $\psi_{a,b}$

Distance seperation shows: $\langle \Delta x^2 \rangle_{\pm} \overset{\text{boson}}{\underset{\text{fermion}}{=}} \langle \Delta x^2 \rangle_{\text{distinc.}} \mp 2|\langle x \rangle_{ab}|^2$

(or more accurately symmetric ⇔ attraction)
Boson attraction integer spin
Fermion repulsion half-spin

App. (Explain Covalent bond) Add spin!

Fermion ⇒ antisym $\psi = \psi(\vec{r})\chi(\vec{s})$ — @ ground state $\begin{cases} \chi \text{ singlet} \\ \psi \text{ sym} \end{cases}$ $\Rightarrow \langle \Delta x^2 \rangle$ closer

ex $\psi(x_1, x_2, x_3) = \psi(x_1, x_3, x_2)$ sym under permutation.
Boson

$\psi(x_1, x_2, x_3) = \varepsilon_{ijk}\psi(x_i, x_j, x_k)$
Fermion.

Fermion ψ. show Pauli principle.
b/c two identical fermion cannot occupy same state
else $\psi_- = 0$ has no wavefunction.

ex CO_2

$(1s)^2(2s)^2(2p)^2$
8 electron state cap
4 filled

$(1s)^2(2s)^2(2p)^4$
8 cap
6 filled
need 2 more

So $\psi = \psi(\vec{r})\chi(\vec{s})$
ground state singlet. → $\psi(\vec{r})$ sym.

we have covalent bond!
$\chi(\vec{s})$ tells us covalent bond requires two electrons to occupy the singlet state w/ total spin "0".