Constant	Symbol	Value
Avogadro's number	N_0	$6.022\,05 \times 10^{23}\,\mathrm{mol}^{-1}$
Proton charge	e	$1.602\,19 \times 10^{-19}\,\mathrm{C}$
Planck's constant	h	$6.626\,18 \times 10^{-34}\,\mathrm{J\,s}$
	$\hbar$	$1.054\,50 \times 10^{-34}\,\mathrm{J\,s}$
Speed of light in vacuum	c	$2.997\,925 \times 10^{8}\,\mathrm{m\,s}^{-1}$
Atomic mass unit	amu	$1.660\,56 \times 10^{-27}\,\mathrm{kg}$
Electron rest mass	m_e	$9.109\,53 \times 10^{-31}\,\mathrm{kg}$
Proton rest mass	m_p	$1.672\,65 \times 10^{-27}\,\mathrm{kg}$
Boltzmann constant	k_B	$1.380\,66 \times 10^{-23}\,\mathrm{kg}$
Molar gas constant	R	$8.314\,41\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}$
Permittivity of a vacuum	ϵ_0	$8.854\,188 \times 10^{-12}\,\mathrm{C}^2\,\mathrm{s}^2\,\mathrm{kg}^{-1}\,\mathrm{m}^{-3}$
	$4\pi\epsilon_0$	$1.112\,650 \times 10^{-10}\,\mathrm{C}^2\,\mathrm{s}^2\,\mathrm{kg}^{-1}\,\mathrm{m}^{-3}$
Rydberg constant		
(infinite nuclear mass)	R_∞	$2.179\,914 \times 10^{-23}\,\mathrm{J}$
First Bohr radius	a_0	$5.291\,77 \times 10^{-11}\,\mathrm{m}$
Bohr magneton	μ_B	$9.274\,09 \times 10^{-24}\,\mathrm{J\,T}^{-1}$
Stefan-Boltzmann constant	σ	$5.670\,32 \times 10^{-8}\,\mathrm{J\,m}^{-2}\,\mathrm{K}^{-4}\,\mathrm{s}^{-1}$

0.1 Integrals

$\int_0^a x(a-x)\sin(\frac{n\pi}{a}x)dx = 2[\frac{a}{n\pi}]^3[1-\cos(n\pi)]$ $\quad$ $\int \sin^2(kx)dx = \frac{1}{2}x - \frac{1}{4k}\sin(2kx) + C$

$\int_0^a x\sin^2(\frac{n\pi}{a}x)dx = \frac{a^2}{4}$ $\quad$ $\int_0^a x^2\sin^2(\frac{n\pi}{a}x)dx = (\frac{a}{2\pi n})(\frac{4\pi^3n^3}{3} - 2n\pi$

$$\int_0^a x\sin(\frac{n\pi}{a}x)\sin(\frac{m\pi}{a}x)dx = \begin{cases} \frac{-4a^2nm}{(n+m)^2(n-m)^2\pi^2} & (m+n)\text{ odd} \\ 0 & (m+n)\text{ even} \end{cases}$$

$\int \sin^2(x)dx = \frac{1}{4}\sin(2x) - \frac{1}{2}x + C$ $\quad$ $\int \cos^2(x)dx = \frac{1}{4}\sin(2x) + \frac{1}{2}x + C$

$\int_0^\infty x^n e^{-ax}dx = \frac{n!}{a^{n+1}}$ $\quad$ $\int_0^\infty e^{-ax^2}dx = (\frac{\pi}{4a})^{1/2}$

$\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{\sum_{k=1}^{n}(2n-1)}{2^{n+1}a^n}(\frac{\pi}{a})^{1/2}$ $\quad$ $\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}}$

$$\int_0^a \sin(\frac{n\pi x}{a})\sin(\frac{m\pi x}{a})dx = \int_0^a \cos(\frac{n\pi x}{a})\cos(\frac{m\pi x}{a})dx = \frac{a}{2}\,\delta_{nm} \qquad \delta_{nm} = \begin{cases} 1 & m=n \\ 0 & \end{cases}$$

0.2 Even/Odd

$\int_{-\infty}^\infty e(x)dx = 2\int_0^\infty e(x)dx$ $\quad$ $\int_{-\infty}^\infty o(x)dx = 0$

Even	g_1+g_2	g_1g_2	u_1u_2	u_1'	$g_1\circ g_2$	$g_1\circ u_1$	$u_1\circ g_1$
Odd	u_1+u_2	u_1g_1		g_1'	$u_1\circ u_2$		

0.3 Identities

$\sin(\alpha)\sin(\beta) = \frac{1}{2}\cos(\alpha-\beta) - \frac{1}{2}\cos(\alpha+\beta)$ $\quad$ $\cos(\alpha)\cos(\beta) = \frac{1}{2}\cos(\alpha-\beta) + \frac{1}{2}\cos(\alpha+\beta)$

$\sin(\alpha)\cos(\beta) = \frac{1}{2}\sin(\alpha+\beta) + \frac{1}{2}\sin(\alpha-\beta)$

$\sin(\alpha\pm\beta) = \sin(\alpha)\cos(\beta) \pm \cos(\alpha)\sin(\beta)$ $\quad$ $\cos(\alpha\pm\beta) = \cos(\alpha)\cos(\beta) \mp \sin(\alpha)\sin(\beta)$

$e^{\pm i\theta} = \cos(\theta) \pm i\sin(\theta)$

$\cos(\theta) = \frac{e^{i\theta}+e^{-i\theta}}{2}$ $\quad$ $\sin(\theta) = \frac{e^{i\theta}-e^{-i\theta}}{2i}$

$f(x) = \sum_{n=0}^\infty \frac{f^{(n)}(a)(x-a)^n}{n!}$ $\quad$ $e^x = \sum_{n=0}^\infty \frac{x^n}{n!}$

$\cos(x) = \sum_{k=0}^\infty \frac{x^{2k}}{(2k)!}$ $\quad$ $\sin(x) = \sum_{k=1}^\infty \frac{x^{2k+1}}{(2k+1)!}$

1 Schrödinger equation

$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi$ $\int_{-\infty}^{\infty}|\Psi(x,t)|^2dx = 1$

$\int_a^b |\Psi(x,t)|^2dx$ = probability of finding the particle between a and b, at time t.

$\int_{-\infty}^{\infty}|\Psi(x,t=0)|^2dx = 1 \implies \int_{-\infty}^{\infty}|\Psi(x,t)|^2dx = 1$

1.1 Stationary solutions, seperation of variables

$V(x,t) = V(x)$ $Psi(x,t) = \psi(x)\phi(t)$

$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi \Rightarrow i\hbar\frac{1}{\phi}\frac{d\phi}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{d^2\psi}{dx^2} + V$

$\boxed{\frac{d\phi}{dt} = -\frac{iE}{\hbar}\phi \Rightarrow \phi(t) = e^{iEt/\hbar}}$ $\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi}$

To solve for $\psi(x)$ we need $V(x)$ $\hat{H}\psi = E\psi$ $\hat{H}^2\psi = E^2\psi$

$\Psi(x,t) = \psi\cdot e^{i\Theta} \to |\Psi|^2 = e^{-i\Theta}\psi^*\cdot e^{i\Theta}\psi = \psi^*\psi = |\psi|^2$

$\langle H\rangle = E$ $\sigma_H^2 = 0$ $\Psi_n(x,t)$ are complete!

1.1.1 Case $V(x) \equiv 0$

$\rightarrow \frac{d^2\psi}{dx^2} = -k^2\psi$ leads to 2 general solutions:

$$\begin{cases} \text{Travelling Waves} & \psi(x) = Ce^{ikx} + De^{-ikx} \\ \text{Standing Waves} & \psi(x) = A\sin(kx) + B\cos(kx) \end{cases}$$

1.1.2 The free particle, travelling waves

$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$ $\psi(x) = Ce^{ikx} + De^{-ikx}$ $\psi_k(x) = C'e^{ikx}$

$\Psi_k(x,t) = \psi_k(x)e^{-iEt/\hbar}$ with $E = \frac{\hbar^2k^2}{2m}$ $p = \hbar k$

$\Psi_k(x,t) = C'e^{i(kx-\frac{\hbar k^2}{2m}t)}$ and $\begin{cases} k > 0 & \Rightarrow \text{going right} \\ k < 0 & \Rightarrow \text{going left} \end{cases}$

$$\boxed{|\Psi_k(x,t)|^2 = |C'|^2 \to \int_{-\infty}^{\infty}|\Psi_k|^2dx = \infty \neq 1!}$$

Thus a free particle with definite energy does not exist!

$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}g(k)\exp(i(kx - \frac{\hbar k^2}{2m}t))dk$ $c_n = \frac{g(k)dk}{\sqrt{2\pi}}$

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

$$\boxed{f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}F(k)e^{ikx}dk \Leftrightarrow F(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(x)e^{-ikx}dx}$$

Plancherel

If a particles wave packet is localized in position, it contains many k-components, thus the momentum($p = \hbar k$) is unclear. If a particles wave packet is delocalized in position, it contains few k-components, thus the momentum is clearly defined, though the position is not.

1.2 The infinite square well, standing waves

$V(x) = 0 \;\forall\; x \in (0,a) \Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$

$\psi(x) = A\sin(kx) + B\cos(kx)$.

BC: $\psi(x) = A\sin(kx)$ $k = \frac{n\pi}{a} \Rightarrow E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}$ $|A|^2 = \frac{2}{a}$.

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

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty}c_n\sqrt{\frac{2}{a}}\sin(\frac{n\pi}{a}x)e^{-i(n^2\pi^2\hbar/2ma^2)t}}$$

$c_n = \sqrt{\frac{2}{a}}\int_0^a sin(\frac{n\pi}{a}x)\Psi(x,0)dx$ $\langle\hat{H}\rangle = \sum_{n=1}^{\infty}|c_n|^2E_n$

$\sum_{n=1}^{\infty}|c_n|^2 = 1$ $|c_n|^2$ probability to measure E_n.

1.3 The harmonic Oscillator

$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$ $\omega = \sqrt{\frac{k}{m}}$

1.3.1 Ladder Operators

$$\boxed{\hat{a}_\pm = \frac{1}{\sqrt{2\hbar m\omega}}(\mp i\hat{p} + m\omega\hat{x}) \qquad \hat{N} = \hat{a}_+\hat{a}_- \qquad \langle\hat{N}\rangle = n}$$

$\hat{H} = \hbar\omega(a_-a_+ - \frac{1}{2})$ $\hat{H} = \hbar\omega(a_+a_- + \frac{1}{2})$ $[a_-, a_+] = 1$

$$\boxed{\psi_n\hat{a}_+ = \psi_{n+1} \text{ has } E = E_n + \hbar\omega}$$

$$\boxed{\psi_0\hat{a}_- = 0 \qquad \psi_0 = (\frac{m\omega}{\pi\hbar})^{1/4}e^{-\frac{m\omega}{2\hbar}x^2} \qquad E_0 = \frac{1}{2}\hbar\omega}$$

$$\boxed{\psi_1 = (\frac{m\omega}{\pi\hbar})^{\frac{1}{4}}\;(\frac{2m\omega}{\hbar})^{\frac{1}{2}}\;x\;e^{-\frac{m\omega}{2\hbar}x^2}}$$

$$\boxed{\psi_n = A_n(a_+)^n\psi_0 \qquad E_n = (n+\frac{1}{2})\hbar\omega) \qquad A_n = \frac{1}{\sqrt{n!}}}$$

- ψ_n alternate between even and odd.
- ψ_n are mutually orthogonal: $\int_{-\infty}^{\infty}\psi_m^*\psi_ndx = \delta_{mn}$
- classical turning point x_p from $E_n = V(x)$

1.4 Delta-Function potential

$V(x) = -\alpha\delta(x)$ $-\frac{\hbar^2}{2m}\cdot\frac{\partial^2\psi}{\partial x^2} - \alpha\delta(x)\psi = E\psi$

1.4.1 Bound state

$$\psi(x)\begin{cases} Be^{\kappa x} & (x \le 0) \\ Be^{-\kappa x} & (x \ge 0) \end{cases} \qquad \kappa = \frac{m\alpha}{\hbar^2} \qquad B = \frac{\sqrt{m\alpha}}{\hbar}$$

$\boxed{\psi(x) = \frac{\sqrt{m\alpha}}{\hbar}e^{-m\alpha|x|/\hbar^2} \qquad E = -\frac{m\alpha^2}{2\hbar^2}}$ single bound state

1.4.2 Scattering states

$\psi(x<0) = Ae^{ikx} + Be^{-ikx}$ $\psi(x>0) = Fe^{ikx} + Ge^{-ikx}$

A - incident wave; B - reflected wave; F - transmitted wave; G = 0

$$\boxed{B = \frac{i\beta}{1-i\beta}A, \quad F = \frac{1}{1-i\beta}A \qquad \beta = \frac{m\alpha}{\hbar^2k} \quad k = \frac{\sqrt{2mE}}{\hbar}}$$

$\boxed{R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1+\beta^2} = \frac{1}{1+(2\hbar^2E/m\alpha^2)}}$ reflection coeff.

$\boxed{T = \frac{|F|^2}{|A|^2} = \frac{1}{1+\beta^2} = \frac{1}{1+(m\alpha^2/2\hbar^2E)}}$ transmission coeff.

$R + T = 1$ higher E $\rightarrow$ higher probability of transmission

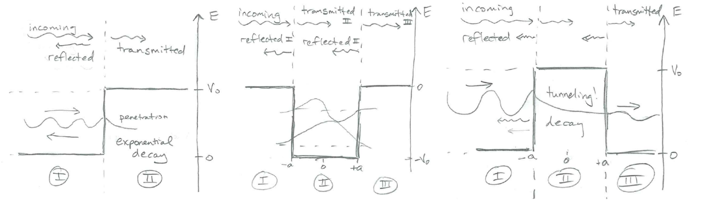
1.4.3 Delta barrier

- Change sign of $\alpha \rightarrow$ no bound state.
- r. and t. coefficients unaffected.
- transmission $\rightarrow$ tunneling

1.5 Finite step, finite well, finite barrier

Divide in regions and solve T.I.S.E. in each of them.

BC: [ψ finite, continuous, $\frac{d\psi}{dx}$ continuous]



1.5.1 Sharp potential change

- Higher energy $\rightarrow$ reflection, transmission.
- Lower energy $\rightarrow$ reflection, penetration.
- Pentration: with exponentially decaying probability, can lead to tunneling.

1.5.2 Scattering and bound states

$E > V(\pm\infty) \Rightarrow$ scattering state

$E < V(\pm\infty) \Rightarrow$ bound state

2 Formalism

2.1 Statistics

probability density: $\rho(x)$ $\quad P_{a,b} = \int_a^b \rho(x)dx$

$1 = \int_{-\infty}^{\infty} \rho(x)dx$ $\quad \langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)dx$

$\langle f(x) \rangle = \int_{-\infty}^{\infty} f(x)\rho(x)dx$ $\quad \sigma^2 = \langle(\Delta x)^2\rangle = \langle x^2 \rangle - \langle x \rangle^2$

2.2 Inner products

$\langle \alpha|\beta \rangle = a_1^* b_1 + a_2^* b_2 + \cdots + a_N^* b_N$ $\quad \langle f|g \rangle \equiv \int_a^b f(x)^* g(x)dx$

$$\boxed{|\int_a^b f(x)^* g(x)dx| \le \sqrt{\int_a^b |f(x)|^2 dx \int_a^b |g(x)|^2 dx}}$$

The inner product of square-integrable functions converges.

$\langle f|g \rangle = \langle g|f \rangle$ $\quad \langle f|f \rangle = \int_{-\infty}^{\infty} |f(x)|^2 dx$

$\{f_n\}$ is complete if for any function $F(x) = \sum_{n=1}^{\infty} c_n f_n(x)$

2.2.1 Fouriers trick

orthonormal set of functions: $\{f_n(x)\}$ $\quad \rightarrow c_n = \langle f_n|f \rangle$

$F(x) = \sum_{n=1}^{\infty} \langle f_n|f \rangle \cdot f_n(x)$

2.3 Hilbert Space

$f(x) \ : \ \int_a^b |f(x)|^2 dx < \infty$ respectively $\Psi \ : \ \int_{-\infty}^{\infty} |\Psi|^2 dx = 1$

$\lim_{x\to\pm\infty} \frac{df}{dx} = 0$

2.4 Observables and Operators

$Q(x,p)$ and $\hat{Q}(x, \frac{\hbar}{i}\frac{\partial}{\partial x})$ $\quad \langle Q \rangle = \int \Psi^* \hat{Q} \Psi dx = \langle \Psi | \hat{Q} \Psi \rangle$

$\hat{x} = x$ $\quad \hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$ $\quad \langle p \rangle = \frac{m d\langle x \rangle}{dt}$ $\quad$ (Ehrenfest)

$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ $\quad \langle H \rangle = \frac{\sum_{n=1}^{\infty} |c_n|^2 E_n}{N}$

$\boxed{\text{Hermitian operator } \langle f|\hat{Q}g \rangle = \langle \hat{Q}f|g \rangle}$

$\boxed{\text{Observables are represented by hermitian operators.}}$

$\langle f|(\hat{Q}_1 + \hat{Q}_2)g \rangle = \langle (\hat{Q}_1 + \hat{Q}_2) f|g \rangle$

$\langle f|\hat{Q}(\hat{R}f) \rangle = \langle \hat{Q}f|\hat{R}f \rangle = \langle \hat{R}(\hat{Q}f)|f \rangle \ \forall \hat{Q}, \hat{R} \ : \ [\hat{Q}, \hat{R}] = 0$

2.5 Commutators

$[A,B] = AB - BA$ $\quad [\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] - [\hat{A}, \hat{C}]\hat{B}$

$[\hat{x}, \hat{p}_x] = i\hbar$ $\quad [\hat{a_-}, \hat{a_+}] = 1$ $\quad [\hat{x}^n, \hat{p}_x] = i\hbar n x^{n-1}$ $\quad [f(\hat{x}), \hat{p}] = i\hbar \frac{\partial f}{\partial x}$

$[\hat{H}, \hat{x}] = \frac{i^2\hbar^2}{m}\frac{\partial}{\partial x} = -\frac{i\hbar\hat{p}}{m}$ $\quad [\hat{x}, \hat{y}] = [\hat{x}, \hat{p}_y] = [\hat{p}_x, \hat{p}_y] = 0$

$[\hat{L}_z, \hat{x}] = i\hbar y$ $\quad [\hat{L}_z, \hat{y}] = -i\hbar x$ $\quad [\hat{L}_z, \hat{z}] = 0$

$[\hat{L}_z, \hat{p}_y] = -i\hbar\hat{p}_x = -\hbar^2\frac{\partial}{\partial x}$ $\quad [\hat{L}_z, \hat{p}_x] = i\hbar\hat{p}_y = \hbar^2\frac{\partial}{\partial y}$

$[\hat{L}_z, \hat{p}_z] = 0$ $\quad [\hat{L}_z, \hat{r}^2] = 0$ $\quad [\hat{L}_z, \hat{p}^2] = 0$ $\quad [\hat{H}, \hat{L}^2, \hat{L}_z] = 0$

for H: $\langle x \rangle = 0$ $\quad \langle x^2 \rangle = ? \rightarrow \langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\langle x^2 \rangle$

2.6 Determinate States

$\hat{Q}\Psi = q\Psi$ $\quad$ Spectrum of $\hat{Q}$: $\{q_n\}$ $\quad$ Eigenfunctions Ψ_n

$\boxed{\text{Determinate states are eigenfunctions of } \hat{Q}}$

Degenrate states: $\quad \hat{Q}\Psi_1 = \hat{Q}\Psi_2 = q\Psi$

$\boxed{\text{Eigenfunctions of a hermitian operator are } \textit{complete}}$

$\langle \hat{Q} \rangle = \sum_n |c_n|^2 q_n$ $\quad \sum_n |c_n|^2 = 1$

2.6.1 Examples of Eigenfunctions

Position $\hat{X} g_{x'}(x) = x' g_{x'}(x)$ $\quad g_{x'}(x) = \delta(x - x')$

Momentum $\hat{p} f_p(x) = p f_p(x)$ $\quad f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}$

Dirac Orthonormality:

$\langle g_{x'}|g_{x''} \rangle = \delta(x' - x'')$ $\quad \langle f_{p'}|f_{p''} \rangle = \delta(p' - p'')$

2.7 Dirac Notation

$\langle f|g \rangle \equiv \int_a^b f(x)^* g(x)dx$ with **bra** $\langle \alpha|$ and **ket** $|\beta\rangle$.

bra $\langle \alpha|$ - linear function of vectors

ket $|\beta\rangle$ - vector

Operator $\hat{Q}$ - matrix

$\Psi(x,t) = \langle x|\int(t) \rangle$ $\quad \Phi(p,t) = \langle p|\int(t) \rangle$ $\quad c_n(t) = \langle n|\int(t) \rangle$

$\Psi(x,t), \Phi(p,t), c_n(t)$ are the coefficients in the expansion of $|\int\rangle$ in the basis of the corresponding eigenfunctions.

$\Psi(x,t) = \int \Psi(y,t)\delta(x-y)dy = \int \Phi(p,t)\frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar} dp = \sum c_n e^{iE_n t/\hbar} \psi_n(x)$

2.8 Compatible Observables / Uncertainty Principle

$\boxed{\text{Two observables can be precisely determined iff } [\hat{Q}_1, \hat{Q}_2] = 0}$

$$\boxed{\sigma_{\hat{Q}_1}^2 \sigma_{\hat{Q}_2}^2 = (\tfrac{1}{2i}\langle[\hat{Q}_1, \hat{Q}_2]\rangle)^2 \qquad \sigma_x \sigma_p \ge \tfrac{\hbar}{2} \qquad \Delta t \Delta E \ge \tfrac{\hbar}{2}}$$

$$\boxed{\frac{d}{dt}\langle Q\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{Q}]\rangle + \langle\frac{d\hat{Q}}{dt}\rangle \quad \text{is } \langle\frac{d\hat{Q}}{dt}\rangle \neq 0 \text{ ?} \quad \Delta t = \frac{\sigma_{\hat{Q}}}{|\frac{d\langle\hat{Q}\rangle}{dt}|}}$$

2.9 Classical Physics

$p = \frac{h}{\lambda}$ de Broglie formula $\qquad E = \frac{p^2}{2m}$

Wave function $f(x) = Ae^{ikx} \qquad k = \frac{2\pi}{\lambda}$

3 QM in 3 dimensions

3.1 Generalization

$p = \frac{\hbar}{i}\nabla \qquad i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$ (TDSE)

$\Psi_n(r,t) = \Psi_n(r)e^{-iE_nt/\hbar} \qquad -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$ (TISE)

ISW: $\psi(x,y,z) = \frac{2}{a}^{3/2}\sin(\frac{n_x\pi}{a}x)\sin(\frac{n_y\pi}{a}y)\sin(\frac{n_z\pi}{a}z)$

3.2 Spherical coordinates

$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}(\frac{\partial^2}{\partial\phi^2})$

$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}(r^2\frac{\partial\psi}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\psi}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}(\frac{\partial^2\psi}{\partial\phi^2})\right] + V\psi = E\psi$

3.3 Seperation of Variables

$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

$$\underbrace{\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]\right\}}_{\text{A, depends on r}} + \underbrace{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{dY}{d\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}}_{\text{B, depends on }\theta,\ \phi} = 0$$

thus each part has to be constant $\rightarrow$ seperation constant:

$A(r) = l(l+1) \qquad B(\theta,\phi) = -l(l+1)$

3.3.1 Angular Equation

$\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{dY}{d\theta}\right) + \frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)\sin^2\theta Y$

$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$

$$\underbrace{\left\{\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta\right\}}_{\text{C, depends on }\theta} + \underbrace{\frac{1}{\Psi}\frac{d^2\Psi}{d\psi^2}}_{\text{D, depends on }\phi} = 0$$

thus each part has to be constant $\rightarrow$ seperation constant:

$C(\theta) = m^2 \qquad D(\phi) = -m^2$

3.4 Solution, ϕ-equation

$\Phi(\phi) = e^{im\phi} \qquad \Phi(\phi + 2\pi) = \Phi(\phi) \qquad m = 0,\ \pm1,\ \pm2,\ \ldots$

3.5 Solution, θ-equation

$\Theta(\theta) = AP_l^m(\cos\theta)$

associated Legendre function:

$P_l^m \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|}P_l(x)$

Legendre polynomial defined by Rodrigues formula:

$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l(x^2-1)^l$

3.6 From this: Spherical Harmonics

$$\boxed{Y_l^m(\theta,\phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\ e^{im\phi}\ P_l^m(\cos\theta)}$$

$$\epsilon = \begin{cases} (-1)^m & m \geq 0 \\ 1 & m \leq 0 \end{cases}$$

Spherical harmonics are orthogonal!

$\langle Y_l^m|Y_{l'}^{m'}\rangle = \delta_{ll'}\delta mm'$

3.7 The radial equation

$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r)-E]R = l(l+1)R$

$u(r) = rR(r)$

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu}$$

Identical to the one-dimensional SE, except for the effective potential.

$$V_{eff} = V + \underbrace{\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}}_{\text{centrifugal term}}$$

The centrifugal term tends to throw the particle away from the origin.

$\lim_{r\to0} V_{eff} = \infty$

4 The Hydrogen Atom

$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu$

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{e\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} \qquad n = 1,\ 2,\ 3,\ \ldots}$$

$$\boxed{\text{ground state: } E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\,\text{eV}}$$

$$\boxed{\text{Bohr radius: } a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.592\times10^{-10}\,\text{m}}$$

$$\boxed{R_{nl}(r) = \sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^2}}\exp(-\frac{r}{na})\left(\frac{2r}{na}\right)^l L_{(n+l)-(2l+1)}^{2l+1}\left(\frac{2r}{na}\right)}$$

$$\boxed{\psi_{nlm_l}(r,\theta,\phi) = R_{nl}Y_l^{m_l}(\theta,\phi)}$$

$n = 1,\ 2,\ 3,\ \ldots$	principal quantum number
$l = 0,\ 1,\ 2,\ \ldots,\ n-1$	azimuthal quantum number
$m_l = -l, -l+1, .., -1, 0, 1, .., l-1, l$	magnetic quantum number

4.1 Angular Momentum

Classically $\mathbf{L} = \mathbf{r}\times\mathbf{p} \qquad [\hat{H},\hat{L}^2,\hat{L}_z] = 0$

$L_x = yp_z - zp_y \qquad L_y = zp_x - xp_z \qquad L_z = xp_y - yp_x$

$$\boxed{[L_x,L_y] = i\hbar L_z;\ [L_y,L_z] = i\hbar L_x;\ [L_z,L_x] = i\hbar L_y}$$

$L^2 = L_x^2 + L_y^2 + L_z^2 \qquad |\vec{L}| = \sqrt{L^2} \qquad [L^2, L_{x,y,z}] = 0$

$$\boxed{L^2 f_l^m = \hbar^2 l(l+1)f_l^m \qquad L_z f_l^m = \hbar m f_l^m}$$

$$\boxed{L_\pm \equiv L_x \pm iL_y \text{ where } L_z(L_\pm f) = (\mu\pm\hbar)(L_\pm f)}$$

4.1.1 Eigenfunctions f_l^m

$\vec{L} = \vec{r} \times \vec{p} = \frac{\hbar}{i}(\vec{r} \times \vec{\nabla}) = \frac{\hbar}{i}\left(\vec{u_\phi}\frac{\partial}{\partial\theta} - \vec{u_\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right)$

in spherical coordinates: $\vec{\nabla} = \vec{u_r}\frac{\partial}{\partial r} + \frac{\vec{u_\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\vec{u_\phi}}{r\sin\theta}\frac{\partial}{\partial\phi}$

$$\hat{L_x} = \frac{\hbar}{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cos\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$
$$\hat{L_y} = \frac{\hbar}{i}\left(\cos\phi\frac{\partial}{\partial\theta} - \sin\phi\cot\theta\frac{\partial}{\partial\phi}\right)$$
$$\hat{L_x} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$
$$\hat{L^2} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

$\hat{L}^2 f_l^{m_l} = \hbar^2 l(l+1) f_l^{m_l} \qquad \hat{L_z} f_l^{m_l} = \hbar m_l f_l^{m_l}$

leads to $\boxed{f_l^{m_l} = Y_l^{m_l}}$ which proves $Y_l^{m_l}$ are orthogonal, because they are the eigenfunctions of a hermitian operator.

4.2 Spin

$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \qquad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x \qquad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$

$$\boxed{S^2|sm\rangle = \hbar^2 s(s+1)|sm\rangle \qquad S_z|sm\rangle = \hbar m|sm\rangle}$$

$$\boxed{S^2 f_s^{m_s} = \hbar^2 s(s+1) f_s^{m_s} \qquad S_z f_s^{m_s} = \hbar m_s f_s^{m_s}}$$

$$\boxed{S_\pm \equiv S_x \pm iS_y}$$

Electron $\to s = \frac{1}{2}$ Photon $\to s = 1$

For the electron: Only two eigenstates $f_{\frac{1}{2}}^{\frac{1}{2}}$ and $f_{\frac{1}{2}}^{-\frac{1}{2}}$.

Dirac notation: $f_s^{m_s} \to |s, m_s\rangle$

$f_{\frac{1}{2}}^{\frac{1}{2}} \to |\frac{1}{2}, \frac{1}{2}\rangle \to$(up) $\qquad f_{\frac{1}{2}}^{-\frac{1}{2}} \to |\frac{1}{2}, -\frac{1}{2}\rangle \to$(down)

general spin: $|\chi\rangle = a|\frac{1}{2}, \frac{1}{2}\rangle + b|\frac{1}{2}, -\frac{1}{2}\rangle$

$$\boxed{|\chi\rangle = a\underbrace{\begin{pmatrix}1\\0\end{pmatrix}}_{\text{up}} + b\underbrace{\begin{pmatrix}0\\1\end{pmatrix}}_{\text{down}}}$$

Probability to measure spin up: $|a|^2$

$|\chi\rangle = \begin{pmatrix}3i\\4\end{pmatrix}\frac{1}{5} \to \langle\chi|\chi\rangle = 1 = \frac{1}{25}\begin{pmatrix}-3i & 4\end{pmatrix}\begin{pmatrix}3i\\4\end{pmatrix}$

4.2.1 Operators

$\hat{S}^2 \to \frac{3}{4}\hbar^2\begin{pmatrix}1&0\\0&1\end{pmatrix} \qquad \hat{S}_z \to \frac{\hbar}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}$

$\hat{S}_x \to \frac{\hbar}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix} \qquad \hat{S}_y \to \frac{\hbar}{2}\begin{pmatrix}0&-i\\i&0\end{pmatrix}$

$\hat{S_+} \to \hbar\begin{pmatrix}0&1\\0&0\end{pmatrix} \qquad \hat{S_-} \to \hbar\begin{pmatrix}0&0\\1&0\end{pmatrix}$

for example $\hat{S_+}|\frac{1}{2}, -\frac{1}{2}\rangle = \hbar|\frac{1}{2}, \frac{1}{2}\rangle$ raises S_z by $\hbar$

What values at which probabilities? $\to$ Find EV of $\hat{S}_y$, normalize, project $|\chi\rangle$ onto EV_i, $abs()^2$ gives probability.

5 Identical Particles

5.1 Two-particle systems

$\Psi(\vec{r}_1, \vec{r}_2, t)$

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

probability to find particle 1 in volume $d^3\vec{r_1}$ **and** particle two in volume $d^3\vec{r_2}$: $\boxed{|\Psi(\vec{r}_1, \vec{r}_2, t)|^2 d^3\vec{r}_1 d^3\vec{r}_2}$

5.1.1 Seperation

Center of mass motion:	$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$	$\vec{r}_1 = \vec{R} + \frac{m_r}{m_1}\vec{r}$
reduced mass:	$m_r = \frac{m_1 m_2}{m_1+m_2}$	$\vec{r}_2 = \vec{R} - \frac{m_r}{m_2}\vec{r}$
Relative motion:	$\vec{r} = \vec{r}_1 - \vec{r}_2$	$\nabla_1 = \nabla_r + \frac{m_r}{m_2}\nabla_R$

$\nabla_2 = -\nabla_r + \frac{m_r}{m_1}\nabla_R \qquad [-\frac{\hbar^2}{2(m_1+m_2)}\nabla_R^2 - \frac{\hbar^2}{2m_r}\nabla_r^2 + V(\vec{r})]\psi = E\psi$

$$\boxed{\psi(\vec{r}_1, \vec{r}_2) \Rightarrow \psi = \psi_R(\vec{R}) \cdot \psi(\vec{r})}$$

ψ_R satisfies one particle SE with $m = m_1 + m_2,\ V = 0,\ E = E_R$

ψ_r satisfies one particle SE with $m = m_r,\ V = V(\vec{r}),\ E = E_r$

$E_{tot} = E_R + E_r$

5.2 Distinguishable particles

$$\boxed{\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r})\psi_b(\vec{r}_2) \text{ or } \psi(\vec{r}_1, \vec{r}_2) = \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)}$$

5.3 Indistinguishable particles

$$\boxed{\begin{aligned}\psi_+(\vec{r}_1, \vec{r}_2) &= A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right]\\ \psi_-(\vec{r}_1, \vec{r}_2) &= A\left[\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\right]\end{aligned}}$$

5.3.1 Exchange force

$$\boxed{\hat{P}f(\vec{r}_1, \vec{r}_2) \longrightarrow f(\vec{r}_2, \vec{r}_1) \qquad [\hat{P}, \hat{H}] = 0 \qquad EV_P = \pm 1}$$

$\langle(x_1 - x_2)^2\rangle$ for ψ_+ and ψ_-:

ψ_+	lower energy, forms bond, closer together
ψ_-	higher energy, forms antibond, farther apart

5.3.2 Axiom for Bosons and Fermions

Bosons	**Fermions**
photons, gravitons	electrons, protons, neutrons
integer Spin	$\frac{1}{2}$-integer Spin
symmetric	antisymmetric

Electrons are fermions $\to \psi$ should be antisymmetric **but** ψ_- is unbonding!

$\to$ consider **spin**

Possible spins for 2 electrons:

both spin up	$\uparrow\uparrow$	symmetric triplet
both spin down	$\downarrow\downarrow$	
one up one down	$\frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$	
or	$\frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$	antisymmetric singlet

5.3.3 Overall Wavefunction

$\underbrace{\psi(\vec{r})}_{\text{spatial}} \cdot \underbrace{\chi(s)}_{\text{spin}} = \psi_+ \cdot (singlet)$ yields a bonding electron pair!

6 Atoms

$$\boxed{\hat{H} = \sum_{j=1}^{Z} \left[\left\{ -\frac{\hbar^2}{2m}\nabla_j^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r_j} \right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0} \sum_{k\neq j}^{Z} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} \right) \right]}$$

First part in {}: Kinetic energy + interaction of nucleus with j_{TH} electron.

Second part in (): Repulsive interaction between electron j and k. Factor $\frac{1}{2}$ avoids double counting.

6.1 Placement of electrons

Each electron placed in a single-particle hydrogenic state: ψ_{n,l,m_l,m_s}.

$n = 1,\ 2,\ 3,\ \dots$	shell (K,L,M,N)
$l = 0,\ 1,\ 2,\ \dots,\ n-1$	subshell (or shape) s,p,d,f,g,...
$m_l = -l, -l+1, .., -1, 0, 1, .., l-1, l$	orientation of orbital p_x, p_y, p_z
$m_s = \pm\frac{1}{2}$	spin of electron

$\boxed{\text{Hydrogenic state of the same n are degenerate.}}$

$\boxed{\text{In reality screening prevents this.}}$

$[Cr] = [Ar]4s3d^5$ $[Cu] = [Ar]4s3d^{10}$

6.2 Angular momentum in multiparticle systems

L	$\equiv$ total orbital angular momentum
S	$\equiv$ total spin angular momentum
$J = L + S$	$\equiv$ total angular momentum
M_L	$\equiv \sum_i m_{li}$
M_S	$\equiv \sum_i m_{si}$
$M_J = M_L + M_S$	$\equiv$ related to projection along z-axis

Filled subshell: $M_s = 0 \Rightarrow S = 0 \quad M_L = 0 \Rightarrow L = 0$

$\boxed{\text{Filled subshells never contribute to L,S,J}}$

6.2.1 Addition rule

given j_1 and j_2, $J = j_1 + j_2$

$$\boxed{J = (j_1 + j_2), (j_1 + j_2 - 1), (j_1 + j_2 - 2), \dots, |j_1 - j_2|}$$

6.2.2 Labelling

${}^{2S+1}L_J$

for L use: S,P,D,F,G,...

if $S = 0 \Rightarrow$ called single state

if $S = 1 \Rightarrow$ called triplet state

6.3 Hund's Rules

- The state with the largest S is the most stable.
- For states with the same S the largest L is most stable.
- For states with the same S and L:
  - smallest J is most stable for subshells less than half full.
  - largest J is most stable for subshells more than half full.

7 Solids

$\rightarrow$ 3D particle-in-a-box

$\rightarrow E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2}\right)$

$\Delta E = 1 \times 10^6\,\text{eV} \ll k_B T$ at room temperature

ΔE very small $\rightarrow$ continuous electron-bands.

7.1 Fermi level

Fill up the band with electrons $\rightarrow$ highest occupied level?

K-space, each point represents a combination of n_i.

1D	2D	3D
$E_{n_x} = \frac{\hbar^2 k_x^2}{2m}$	$E_{n_{x,y}} = \frac{\hbar^2(k_x^2+k_y^2)}{2m}$	$E_{n_{x,y,z}} = \frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2m}$
$k_F = k_x$	$k_F = \sqrt{k_x^2 + k_y^2}$	$k_F = \sqrt{k_x^2 + k_y^2 + k_z^2}$
$V_1 = \frac{\pi}{L_x}$	$V_2 = \frac{\pi^2}{L_x L_y}$	$V_3 = \frac{\pi^3}{L_x L_y L_z}$
$V_{tot,1} = k_F$	$V_{tot,2} = \frac{1}{4}k_F^2\pi$	$V_{tot,3} = \frac{1}{8}\cdot\frac{4}{3}k_F^3\pi$

$k = \frac{N\pi}{L}$ $n = \frac{M}{L^{(D)}}$ $N = \frac{M}{2}$

$V_{tot,D} = V_D N = V_D \frac{M}{2}$ $L_i = L$ $\rightarrow E_F(k_F) = ?$

$E_F = \frac{\hbar^2 k_F^2}{2m}$

$E_{F,1} = \frac{h^2 n^2}{32 m_e}$ $E_{F,2} = \frac{h^2 n}{4\pi m_e}$ $E_{F,3} = \frac{h^2}{8m_e}\cdot\frac{3n}{\pi}^{2/3}$

N_q - number of occupied 1-electron levels

$$\boxed{N_q = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{2/3} \qquad D(E) = \frac{\partial N_q}{\partial E} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}}$$

7.2 Insulators and semiconductors

Periodic potential $V(x) = V(x+a)$

$|\psi(x+a)|^2 = |\psi(x)|^2 \rightarrow |\psi(x)|^2$ is periodic.

Displacement operator $\hat{D}$, $\hat{D}f(x) = f(x+a)$

$\Rightarrow [\hat{D}, \hat{H}] = 0 \rightarrow \psi(x)$ are eigenfunctions of $\hat{D}$

$$\boxed{\text{Bloch's theorem: } \psi(x+a) = e^{iKa}\psi(x)}$$

Boundary condition $\psi(x) = \psi(Na + x) \overset{\text{Bloch}}{=} e^{iKNa}\psi(x)$

$\rightarrow e^{iKNa} = 1 \Rightarrow K = \frac{2\pi s}{Na}$

7.3 Dirac's comb

$V(x) = \alpha \sum_{j=0} N - 1\delta(x - ja)$

for $0 < x < a$: $\psi(x) = A\sin(kx) + B\cos(kx)$

Boundary conditions: Bloch, continuity of $\psi(x)$ and $\frac{\partial\psi(x)}{\partial x}$

$$\boxed{\cos(Ka) = \cos(ka) + \frac{m\alpha}{\hbar^2 k}\sin(ka)}$$

$\rightarrow$ LHS $\in [-1, 1]$ but RHS is not!

$\boxed{\text{Only certain ranges of E are allowed!}}$

7.4 Impurities

$n_{electrons} = N_D \exp(\frac{-E_D}{k_B T})$

8 Perturbation Theory

8.1 non-degenerate

Perturbed potential → new Hamiltonian: $H = H^0 + \lambda H'$

$\psi_n = \phi_n^0 + \lambda \psi_n^1 + \cdots \qquad E_n = E_n^0 + \lambda E_n^1 + \cdots$

1_{st} order: $H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

→ multiply by $(\psi_n^0)^*$ and integrating → Inner product.

$$\boxed{E_n^1 = \langle \psi_n^0 | H' | \psi_n^0 \rangle} \qquad \boxed{E_n^2 = \sum_{m \neq n} \frac{|\langle \psi_m^0 | H' | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0}}$$

$$\boxed{\psi_n^1 = \sum_{m \neq n} \frac{\langle \psi_m^0 | H' | \psi_n^0 \rangle}{(E_n^0 - E_m^0)} \psi_m^0}$$

The denominator is safe as long as the unperturbed Energy spectrum is nondegenerate.

8.2 degenerate

$H^0 \psi_a^0 = E^0 \psi_a^0 \qquad H^0 \psi_b^0 = E^0 \psi_b^0 \qquad \rightarrow \psi_0 = \alpha \psi_a^0 + \beta \psi_b^0$

When increasing the perturbation from 0 to 1, E^0 is split into two.

As before, 1_{st} order: $H^0 \psi_n^1 + H' \psi_n^0 = E_n^0 \psi_n^1 + E_n^1 \psi_n^0$

Taking the inner product with ψ_a^0, ψ_b^0 respectively:

$\alpha W_{aa} + \beta W_{ab} = \alpha E^1 \qquad \alpha W_{ba} + \beta W_{bb} = \beta E^1$

$$\boxed{W_{ij} \equiv \langle \psi_i^0 | H' | \psi_j^0 \rangle}$$

$$\boxed{E_\pm^1 = \frac{1}{2} \left[W_{aa} + W_{bb} \pm \sqrt{(W_{aa} - W_{bb})^2 + 4 |W_{ab}|^2} \right]}$$

This is equivalent to finding the eigenvalues of the W-matrix

$$\boxed{\begin{pmatrix} W_{aa} & W_{ab} \\ W_{ba} & W_{bb} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E^1 \begin{pmatrix} \alpha \\ \beta \end{pmatrix}}$$

If the W-matrix is diagonal, i.e. ψ_a^0 and ψ_b^0 are already the proper eigenstates:

$E_+^1 = W_{aa} = \langle \psi_a^0 | H' \psi_a^0 \rangle$

$E_-^1 = W_{bb} = \langle \psi_b^0 | H' \psi_b^0 \rangle$

9 Variational Principle

$$\boxed{E_{gs} \leq \langle \psi_{trial} | \hat{H} \psi_{trial} \rangle \equiv \langle \hat{H} \rangle}$$

9.1 Proof

$\psi_{trial} = \sum_n c_n \psi_n$ with $\hat{H} \psi_n = E_n \psi_n$

$\langle \hat{H} \rangle = \langle \sum_m c_m \psi_m | \hat{H} \sum_n c_n \psi_n \rangle = \sum_m \sum_n c_m^* c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$

$\sum_n |c_n|^2 \equiv 1 \qquad E_n \geq E_{gs} \Rightarrow \langle \hat{H} \rangle \geq E_{gs}$

9.2 Application

$\psi_{trial} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}$

$\Rightarrow E_{gs} \leq \langle \psi_{trial} | \hat{H} \psi_{trial} \rangle =$

$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-\alpha x^2/2} \cdot \left[-\frac{\hbar^2}{2m} \cdot \frac{\partial^2}{\partial x^2} + c x^4 \right] \cdot e^{-\alpha x^2/2}$

$E_{gs} \leq \frac{\hbar^2 \alpha}{4m} + \frac{3c}{4\alpha^2} \Rightarrow \frac{\partial}{\partial \alpha} E(\alpha) = 0 \Rightarrow \alpha_{min} = \left(\frac{6mc}{\hbar^2}\right)^{1/3}$

$$\boxed{E_{ges} \leq E(\alpha_{min})}$$