1. THE WAVE FUNCTION

1.1 The Schrödinger Equation

$i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\vec{\nabla}^2\Psi(\vec{r},t) + V(\vec{r},t)\Psi(\vec{r},t)$, $\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^3}{\partial z^3}$

Solve for the particle's wave function $\Psi(x,t)$

$\hbar = \frac{h}{2\pi} = 1.054572 \times 10^{-34}$ Js

1.2 The Statistical Interpretation

$\int_a^b |\Psi(x,t)|^2 dx = \{\text{P of finding the particle btwn } a \text{ and } b, \text{ at } t\}$

1.3 Probability

Standard deviation: $\sigma = \sqrt{\langle j^2\rangle - \langle j\rangle^2}$

Expectation value of x given Ψ: $\langle x\rangle = \int x|\Psi|^2 dx$

Probability current: $J(x,t) = \frac{i\hbar}{2m}(\Psi\frac{\partial\Psi^*}{\partial x} - \Psi^*\frac{\partial\Psi}{\partial x})$

1.4 Normalization

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

The Schrödinger equation produces unitary time evolution:

$\vec{J} = -\frac{i\hbar}{2m}(\psi(\vec{(r)},t)^*\vec{\nabla}\psi(\vec{r},t) - \psi(\vec{r},t)\vec{\nabla}\psi(\vec{r},t)^*)$

The probability density satisfies the continuity equation, $\frac{\partial}{\partial t}\mathcal{P} + \vec{\nabla}\cdot J = 0$

Because the probability for finding the particle at infinity is 0 (otherwise non-normalizable), $\vec{J} = 0$ at infinity.

Therefore, $\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\mathcal{P}d^3\vec{r} = \frac{\mathrm{d}}{\mathrm{d}t}P = 0$, where P is the total probability $\to$ the total probability is constant in time.

1.5 Momentum

For a particle in state Ψ, the expectation value of x and p is

$$\langle x\rangle = \int_{-\infty}^{+\infty} x|\Psi(x,t)|^2 dx \qquad \langle p\rangle = m\frac{d\langle x\rangle}{dt} = -i\hbar\int(\Psi^*\frac{\partial\Psi}{\partial x})dx$$

Expectation value of any quantity, $Q(x,p)$: $\langle Q(x,p)\rangle = \int\Psi^* Q(x, \frac{\hbar}{i}\frac{\partial}{\partial x})\Psi dx$

Position and momentum operators: $\widehat{\vec{r}} = \vec{r}$, $\widehat{\vec{p}} = -i\hbar\vec{\nabla}$

1.6: The Uncertainty Principle

The wavelength of Ψ is related to the momentum of the particle by the de Broglie formula: $p = \frac{h}{\lambda} = \frac{2\pi\hbar}{\lambda}$

Heisenberg's uncertainty principle: $\sigma_x\sigma_p \geq \frac{\hbar}{2}$

Commutation relation btwn position and momentum:

$$\widehat{p}_x(\widehat{x}\psi(x,t)) = -i\hbar\frac{\partial}{\partial x}[x\psi(x,t)] = -i\hbar\psi(x,t) - i\hbar x\frac{\partial}{\partial x}\psi(x,t)$$

$$\widehat{x}(\widehat{p}_x\psi(x,t)) = x(-i\hbar\frac{\partial}{\partial x}\psi(x,t))$$

$\widehat{x}\widehat{p}_x - \widehat{p}_x\widehat{x} = [\widehat{x},\widehat{p}_x] = i\hbar$

$[\widehat{x}_i,\widehat{p}_j] = i\hbar\delta_{ij}$, $[\widehat{x}_i,\widehat{x}_j] = [\widehat{p}_i,\widehat{p}_j] = 0$. $\delta_{ij} = 1$ for $i = j$, $\delta_{ij} = 0$ for $i \neq j$

Given three operators $\widehat{A},\widehat{B},\widehat{C}$, we have $[\widehat{A},\widehat{B}\widehat{C}] = [\widehat{A},\widehat{B}]\widehat{C} + \widehat{B}[\widehat{A},\widehat{C}]$.

2. Time-Independent Schrödinger Equation

2.1 Stationary States

Suppose PE is independent of time, $V(\vec{r},t) = V(\vec{r})$.

Separation of variables: $\Psi(\vec{r},t) = \psi(\vec{r})\varphi(t)$

Eq of motion for $\varphi(t)$: $\varphi(t) = e^{-iEt/\hbar}$

Eq of motion for $\psi(\vec{r})$ is the TISE: $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(\vec{r})}{\mathrm{d}x^2} + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$

TD of the wavefunction that corresponds to the constant E is easily written once we solve the TISE: $\Psi_E(\vec{r},t) = \psi_E(\vec{r})e^{-iEt/\hbar}$

Properties of solutions for TI potentials:

- **The constant E must be real.**
- **Stationary wavefunction.** $\mathcal{P}(\vec{r},t) = |\psi_E(\vec{r},t)|^2 = |\psi_E(\vec{r})|^2$ (TD cancels).
- **Stationary wavefunction is a state of definite energy.**

  Total E (kinetic + potential) is the Hamiltonian: $H(x,p) = \frac{p^2}{2m} + V(x)$

  Hamiltonian operator: $\widehat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$. TISE: $\widehat{H}\psi = E\psi$

  $\langle\widehat{H}\rangle = E$, $\langle\widehat{H}^2\rangle = E^2$, $\Delta E = \sqrt{\langle\widehat{H}^2\rangle - \langle\widehat{H}\rangle^2} = 0$
- **Spatial part of stationary wavefunction can be chosen to be real.**
  $\psi^*(\vec{r})$ is a soln w/ same E

  Solns can be chosen to be real: $\psi(\vec{r}) + \psi^*(\vec{r})$ and $\frac{\psi(\vec{r})-\psi^*(\vec{r})}{i}$.
- **Parity symmetry: even and odd wavefunctions.** Suppose $V(-\vec{r}) = V(\vec{r})$.
  Then, $\psi_E(-\vec{r})$ is a soln w the same energy.
  $\psi_E(\vec{r}) + \psi_E(-\vec{r})$ is even under reflection, $\psi_E(\vec{r}) - \psi_E(-\vec{r})$ is odd.
  When the potential is symmetric under reflection, we can choose the stationary states to be either even or odd under reflection.
- **Orthogonality/orthonormality.**
  $\int\psi_m(\vec{r})^*\psi_n(\vec{r})d^3\vec{r} = \delta_{mn}$ where δ_{mn} is 0 if $m \neq n$ and 1 if $m = n$.
- **Linearity.**
  The SE is linear. Given stationary states, a linear combo of these
  $$\psi(\vec{r},t) = \sum_n c_n\psi_n(\vec{r},t) = \sum_n c_n\psi_n(\vec{r})e^{-\frac{i}{\hbar}E_n t}$$
  where c_n are complex constants, is a soln the TDSE $i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t} = \widehat{H}\psi(\vec{r},t)$
- **Time evolution.** Given $\psi(\vec{r},0) = \sum_n c_n\psi_n(\vec{r},0) = \sum_n c_n\psi_n(\vec{r})$ at time t, the time evolution is
  $\psi(\vec{r},t) = \sum_n c_n\psi_n(\vec{r},t) = \sum_n c_n\psi_n(\vec{r})e^{-\frac{i}{\hbar}E_n t}$
  Once we've expanded a given initial wavefunction in terms of a linear combo of the stationary wavefunctions $\psi_n(\vec{r})$, the time evolution follows simply by putting a factor of $e^{-i/\hbar E_n t}$ to each term containing $\psi_n(\vec{r})$.
- **Normalization.** The constant coefficients are constrained by $\sum_n |c_n|^2 = 1$
- **Completeness.** The stationary states form a complete set if
  $\sum_n\psi_n(\vec{r'},t)^*\psi_n(\vec{r},t) = \delta^3(\vec{r'} - \vec{r})$, where $\delta^3(\vec{r'} - \vec{r})$ is the Dirac-delta function in 3D defined by $\int d^3\vec{r'}\psi(\vec{r'},t)\delta^3(\vec{r'} - \vec{r}) = \psi(\vec{r},t)$

Euler's formula: $e^{i\theta} = \cos\theta + i\sin\theta$

sin and cos: $\cos(\theta) = \frac{1}{2}(e^{i\theta} + e^{-i\theta})$, $\sin(\theta) = \frac{1}{2}(e^{i\theta} - e^{-i\theta})$

One-dimensional systems

Wavefunction for a system containing a single particle of mass m in 1D with TI potentials. $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x)$

Time dependence: $\psi_E(x,t) = \psi_E(x)e^{-\frac{i}{\hbar}Et}$

Boundary conditions

1. When the potential $V(x)$ has a finite jump at $x = a$, both $\psi(x)$ and $\psi'(x)$ are continuous across $x = a$.
2. When the potential $V(x)$ has an infinite jump at $x = a$, $\psi(x)$ is continuous but $\psi'(x)$ is discontinuous across $x = a$.

Wavefunction must vanish at $x = \pm\infty$ to be normalizable.

2.2 The Infinite Square Well

$V(x) = \{0 \text{ if } 0 \leq x \leq a; \quad \infty \text{ otherwise}\}$

$\psi(x) = 0$ for $x < 0$ and $x > a$ For $0 \leq x \leq a$, $V(x) = 0$. The SE:

$$\psi''(x) + k^2\psi(x) = 0, \text{ where } k = \sqrt{\frac{2mE}{\hbar^2}} \text{ and } E > 0$$

Classic **simple harmonic oscillator**: $\psi(x) = A\sin(kx) + B\cos(kx)$

Boundary conditions:

Continuity of $\psi(x)$ at $x = 0$ sets $\psi(0) = B = 0 \to \psi(x) = A\sin(kx)$

at $x = a$ sets $\psi(a) = A\sin(ka) = 0$

$$k_n = \frac{n\pi}{a}, n = 1,.. \quad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right) \quad E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

They are complete, in the sense that any other function, $f(x)$, can be expressed as a linear combination of them (Fourier series), Dirichlet's theorem:

$$f(x) = \sum_{n=1}^{\infty}c_n\psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty}c_n\sin\left(\frac{n\pi}{a}x\right)$$

Fourier's trick: $c_n = \int\psi_n(x)^* f(x)dx$

$$c_m = \frac{2}{a}\int_0^a f(x)\sin\left(\frac{m\pi x}{a}\right)dx$$

$|c_n|^2$: probability that a measurement of the energy would yield the value E_n.

Sum of these probabilities should be 1: $\sum_{n=1}^{\infty}|c_n|^2 = 1$

The expectation value of the energy is $\langle H\rangle = \sum_{n=1}^{\infty}|c_n|^2 E_n$

2.3 The Harmonic Oscillator

Hooke's law (mass m w/ spring constant k): $F = -kx = m\frac{d^2x}{dt^2}$

Solution is $x(t) = A\sin(\omega t) + B\cos(\omega t)$, where $\omega = \sqrt{\frac{k}{m}}$

Potential energy: $V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2x^2$

Expanding $V(x)$ in a **Taylor series** about the min:

$V(x) = V(x_0) + V'(x_0)(x - x_0) + \frac{1}{2}V''(x_0)(x - x_0)^2 + \cdots$

Simple harmonic oscillaton, $V(x) \cong \frac{1}{2}V''(x_0)(x - x_0)^2, k = V''(x_0)$

SE for the harmonic oscillator: $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$

Boundary conditions: $\psi(-\infty) = 0, \qquad \psi(+\infty) = 0$

1. Simplify notation with change of variables

Introduce $\xi \equiv \sqrt{\frac{m\omega}{\hbar}}x$. SE becomes $\frac{\mathrm{d}^2\psi}{\mathrm{d}\xi^2} = (\xi^2 - K)\psi$, where $K \equiv \frac{2E}{\hbar\omega}$.

2. Asymptotic behavior

Working in the large $\xi^2 >> K$ region,

Hermite eqn: $H''(\xi) - 2\xi H'(\xi) + (K-1)H(\xi) = 0$

Hermite polynomials: $H_0 = 1$, $H_1 = 2\xi$, $H_2 = 4\xi^2 - 2$, $H_3 = 8\xi^3 - 12\xi$, $H_4 = 16\xi^4 - 48\xi^2 + 12$, $H_5 = 32\xi^5 - 160\xi^3 + 120\xi$

3. Method of power series

Recursion: $a_{j+2} = \frac{(2j+1-K)}{(j+1)(j+2)}a_j$. For allowed K: $a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)}a_j$

$h(\xi) = a_0 + a_1\xi + a_2\xi^2 + \cdots = \sum_{j=0}^{\infty}a_j\xi^j$, $h(\xi) = h_{\text{even}}(\xi) + h_{\text{odd}}(\xi)$

4. Infinite series produces a diverging function For large n, $a_{n+2} \approx \frac{2}{n}a_n$

5. Truncate series $K = 2n + 1$, so $E_n = (n + \frac{1}{2})\hbar\omega$

Normalized stationary states: $\psi_n(x) = (\frac{m\omega}{\pi\hbar})^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\xi)e^{-\xi^2/2}$

Rodrigues formula: $H_n(\xi) = (-1)^n e^{\xi^2}(\frac{\mathrm{d}}{\mathrm{d}\xi})^n e^{-\xi^2}$

2.4 The Free Particle

$E > V(x)$ for all x, $V(x) = 0, -\infty < x < \infty$

We have $x(t) = v_{cl}t$, where v_{cl} is the classical velocity of the particle.

$\psi''(x) + k^2\psi(x) = 0, k \equiv \sqrt{\frac{2mE}{\hbar^2}}$

$\Psi(x,t) = Ae^{ikx - i\frac{\hbar k^2}{2m}t} + Be^{-ikx - i\frac{\hbar k^2}{2m}t} =$
$Ae^{i(kx-wt)} + Be^{-i(kx+\omega t)} = Ae^{ik(x-v_p t)} + Be^{-ik(x+v_p t)}$, where

$\omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}$ is angular vel, $v_p = \frac{\omega}{k} = \frac{\hbar k}{2m} = \frac{p}{2m} = \frac{1}{2}v_{cl}$ is phase velocity.

Not normalizable. General sol to the TISE: wave packet,

$\Psi(x,t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\phi(k)e^{i(kx - \frac{\hbar k^2}{2m}t)}dk$, $\phi(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}\Psi(x,0)e^{-ikx}dx$

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

$F(k)$ is Fourier transform of $f(x)$; $f(x)$ is inverse Fourier transform of $F(k)$

2.5 The Delta-Function Potential

Dirac delta function, area is 1: $\delta(x) = \{0, \text{ if } x \neq 0; \quad \infty, \text{ if } x = 0\}$

$f(x)\delta(x-a) = f(a)\delta(x-a)$ bc the product is 0 anyway except at a.

In particular, $\int_{-\infty}^{\infty}f(x)\delta(x-a)dx = f(a)$

$V(x) = -\alpha\delta(x)$, where α is positive constant. $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \alpha\delta(x)\psi = E\psi$

Bound states ($E < 0$):

REGION I, $x < 0, V(x) = 0$

$\frac{\mathrm{d}^2\psi_I}{\mathrm{d}x^2} - \kappa^2\psi_I = 0$, where $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$.

General sol: $\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}$ But $A = 0$, so

$\psi(x) = Be^{-\kappa x}, (x < 0)$.

REGION II, $x > 0, V(x) = 0$ $\psi(x) = Fe^{-\kappa x} + Ge^{\kappa x}$

But $G = 0$, so $\psi(x) = Fe^{-\kappa x}, (x > 0)$.

The first boundary condition tells us that $F = B$, so

$\psi(x) = \{Be^{\kappa x}, (x \leq 0), \qquad Be^{-\kappa x}, (x \geq 0)\}$

The discontinuity of $\psi'(x)$ across $x = 0$ follows from

$$\psi'_{II}(0) - \psi'_I(0) = \lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}\psi''(x)dx = \lim_{\epsilon\to 0}\int_{-\epsilon}^{\epsilon}\frac{2m}{\hbar^2}(V(x) - E)\psi(x)dx$$

$$= -\frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon}\alpha\delta(x)\psi(x)dx = \frac{2m}{\hbar^2}\alpha\psi(0) = -\frac{2m}{\hbar^2}\alpha F$$

Taking the derivatives directly, $\psi'_{II}(0) - \psi'_I(0) = -\kappa F - \kappa B$. Therefore,

$\kappa F + \kappa B = \frac{2m}{\hbar^2}\alpha F \to \kappa = \frac{m\alpha}{\hbar^2} \to E = -\frac{m\alpha^2}{2\hbar^2}$

Only one E, so only one bound state.

Normalizing: $1 = \int_{-\infty}^{0}B^2e^{2\kappa x} + \int_0^{\infty}B^2e^{-2\kappa x} = B^2\frac{1}{2\kappa} + B^2\frac{1}{2\kappa} = \frac{B^2}{\kappa}$,

which gives $B = \sqrt{\kappa}$.

The normalized wavefunction is:

$$\psi(x) = \begin{cases}\sqrt{\kappa}e^{-\kappa x} = \sqrt{\frac{m\alpha}{\hbar^2}}e^{-\frac{m\alpha}{\hbar^2}x}, & x > 0\\ \sqrt{\kappa}e^{\kappa x} = \sqrt{\frac{m\alpha}{\hbar^2}}e^{\frac{m\alpha}{\hbar^2}x}, & x < 0\end{cases}$$

Scattering states ($E > 0$) – reflection and transmission:

For $x < 0$ the SE reads

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{2mE}{\hbar^2}\psi = -k^2\psi, \qquad k \equiv \frac{\sqrt{2mE}}{\hbar}$$

General sol is $\psi(x) = Ae^{ikx} + Be^{-ikx}$

For $x > 0$, $\psi(x) = Fe^{ikx} + Ge^{-ikx}$

Continuity of $\psi(x)$ at $x = 0$: $F + G = A + B$

Reflection coefficient: $R \equiv \frac{|B|^2}{|A|^2}$, Transmission coefficient: $T \equiv \frac{|F|^2}{|A|^2}$
$R+T=1$, $R=\frac{1}{1+(2\hbar^2E/m\alpha^2)}$, $T=\frac{1}{1+m\alpha^2/2\hbar^2E)}$
Higher $E \to$ greater probability of transmission.

Step potential

Particle of energy $E>V_0$ approaching a step potential from the left in the $x<0$ region with $V(x)=\{0, x<0; \quad V_0, x>0\}$.
Incident and reflected waves in region I, only transmitted wave in region II:
$\psi_I(x)=Ae^{ikx}+Be^{-ikx}, \quad \psi_{II}(x)=Ce^{i\kappa x}$
where $k=\sqrt{\frac{2mE}{\hbar^2}}$, $\kappa=\sqrt{\frac{2m(E-V_0)}{\hbar^2}}$
$\psi(x)$ and $\psi'(x)$ across $x=0$: $A+B=C$, $ik(A-B)=i\kappa C$
Solving for B and C in terms of A, $B=\frac{k-\kappa}{k+\kappa}A, \quad C=\frac{2k}{k+\kappa}A$
Speed of particle is diff in two regions, use probability current.
$J_{inc}=\frac{\hbar k}{m}|A|^2, \quad J_{ref}=\frac{\hbar k}{m}|B|^2, \quad J_{tra}=\frac{\hbar \kappa}{m}|C|^2$
$R=\frac{J_{ref}}{J_{inc}}=|\frac{B}{A}|^2=(\frac{k-\kappa}{k-\kappa})^2=(\frac{\sqrt{E}-\sqrt{E-V_0}}{\sqrt{E}+\sqrt{E-V_0}})^2$
$T=\frac{J_{tra}}{J_{inc}}=\frac{\kappa}{k}|\frac{C}{A}|^2=\frac{4k\kappa}{(k+\kappa)^2}=\frac{4\sqrt{E}\sqrt{E-V_0}}{(\sqrt{E}+\sqrt{E-V_0})^2}$
$R+T=1$

Tunneling

Consider a particle mass m and energy $E<V_0$ approaching from the left a potential barrier of height V_0:

$$V(x)=\{V_0, -a<x<a; \quad 0, |x|>a\}$$

$\psi_I(x)=Ae^{ikx}+Be^{-ikx}, \psi_{II}(x)=Ce^{\kappa x}+De^{-\kappa x}, \psi_{III}(x)=Fe^{ikx}$
where $k=\frac{2mE}{\hbar^2}$, $\kappa=\sqrt{\frac{2m(V_0-E)}{\hbar^2}}$
Applying continuity of $\psi(x)$ and $\psi'(x)$ at $x=\pm a$:
$B=\frac{e^{-2iak}(e^{4a\kappa}-1)(k^2+\kappa^2)}{e^{4a\kappa}(k+i\kappa)^2-(k-i\kappa)^2}A$, $C=...A, D=...A, F=...A$
Bc the speeds of particles in I and II are same,
$T=|\frac{F}{A}|^2=\frac{(2k\kappa)^2}{(k^2+\kappa^2)^2\sinh^2(2\kappa a)+(2k\kappa)^2}$
$T\approx e^{-2\gamma}$, where $\gamma=\int_a^b\sqrt{\frac{2m(V(x)-E)}{\hbar^2}}dx$
Lifetime of a particle of mass m and energy E:
Particle has velocity $v=\sqrt{\frac{2E}{m}}$ and bounced back and forth in the wall. When it hits the right wall, it has probability $T=e^{-2\gamma}$ for tunneling, where $\gamma=\sqrt{\frac{2m(V_0-E)}{\hbar^2}}(b-a)$ ($b-a$ is width of well). It needs a number N of bounces on the right wall st $NT\sim 1$ for it to tunnel. Therefore, $N\sim\frac{1}{T}=e^{2\gamma}$. The time interval btwn bounces off the right wall is $t=\frac{2a}{v}$ (a is length to the left). Lifetime is $\tau\sim Nt=\frac{2a}{\sqrt{\frac{2E}{m}}}e^{2\sqrt{\frac{2m(V_0-E)}{\hbar^2}}(b-a)}$.

2.6 The Finite Square Well

$$V(x)=\begin{cases}-V_0, & \text{for } -a<x<a\\ 0, & \text{for } |x|>a\end{cases}$$

Bound states:
REGION I $-\frac{\hbar}{2m}\frac{d^2\psi}{dx^2}=E\psi$, or $\psi_I''(x)-\kappa^2\psi_I(x)=0, \quad \kappa\equiv\sqrt{-\frac{2mE}{\hbar}}$
where $E<0$ for a bound state. General sol: $\psi_I(x)=Ae^{-\kappa x}+Be^{\kappa x}$.
$x=-\infty\to\psi(x)=0$, so $A=0$, and we have $\psi_I(x)=Be^{\kappa x}$

REGION II $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}-V_0\psi=E\psi$, or $\psi''=-l^2\psi, \quad l\equiv\sqrt{\frac{2m(E+V_0)}{\hbar}}$
General sol: $\psi(x)=C\sin(lx)+D\cos(lx)$, for $-a<x<a$

REGION III $x=\infty\to\psi(x)=0$, so $G=0$ and $\psi_{III}(x)=Fe^{-\kappa x}$

Even bound states: $\psi(-x)=\psi(x)$, $\psi_{II}(x)=D\cos(lx)$
Bc the potential has only a finite discontinuity at $x=\pm a$, both ψ and ψ' must be continuous at $x=\pm a$.
$x=a$, $\psi_{II}(a)=\psi_{III}(a)$ imposes $D\cos(la)=Fe^{-\kappa a}$
$x=a$, $\psi_{II}'(a)=\psi_{III}(a)'$ imposes $-lD\sin(la)=-\kappa Fe^{-\kappa a}$
Continuity of $\psi(x)$ and $\psi'(x)$ at $x=-a$ does not add anything new.
Dividing the above two, we get $\kappa=l\tan(la)$
This is a formula for the allowed energies, since κ and l are both functions of E.
Let $z\equiv la$, and $z_0\equiv\frac{a}{\hbar}\sqrt{2mV_0}$. $\kappa^2+l^2=2mV_0/\hbar^2$, so $\kappa a=\sqrt{{z_0}^2-z^2}$.

Transcendental eq for z (and hence E) as a function of z_0 (which is a measure of size of well): $\tan z=\sqrt{(\frac{z_0}{z})^2-1}$
Odd bound states $\psi_{II}(x)=C\sin(lx)$
$x=-a, \psi_{II}(-a)=\psi_I(-a)$ imposes $C\sin(la)=Be^{-\kappa a}$
$x=-a, \psi_{II}'(-a)=\psi_I'(-a)$ imposes $lC\cos(la)=-\kappa Be^{-\kappa a}$
Dividing, $l\cot(la)=-\kappa$. In terms of z and z_0, $\cot(z)=-\sqrt{(\frac{z_0}{z})^2-1}$
V_1 does not support an odd bound state, since there is no intersection pt, V_2 produces only one bound state, and V_3 produces two bound states. Finite well potential supports at least one even state, the ground state, and it may not support any of the excited states.

Wide and deep well:
$z_n\approx\frac{n\pi}{2}, n=1,2,3,..., \quad E_n=-V_0+\frac{\hbar^2\pi^2n^2}{2m(2a)^2}, n=1,2,...$
Thus, the energy levels of the infinite square well of width $2a$ are reproduced for $E_n-(-V_0)=E_n+V_0$, which is the energy above the bottom of the well.
As $V_0\to\infty$, finite sq well goes to infinite sq well.

Shallow and narrow well Need $z_0=\sqrt{\frac{2mV_0a^2}{\hbar^2}}\geq\frac{\pi}{2}$ to support any odd state.

3. PRINCIPLES OF QM

Axiomatic principles

State vector axiom: State vector at t is ket $\psi(t)$, or $|\psi\rangle$.
Probability axiom: Given a system in state $|\psi\rangle$, a measurement will find it in state $|\phi\rangle$ with probability amplitude $\langle\phi|\psi\rangle$.
Hermitian operator axiom: Physical observable is represented by a linear and Hermitian operator.
Measurement axiom: Measurement of a physical observable results in eigenvalue of observable. Observable $\widehat{A}$, we have $\widehat{A}|a\rangle=a|a\rangle$, where a is eigenvalue and $|a\rangle$ is eigenvector. Measurement of physical quantity represented by $\widehat{A}$ collapses the state $|\psi\rangle$ before measurement into an eigenstate $|a\rangle$ of $\widehat{A}$.
Time evolution axiom: $i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle=\widehat{H}|\psi(t)\rangle$, w/o consider x or p.

Vector space

State vector is neither in position nor momentum space. Basis vectors: $|0\rangle, |1\rangle, |n\rangle$
Linearity : Because the SE is linear, given two states $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$, $|\psi(t)\rangle=c_1|\psi_1(t)\rangle+c_2|\psi_2(t)\rangle$ is also a sol. (c's are complex).
Dual vector space $c|\psi\rangle$ is mapped to $c^*\langle\psi|$. Given a vector, $|\psi\rangle=\begin{bmatrix}\vdots\\ \alpha\\ \vdots\end{bmatrix}$, the dual vector is $\langle\psi|=\begin{bmatrix}\cdots & \alpha^* & \cdots\end{bmatrix}$.
Dual basis vectors are $\langle 0|=\begin{bmatrix}1 & 0 & \cdots\end{bmatrix}, \cdots, \langle n|\begin{bmatrix}0 & \cdots & 1\end{bmatrix}$.
Inner product : $\langle\phi|\psi\rangle=c$, where c is complex.
$\langle\phi|\psi\rangle=\langle\psi|\phi\rangle^*\to\langle\psi|\psi\rangle$ is real, positive, and finite for a normalizable ket vector. Can choose $\langle\psi|\psi\rangle=1$. $\langle\psi_m|\psi_n\rangle=\delta_{mn}$

Operators

A matrix operator $\widehat{A}$ acting on a state vector $|\psi\rangle$ transforms it into another state vector $|\phi\rangle$, $\widehat{A}|\psi\rangle=|\phi\rangle$. It is linear.
Hermitian conjugate (Hermitian adjoint) operator in the dual space
Hermitian adjoint operator $\widehat{A}^\dagger$ acts on the dual vector $\langle\psi|$ from the right as $\langle\psi|\widehat{A}^\dagger\rangle$, where $\widehat{A}^\dagger=(\widehat{A})^{T*}$.

$$(\widehat{A}|\psi\rangle)^\dagger=|\psi\rangle^\dagger\widehat{A}^\dagger=\langle\psi|\widehat{A}^\dagger \qquad \langle\psi|=|\psi\rangle^\dagger \qquad \langle\psi|^\dagger=|\psi\rangle$$
$$(\widehat{A}\widehat{B})^\dagger=(\widehat{A}\widehat{B})^{T*}=(\widehat{B}^T\widehat{A}^T)^*=\widehat{B}^{T*}\widehat{A}^{T*}=\widehat{B}^\dagger\widehat{A}^\dagger, \quad (c\widehat{A})^\dagger=c^*\widehat{A}^\dagger$$

Outer product operators : $|\psi\rangle\langle\phi| \qquad [|\psi\rangle\langle\phi|]\chi\rangle=|\psi\rangle\langle\phi|\chi\rangle$
Matrix elements of operators $\langle\phi|\widehat{A}|\psi\rangle$ (complex num)
Hermitian equiv to complex conj $\langle\phi|\widehat{A}|\psi\rangle^\dagger=\langle\psi|\widehat{A}^\dagger|\phi\rangle=\langle\phi|\widehat{A}|\psi\rangle^*$
Hermitian operators : $\widehat{A}^\dagger=\widehat{A}$, so given $\widehat{A}|\phi\rangle$ in the vector space, we have $\langle\psi|\widehat{A}^\dagger=\langle\phi|\widehat{A}$ in the dual vector space.
Matrix elements of a Hermitian operator
$\langle\phi|\widehat{A}|\psi\rangle^\dagger=\langle\phi|\widehat{A}|\psi\rangle^*=\langle\psi|\widehat{A}^\dagger|\phi\rangle=\langle\psi|\widehat{A}|\phi\rangle$
Hermitian operator, real expectation vals: $\langle\psi|\widehat{A}|\phi\rangle^*=\langle\psi|\widehat{A}|\phi\rangle\equiv\langle\widehat{A}\rangle$
Same result whether $\widehat{A}$ acts to right or left: $\langle\phi|\widehat{A}|\psi\rangle=\langle\phi|\widehat{A}^\dagger|\psi\rangle$
Eigenvals and eigenvecs of Hermitian operators : $\widehat{A}|a_n\rangle=a_n|a_n\rangle$
Normalized eigvecs $\langle a_m|a_n\rangle=\delta_{mn}$. Gram-Schmidt, degenerate evec.
Completeness of eigenvector of a Hermitian operator Set $|a_n\rangle$ is complete if $\sum_n|\langle a_n|\psi\rangle|^2=1$. $\sum_n|a_n\rangle\langle a_n|=1$ (identity operator)

Continuous spectra of a Hermitian operator Hermitian operator $\widehat{A}$, $\widehat{A}|a\rangle=a|a\rangle$, where a is continuous.
$\int da'\langle a'|\widehat{A}|a\rangle=a\int da'\langle a'|a\rangle=\int da'a'\langle a'|a\rangle\to\langle a'|a\rangle=\delta(a'-a)$
Continuous condition: $\int da|a\rangle\langle a|=1$
Gram-Schmidt orthogonalization procedure Eigval (like energy level) is n-fold degenerate: n states w same eigval.
Orthogonal eigenstates $\to$ no degeneracy.
1. Normalize each state and define $\alpha_i=\frac{\alpha_i}{\sqrt{\langle a_i|a_i\rangle}}$. 2. $|\alpha_1'\rangle=|\alpha_1\rangle$.
3. $|\alpha_2'\rangle=\frac{|\alpha_2\rangle-|\alpha_1\rangle\langle\alpha_1|\alpha_2\rangle}{\sqrt{\langle\alpha_2|\alpha_2\rangle-\langle\alpha_1|\alpha_2\rangle\langle\alpha_2|\alpha_1\rangle}}=\frac{|\alpha_2\rangle-|\alpha_1\rangle\langle\alpha_1|\alpha_2\rangle}{\sqrt{1-\langle\alpha_1|\alpha_2\rangle\langle\alpha_2|\alpha_1\rangle}}$
4. Subtract components of $|\alpha_3\rangle$ along $|\alpha_1\rangle$ and $|\alpha_2\rangle$, $|\alpha_3\rangle-|\alpha_1\rangle\langle\alpha_1|\alpha_3\rangle-|\alpha_2\rangle\langle\alpha_2|\alpha_3\rangle$, normalize and promote to $|\alpha_3'\rangle$. ...

Position and momentum representation

$\widehat{\vec{r}}|\vec{r}\rangle=\vec{r}|\vec{r}\rangle \quad \langle\vec{r'}|\vec{r}\rangle=\delta^3(\vec{r'}-\vec{r}), \int d^3\vec{r}|\vec{r}\rangle\langle\vec{r}|=1, \langle\vec{r'}|\hat{\vec{r}}|\vec{r}\rangle=\vec{r}\delta^3(\vec{r'}-\vec{r})$
$\widehat{\vec{p}}|\vec{p}\rangle=\vec{p}|\vec{p}\rangle \quad \langle\vec{p'}|\vec{p}\rangle=\delta^3(\vec{p'}-\vec{p}), \int d^3\vec{p}|\vec{p}\rangle\langle\vec{p}|=1$
State vector $|\psi(t)\rangle$ in position space (scalar): $\langle\vec{r}|\psi(x,t)\rangle\equiv\psi(\vec{r},t)$
$\langle\psi|\widehat{\vec{p}}|\psi\rangle=\frac{d}{dt}\langle\psi|\widehat{\vec{r}}|\psi\rangle m$
Representation of momentum operator in position space: $\widehat{\vec{p}}=-i\hbar\vec{\nabla}$.
$\langle x|\widehat{p}|x'\rangle=-i\hbar\frac{\partial}{\partial x}\delta(x-x')=-i\hbar\frac{\partial}{\partial x}\langle x|x'\rangle$.
$\widehat{p}=-i\hbar\frac{\partial}{\partial x}$ is Hermitian, $\frac{\partial}{\partial x}$ is not.
$\langle x|\widehat{p}|p\rangle=p\langle x|p\rangle=-i\hbar\frac{\partial}{\partial x}\langle x|p\rangle$. The solution is $\langle x|p\rangle=\frac{1}{\sqrt{2\pi\hbar}}e^{\frac{i}{\hbar}px}$.
In 3D, $\langle\vec{r}|\vec{p}\rangle=\frac{1}{(2\pi\hbar)^{3/2}}e^{\frac{i}{\hbar}\vec{p}\vec{r}}$.
We can write the normalized wavefunction of definite position in momentum space, $\langle p|x\rangle=\langle x|p\rangle^*$. So, $\langle p|x\rangle=\frac{1}{\sqrt{2\pi\hbar}}e^{-\frac{i}{\hbar}px}$ (particle moving to the left, or with momentum $-p$, in the momentum space). $[x,p]=i\hbar$
Operators and wavefunction in position representation Position and momentum operators in pos space: $\widehat{\vec{r}}=\vec{r}$, $\widehat{\vec{p}}=-i\hbar\vec{\nabla}$.
$\widehat{\vec{r}}$ is Hermitian and $\langle\phi|\widehat{\vec{r}}^\dagger|\psi\rangle=\langle\phi|\widehat{\vec{r}}|\psi\rangle$.
$\widehat{O}(\widehat{\vec{r}},\widehat{\vec{p}})=\widehat{O}(\vec{r},-i\hbar\vec{\nabla})$
The expectation val of the observable should be indep of representation. In state $\psi(t)$, $\langle\widehat{O}\rangle=\langle\psi(t)|\widehat{O}|\psi(t)\rangle$.
Insert $\int d^2\vec{r}|\vec{r}\rangle\langle\vec{r}|=1$ to get $\langle\widehat{O}\rangle=\int d^2\vec{r}\langle\psi(t)|\vec{r}\rangle\langle\vec{r}|\widehat{O}|\psi(t)\rangle$
$\psi(\vec{r},t)=\langle\vec{r}|\psi(t)\rangle, \qquad \psi(\vec{r},t)^*=\langle\vec{r}|\psi(t)\rangle^*=\langle\psi(t)|\vec{r}\rangle$,
$\langle\vec{r}|\widehat{O}|\psi(t)\rangle=\widehat{O}(\vec{r},-i\hbar\vec{\nabla})\psi(\vec{r},t), \langle\vec{O}\rangle=\int d^3\vec{r}\psi(\vec{r},t)^*\vec{O}(\vec{r},-i\hbar\vec{\nabla})\psi(\vec{r},t)$
Operators and wavefunction in momentum representation $\widehat{\vec{r}}=i\hbar\vec{\nabla}_{\vec{p}}$, or in 1D, $\widehat{x}=i\hbar\frac{\partial}{\partial p}$, $\widehat{\vec{p}}=\vec{p}$, where $\vec{p}^*=\vec{p}$.
$\widehat{\vec{O}}(\widehat{\vec{r}},\widehat{\vec{p}})=\widehat{O}(i\hbar\vec{\nabla}_{\vec{p}},\vec{p})$
$\langle\widehat{O}\rangle=\langle\psi(t)|\widehat{O}|\psi(t)\rangle\to\langle\widehat{O}\rangle=\int d^2\vec{p}\langle\psi(t)|\vec{p}\rangle\langle\vec{p}|\widehat{O}|\psi(t)\rangle$.
$\psi(\vec{p},t)=\langle\vec{p}|\psi(t)\rangle, \qquad \psi(\vec{p},t)^*=\langle\vec{p}\psi(t)\rangle^*=\langle\psi(t)|\vec{p}\rangle$
$\langle\vec{p}|\widehat{O}|\psi(t)\rangle=\widehat{O}(i\hbar\vec{\nabla}_{\vec{p}},\vec{p}), \langle\vec{O}\rangle=\int d^3\vec{p}\psi(\vec{p},t)^*\widehat{O}(i\hbar\vec{\nabla}_{\vec{p}},\vec{p})\psi(\vec{p},t)$.

$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle=\widehat{H}|\psi(t)\rangle$, where $\widehat{H}=\frac{\widehat{\vec{p}}^2}{2m}+V(\widehat{\vec{r}},t)$ becomes
$i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}=-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r},t)+V(\vec{r},t)\psi(\vec{r},t)$

Commuting operators

If $[\widehat{A},\widehat{B}]=0$ and the states are nondegenerate, $|\psi\rangle$ is a simultaneous eigenstate of $\widehat{A}$ and $\widehat{B}$.
$|\psi\rangle=|ab\rangle$, and $\widehat{A}|ab\rangle=a|ab\rangle$, $\widehat{B}|ab\rangle=b|ab\rangle$

Non-commuting operators and the general uncertainty principle

$(\Delta A)^2(\Delta B)^2\geq(\frac{1}{2i}\langle[\widehat{A},\widehat{B}]\rangle)^2$
Cannot construct simultaneous eigenstates (which correspond to definite eigenvalues) of non-commuting observables.

Time evolution of expectation value of an operator and Ehrenfest's theorem

Ehrenfest's theorem: how observable $\widehat{O}$'s expectation value in state $|\psi(t)\rangle$ evolves in time, $\frac{d}{dt}\langle\widehat{O}\rangle=\langle\frac{\partial\widehat{O}}{\partial t}\rangle+\frac{i}{\hbar}\langle[\widehat{H},\widehat{O}]\rangle$. If operator has no explicit time dep, $\frac{d}{dt}\langle\widehat{O}\rangle=\frac{1}{i\hbar}\langle[\widehat{O},\widehat{H}]\rangle$.
For $\widehat{O}=\widehat{\vec{p}}$ and a Hamiltonian that is TI, $\frac{d}{dt}\langle\widehat{\vec{p}}\rangle=-\langle\vec{\nabla}V(\widehat{\vec{r}})\rangle$, which is just Newton's Second Law! $\to$ QM contains all of classical mech.

The simple harmonic oscillator

$\widehat{H}=\frac{\widehat{p}^2}{2m}+\frac{1}{2}m\omega^2\widehat{x}^2$

Raising and lowering operators Lowering op: $\hat{a} = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} + \frac{i}{m\omega}\hat{p})$, Raising op: $\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} - \frac{i}{m\omega}\hat{p})$.

$[\hat{a},\hat{a}^\dagger]=1 \qquad \hat{x}=\sqrt{\frac{\hbar}{2m\omega}}(\hat a^\dagger+\hat a)$, $\hat p = i\sqrt{\frac{m\omega\hbar}{2}}(\hat a^\dagger - \hat a)$

$\hat H = (\hat N + \frac12)\hbar\omega$, where $\hat N = \hat a^\dagger \hat a$. Now $\hat N$ is Hermitian, and $\hat N|n\rangle = n|n\rangle$.
$[\hat N,\hat a] = -\hat a$, $[\hat N, \hat a^\dagger] = \hat a^\dagger$
$\hat N(\hat a|n\rangle) = (n-1)(\hat a|n\rangle)$, $\hat N(\hat a^\dagger|n\rangle) = (n+1)(\hat a^\dagger|n\rangle)$

Normalized number state vectors Energy levels are not degenerate, so $|n-1\rangle = c_n\hat a|n\rangle \to c_n = \frac{1}{\sqrt n} \to \hat a|n\rangle = \sqrt n|n-1\rangle$.

$|n+1\rangle = d_n\hat a^\dagger|n\rangle \to d_n = \frac{1}{\sqrt{n+1}} \to \hat a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$

Ground state: $|0\rangle$, excited state: $|n\rangle = \frac{(\hat a^\dagger)^n}{\sqrt{n!}}|0\rangle$, $n=0,1,2,\dots$

$\langle n'|\hat x|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}\langle n'|(\hat a^\dagger+\hat a)|n\rangle = \sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\delta_{n',n+1}+\sqrt n\delta_{n',n-1})$

$\langle n'|\hat p|n\rangle = i\sqrt{\frac{m\omega\hbar}{2}}\langle n'|(\hat a^\dagger-\hat a)|n\rangle = i\sqrt{\frac{m\omega\hbar}{2}}(\sqrt{n+1}\delta_{n',n+1}-\sqrt n\delta_{n',n-1})$

Wavefunctions in position representation $E_n = (n+\frac12)\hbar\omega, n=0,1,2,\dots$
The stationary wavefunctions of definite energy: $\psi_n(x)=\langle x|n\rangle$

$\langle x'|\hat a^\dagger|x''\rangle = \delta(x'-x'')\frac{1}{\sqrt{2}\sigma}(x''-\sigma^2\frac{\partial}{\partial x''})$, where $\sigma\equiv\sqrt{\frac{\hbar}{m\omega}}$

$\xi=\frac{x}{\sigma}, \qquad \langle x|n\rangle = \frac{1}{\sqrt{\sqrt\pi n!2^n\sigma}}(\xi-\frac{\partial}{\partial\xi})^n e^{-\frac12\xi^2}$

$\langle x|0\rangle = (\frac{m\omega}{\pi\hbar})^{1/4}e^{-\frac{m\omega}{2\hbar}x^2}, \qquad \langle x|1\rangle = \sqrt2(\frac{m^3\omega^3}{\pi\hbar^3})^{1/4}xe^{-\frac{m\omega}{2\hbar}x^2}$

Classical simple harmonic oscillator Hamiltonian of a simple harmonic is
$H=\frac{p^2}{2m}+\frac12 m\omega^2x^2. \qquad \dot x = \frac{\partial H}{\partial p} = \frac{p}{m}, \qquad \dot p = -\frac{\partial H}{\partial x} = -m\omega^2 x$

Define $\sqrt{\hbar\omega}\alpha = \sqrt{\frac{m\omega^2}{2}}x + \frac{i}{\sqrt{2m}}p$, so $x=\sqrt{\frac{2\hbar}{m\omega}}\alpha_R$ and $p=\sqrt{2m\hbar\omega}\alpha_I$

Rewrite Hamiltonian, $H=\hbar\omega|\alpha|^2, \qquad \dot\alpha = -i\omega\alpha$. The sol is $\alpha=\alpha_0e^{-i\omega t}$.

The quantum simple harmonic oscillator and coherent state Coherent state, superpos of stat states $|n\rangle$: $|\alpha\rangle = e^{-\frac12|\alpha|^2}\sum_{n=0}^\infty\frac{\alpha^n}{\sqrt{n!}}|n\rangle$

$P(n) = |\langle n|\alpha\rangle|^2 = |\alpha_n|^2 = \frac{\langle n\rangle^n e^{-\langle n\rangle}}{n!}$, where $\langle n\rangle = \langle\alpha|a^\dagger a|\alpha\rangle = |\alpha|^2$.

Linear superpos. of all quantum nums which represent the class oscill the most. Has shape of Gaussian of min uncertainty satisfying $\Delta x\Delta p \ge \frac{\hbar}{2}$ regardless of value of energy. Oscillates like a class oscill, w only diff being that the particle's loc is not represented by a point (or a delta func) but by a Gaussian func.

4. 3D SYSTEMS

Three-dimensional infinite square well

$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\psi(x,y,z) = E\psi(x,y,z)$ for $0\le x\le l_x,\dots$
while $\psi(x,y,z)=0$ outside.
Separation of vars: $\psi(x,y,z)=\psi_1(x)\psi_2(y)\psi_3(z)$
$\to$ SE becomes $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_1(x) = E_1\psi_1(x),\dots$, where $E=E_1+E_2+E_3$.

$\psi_{n_xn_yn_z}(x,y,z)=\sqrt{\frac{8}{l_xl_yl_z}}\sin\left(\frac{n_x\pi}{l_x}x\right)\sin\left(\frac{n_y\pi}{l_y}z\right)\sin\left(\frac{n_z\pi}{l_z}z\right)$

$E_{n_xn_yn_z} = \frac{\hbar^2\pi^2}{2m}(\frac{n_x^2}{l_x^2}+\frac{n_y^2}{l_y^2}+\frac{n_z^2}{l_z^2})$, with $n_x,n_y,n_z=1,2,\dots$.

Wave vector: $\vec k = (k_x,k_y,k_z) = (\frac{n_x\pi}{l_x},\frac{n_y\pi}{l_y},\frac{n_z\pi}{l_z})$

The Schrödinger equation in spherical coordinates

$i\hbar\frac{\partial\psi(\vec r,t)}{\partial t} = -\frac{\hbar^2}{2m}\vec\nabla^2\psi(\vec r,t)+V(\vec r)\psi(\vec r,t)$, where $\vec r=(r,\theta,\phi)$,
$\psi(\vec r,t) = \psi(r,\theta,\phi,t)$ and $\vec\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$.
For a TI and central potential, potential depends only on r, $V(\vec r)=V(r)$.

$\frac{1}{R(r)}[\frac{d}{dr}-\frac{2mr^2}{\hbar^2}(V(r)-E)] = -\frac{1}{Y(\theta,\phi)}[\frac{1}{\sin\theta}\frac{d}{d\theta}+\frac{1}{\sin^2\theta}\frac{d^2Y(\theta,\phi)}{d\phi^2}]$

Each side must be constant and equal (let it be $l(l+1)$).

$\frac{1}{\sin\theta}\frac{d}{d\theta}+\frac{1}{\sin^2\theta}\frac{d^2Y(\theta,\phi)}{d\phi^2} = -l(l+1)Y(\theta,\phi)$

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

Orbital angular momentum

$\hat L_x = \hat y\hat p_z - \hat z\hat p_y, \hat L_y = \hat z\hat p_x - \hat x\hat p_z, \hat L_z = \hat x\hat p_y - \hat y\hat p_x$

$[\hat L_i,\hat L_j] = i\hbar\epsilon_{ijk}\hat L_k$, with $i=1,2,3$ representing the x, y, and z components, and $\epsilon_{123}=\epsilon_{231}=\epsilon_{312}=1$, which is -1 for odd perms of indices, and vanishes when repeated.

$\hat{\vec L}^2 = \hat{\vec L}_x^2+\hat{\vec L}_y^2+\hat{\vec L}_z^2$, $[\hat L^2,\hat L_i]=0$

In pos rep, $\hat{\vec L} = \hat{\vec r}\times\hat{\vec p} = -i\hbar\vec r\times\vec\nabla$. In sph coords,
$\hat{\vec L} = -i\hbar r\hat r\times(\frac{\partial}{\partial r}\hat r + \frac1r\frac{\partial}{\partial\theta}\hat\theta + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\hat\phi) = -i\hbar(\hat\phi\frac{\partial}{\partial\theta}-\hat\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$

$\hat r = \sin\theta\cos\psi\hat x+\sin\theta\sin\phi\hat y+\cos\theta\hat z$

$\hat\theta = \cos\theta\cos\phi\hat x+\cos\theta\sin\phi\hat y-\sin\theta\hat z \qquad \hat\phi = -\sin\phi\hat x - \cos\phi\hat y$

$\hat L_x = i\hbar(\sin\theta\frac{\partial}{\partial\theta}+\cot\theta\cos\phi\frac{\partial}{\partial\phi}) \qquad \hat L_y = i\hbar(-\cos\phi\frac{\partial}{\partial\theta}+\cot\theta\sin\phi\frac{\partial}{\partial\phi})$

$\hat L_z = -i\hbar\frac{\partial}{\partial\phi} \qquad \hat{\vec L}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]$

$\hat{\vec L}^2Y(\theta,\phi) = l(l+1)\hbar^2Y(\theta,\phi)$

$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr} - V_{\rm eff}(r)R(r) = ER(r)$, $V_{\rm eff}(r) = V(r)+\frac{l(l+1)\hbar^2}{2mr^2}$, centrifugal

Spherical harmonics Find sols to angular eqn. Sep vars $Y(\theta,\phi)=\Theta(\theta)\Phi(\phi)$.

$\frac1\Theta[\sin\theta\frac{d}{d\theta}+l(l+1)\sin^2\theta = -\frac1\Phi\frac{d^2\Phi}{d\phi^2} = \text{constant} = m^2$

$\Phi(\phi)=e^{im\phi}$, periodic in ϕ w period 2π gives constraint $m=0,\pm1,\pm2,\cdots$
$\Theta(\theta)$ can be written in terms of $x\equiv\cos\theta$ as

$(1-x^2)\frac{d^2P(x)}{dx^2}-2x\frac{dP(x)}{dx}+(l(l+1)-\frac{m^2}{1-x^2})P(x)=0$

Associated Legendre functions: $P_l^{m_l}(x) = (1-x^2)^{|m_l|/2}(\frac{d}{dx})^{|m_l|}P_l(x)$, where $P_l(x)$ is the l^{th} Legendre polynomial given by the Rodrigues formula $P_l(x)=\frac{1}{2^ll!}(\frac{d}{dx})^l(x^2-1)^l$, with l taking values $l=0,1,2,\dots$
and for each l, m_l takes $2l+1$ values $m_l=-l,-l+1,\dots,l-1,l$.

Spherical harmonics, normalized angular wave functions:
$Y_l^m(\theta,\phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}e^{im\phi}P_l^m(\cos\theta)$, where $\epsilon=(-1)^m$ for $m\ge0$ and $\epsilon=1$ for $m\le0$.

$\hat{\vec L}^2Y_l^{m_l} = l(l+1)\hbar^2Y_l^{m_l}, \qquad \hat{\vec L}_zY_l^{m_l} = m\hbar Y_l^{m_l}$

The Legendre polynomials are normalized s.t. they satisfy the ortho relation $\int_{-1}^1P_{l'}P_l(x)dx = \int_0^\pi P_{l'}(\theta)P_l(\theta)\sin\theta d\theta = \frac{2}{2l+1}\delta_{l'l}$

$P_0^0(\theta)=1, P_1^1(\theta)=\sin\theta, P_1^1(\theta)=\cos\theta$, with $P_l^{-m_l}(x)=P_l^{m_l}(x)$

$\int_{-1}^1 P_{l'}^{m'}(x)P_l^m(x)dx = \int_0^\pi P_{l'}^{m'}(\theta)P_l^m(\theta)\sin\theta d\theta = \frac{(l+m)!}{(2l+1)(l-m)!}\delta_{l'l}\delta_{m',m}$

Satisfy the orthogonality relation

$\int_0^{2\pi}d\phi\int_0^\pi d\theta\sin\theta Y_{l'}^{m_l'*}(\theta,\phi)Y_l^{m_l}(\theta,\phi) = \delta_{l'l}\delta_{m_l'm_l}$

$\hat{\vec L}^2|lm_l\rangle = l(l+1)\hbar^2|lm_l\rangle$, $\hat{\vec L}_z|lm_l\rangle = m\hbar|lm_l\rangle$

$\hat{\vec L}_+ = L_x+iL_y$, $\hat{\vec L}_-L_x - iL_y$, $L_x = \frac12(L_-+L_+)$, $\langle L_x^2\rangle = \frac12\langle L^2-L_z^2\rangle$

$L_\pm|lm\rangle = \hbar\sqrt{(l\mp m)(l\pm m+1)}|l,m\pm1\rangle$

Spherical harmonics are the wavefunctions in pos rep, $Y_l^{m_l}(\theta,\phi) = \langle\vec r|lm_l\rangle$

Parity of the spherical harmonics

$\hat P\psi(x,y,z)=\psi(-x,-y,-z), \qquad \hat P\psi(r,\theta,\phi)=\psi(r,\pi-\theta,\phi+\theta)$

For the Legendre polynomials, $\hat PP_l^{m_l}(\theta) = (-1)^{l-|m_l|}P_l^{m_l}(\theta)$
$\to$ even for $l+|m_l|$ even and odd for $l+|m_l|$ odd.

Azimuthal part of the wavefunction, $\hat Pe^{im_l\phi} = e^{im_l(\phi+\pi)} = (-1)^{m_l}e^{im_l\phi}$.

The spherical harmonics are products of two, and $\hat PY_l^{m_l}(\theta,\phi) = Y_l^{m_l}(\pi-\theta,\phi+\pi) = (-1)^{l-|m_l|+m_l}Y_l^{m_l}(\theta,\phi) = (-1)^lY_l^{m_l}(\theta,\phi)$

The hydrogen atom

Coulomb's law, $\hat V = -\frac{e^2}{4\pi\epsilon_0}\frac1r$

Let $u(r)\equiv rR(r)$, Radial eq: $-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+[-\frac{e^2}{4\pi\epsilon_0}\frac1r+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}]u = Eu$

The radial wave function
$\kappa\equiv\frac{\sqrt{-2mE}}{\hbar}$. Divide by E, $\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = [1-\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)}+\frac{l(l+1)}{(\kappa r)^2}]u$

Introduce $\rho\equiv\kappa r$, $\rho_0\equiv\frac{me^2}{2\pi\epsilon\hbar^2\kappa}$, $\frac{d^2u}{d\rho^2} = [1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}]u$

As $\rho\to\infty$, the constant term in the brackets dominates, so $\frac{d^2u}{d\rho^2}=u$.

General sol is $u(\rho)=Ae^{-\rho}+Be^\rho$, but $B=0\to u(\rho)=Ae^{-\rho}$ for large ρ.

As $\rho\to0$, centriugal term dominates, $\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$

The general sol is $u(\rho)=C\rho^{l+1}+D\rho^{-l}$, but ρ^{-l} blows up as $\rho\to0$, so $D=0$. Thus, $u(\rho)\approx Cp^{l+1}$ for small ρ.

Peel off the asymptotic behavior, let $u(\rho)=\rho^{l+1}e^{-\rho}v(\rho)$
$\frac{du}{d\rho} = \rho^le^{-\rho}[(l+1-\rho)v+\rho\frac{dv}{d\rho}]$
$\frac{d^2u}{d\rho^2} = \rho^le^{-\rho}\{[-2l-2+\rho+\frac{l(l+1)}{\rho}]v+2(l+1-\rho)\frac{dv}{d\rho}+\rho\frac{d^2v}{d\rho^2}\}$

Radial eq in terms of $v(\rho)$, $\rho\frac{d^2v}{d\rho^2}+2(l+1-\rho)\frac{dv}{d\rho}+[\rho_0-2(l+1)]v=0$

Assume $v(p)$ can be expressed as a power series in ρ: $v(\rho)=\sum_{j=0}^\infty c_j\rho^j$.
$\frac{dv}{d\rho} = \sum_{j=0}^\infty jc_j\rho^{j-1} = \sum_{j=0}^\infty(j+1)c_{j+1}\rho^j$,
$\frac{d^2v}{d\rho^2} = \sum_{j=0}^\infty j(j+1)c_{j+1}\rho^{j-1}$
$j(j+1)c_{j+1}+2(l+1)(j+1)c_{j+1}-2jc_j+[\rho_0-2(l+1)]c_j=0$
$c_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$

For large j (corresponding to large ρ), $c_{j+1} = \frac{2j}{j(j+1)}c_j = \frac{2}{j+1}c_j$

If this were exact, $c_j=\frac{2^j}{j!}c_0$, $v(\rho)=c_0\sum_{j=0}^\infty\frac{2^j}{j!}\rho^j = c_0e^{2\rho}$, and hence $u(\rho)=c_0\rho^{l+1}e^\rho$, which blows up at large ρ

$\exists c_{j_{\max}+1}=0$, so $2(j_{max}+l+1)-\rho_0=0$.
Define principle quantum number, $n\equiv j_{\max}+l+1$, so $\rho_0=2n$

$E=-\frac{\hbar^2\kappa^2}{2m} = -\frac{me^3}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$

Bohr formula: $E_n = -[\frac{m}{2\hbar^2}(\frac{e^2}{4\pi\epsilon})^2]\frac{1}{n^2} = \frac{E_1}{n^2} = \frac{-13.6\text{ eV}}{n^2}$, $n=1,2,3,\dots$

$\kappa = (\frac{me^2}{4\pi\epsilon_0\hbar^2})\frac1n = \frac{1}{an}$, Bohr radius: $a\equiv\frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.529\times10^{-10}\text{m}$

$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$, $\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}$

For arbitrary n, $l=0,1,\dots,n-1$, so $d(n)=2\sum_{l=0}^{n-1}(2l+1)=2n^2$

$v(\rho)=L_{n-l-1}^{2l+1}(2\rho)$, where $L_{q-p}^p(x)\equiv(-1)^p(\frac{d}{dx})^pL_q(x)$ is an associated Laguerre polynomial. $L_q(x)\equiv e^x(\frac{d}{dx})^q(e^{-x}x^q)$ is the qth Lag. poly.

Normalized hydrogen wavefunctions:

$$\psi_{nlm} = \sqrt{(\frac{2}{na})^3\frac{(n-l-1)!}{2n[(n+1)!]^3}}e^{-r/na}(\frac{2r}{na})^l[L_{n-l-1}^{2l+1}(2r/na)Y_l^m(\theta,\phi)$$

Wavefunctions are mutually orthogonal.
$\int\psi*_{n'l'm_l'}\psi_{nlm_l}r^2\sin\theta drd\theta d\phi = \delta_{n'n}\delta_{l'l}\delta_{m_l'm_l}$

Spectrum Transitions: $E_\gamma = E_i-E_f = -13.6eV(\frac{1}{n_i^2}-\frac{1}{n_f^2})$

Planck formula, $E_\gamma=h\nu$, wavefunction is $\lambda=c/\nu$.

Rydberg: $\frac1\lambda = R(\frac{1}{n_f^2}-\frac{1}{n_i^2})$, $R\equiv\frac{m}{4\pi c\hbar^3}(\frac{e^2}{4\pi\epsilon_0})^2 = 1.097\times10^7\ \text{m}^{-1}$

General angular momentum

$\hat{\vec J} = (\hat J_x,\hat J_y,\hat J_z) = (\hat J_1,\hat J_2,\hat J_3) \qquad \hat{\vec J}^2 = \hat{\vec J}_x^2+\hat{\vec J}_y^2+\hat{\vec J}_z^2$

$[\hat J_i,\hat J_j] = i\hbar\epsilon_{ijk}\hat J_k$, $[\hat{\vec J}^2,\hat J_i]=0$

Take commuting set to be $\hat{\vec J}^2$ and $\hat J_z$. Trade $\hat J_x$ and $\hat J_y$ for $\hat J_\pm = \hat J_x\pm i\hat J_y$

Commutation relations: $[\hat J_+,\hat J_-] = 2\hbar\hat J_z$, $[\hat J_z,\hat J_\pm] = \pm\hbar\hat J_\pm$, $[\hat{\vec J}^2,\hat J_\pm]=0$

$\hat{\vec J}^2$ and $\hat J_z$ commute $\to$ we can simulaneously diagonalize them. Let the simultaneous eigenstate be $|ab\rangle$ s.t. $\hat{\vec J}^2|ab\rangle = a|ab\rangle$, $\hat J_z|ab\rangle = b|ab\rangle$

$\hat{\vec J}^2(\hat J_\pm|ab\rangle) = a(\hat J_\pm|ab\rangle \qquad \hat J_z(\hat J_\pm|ab\rangle) = (b\pm\hbar)(\hat J_\pm|ab\rangle)$

$\hat J_+$ raises and $\hat J_-$ lowers the eigenvalue b of $\hat J_z$. Assuming $|ab\rangle$ is normalized, $\hat J_\pm|ab\rangle = c_\pm|ab\pm\hbar\rangle$, where $c_\pm$ are normalization constants.

$\hat J_\pm\hat J_\mp = \hat{\vec J}^2-\hat J_z^2\pm\hbar\hat J_z$

$0=\langle ab_{\max}|\hat J_-\hat J_+|ab_{\max}\rangle = a-b_{\max}^2-\hbar b_{\max}$, $0=a-b_{\min}^2+\hbar b_{\min}$

$b_{\max} = \frac{-\hbar+\sqrt{\hbar^2+4a}}{2}$, $b_{\min} = \frac{\hbar-\sqrt{\hbar^2+4a^2}}{2}$, $b_{\max}=-b_{\min}=j\hbar$, $j=0,\frac12,1,\dots$

$j\equiv\frac n2$, then $a=b_{\max}^2+\hbar b_{\max} = j^2\hbar^2+\hbar^2j = j(j+1)\hbar^2$

$\widehat{J}_\pm|jm_j\rangle = \hbar\sqrt{(j\mp m_j)(j\pm m_j+1)}|jm_j\pm 1\rangle$
$\langle j'm_j'|\widehat{J}_\pm|jm_j\rangle = \hbar\sqrt{(j\mp m_j)(j\pm m_j+1)}\langle j'm_j'|jm_j\pm 1\rangle =$
$\hbar\sqrt{(j\mp m_j)(j\pm m_j+1)}\delta_{j'j}\delta_{m_j' m_j\pm 1}$

Spin

Classical orbital and spinning motion Infinitesimal classical angular momentum corresponding to an infinite linear momentum $d\vec{p} = dm\vec{v}$ at position $\vec{r}$ from the axis of rotation is $d\vec{L} = \vec{r}\times d\vec{p}$
The total angular momentum is $\vec{L} = \int \vec{r}\times d\vec{p} = \int \vec{r}\times dm\vec{v}$
Point particle of mass m at radius r spinning w constant angular velocity ω about the z-axis, $\vec{L} = I\omega\widehat{z} = m\omega r^2\widehat{z}$
Considering a particle of mass m and charge q rotating with angular velocity ω at radius r about the z-axis, the angular momentum $\vec{L}$ and the momentum dipole momentum $\vec{\mu}$ are given by $\vec{L} = m\omega r^2\widehat{z}$, $\vec{\mu} = \frac{q}{2}\omega r^2\widehat{z}$, where we used $\mu = I\pi r^2$ with current $I = \frac{q}{2\pi/\omega} = \frac{q\omega}{2\pi}$. Thus, $\vec{\mu} = \frac{q}{2m}\vec{L}$

Spin Electron: $j=\frac{1}{2}$, $m_j = \pm\frac{1}{2}$. Spin-$\frac{1}{2}$: $s=\frac{1}{2}$, use $\widehat{J}\to\widehat{S}$.
Basis vectors are $|\frac{1}{2},\frac{1}{2}\rangle \equiv |1\rangle = \begin{bmatrix}1\\0\end{bmatrix}$, $|\frac{1}{2},-\frac{1}{2}\rangle \equiv |2\rangle = \begin{bmatrix}0\\1\end{bmatrix}$

$\widehat{S}_z$ and $\widehat{S}^2$ are diagonal, since simultaneously diagonalized. Matrix elements:
$\langle s'm_s'|\widehat{S}^2|sm_s\rangle = s(s+1)\hbar^2\delta_{s's}\delta_{m_s'm_s}$,
$\langle s'm_s'|\widehat{S}_z|sm_s\rangle = m_s\hbar\delta_{s's}\delta_{m_s'm_s}$

$\widehat{S}^2 = \frac{3}{4}\hbar^2\begin{bmatrix}1&0\\0&1\end{bmatrix}$, $\widehat{S}_z = \frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}$. $\widehat{S}_+ = \hbar\begin{bmatrix}0&1\\0&0\end{bmatrix}$, $\widehat{S}_- = \frac{\hbar}{2}\begin{bmatrix}1&0\\0&-1\end{bmatrix}$.
$\widehat{S}_x = \frac{1}{2}(\widehat{S}_+ + \widehat{S}_-)$, $\widehat{S}_y = \frac{1}{2i}(\widehat{S}_+ - \widehat{S}_-)$, $\widehat{S}_x = \frac{\hbar}{2}\begin{bmatrix}0&1\\1&0\end{bmatrix}$, $\widehat{S}_y = \frac{\hbar}{2}\begin{bmatrix}0&-i\\i&0\end{bmatrix}$
Spin angular momentum: $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$. Pauli m: $\sigma_x = \begin{bmatrix}0&1\\1&0\end{bmatrix}$, $\sigma_y = \begin{bmatrix}0&-i\\i&0\end{bmatrix}$, $\sigma_z = \begin{bmatrix}1&0\\0&-1\end{bmatrix}$
$[\widehat{S}_i,\widehat{S}_j] = i\hbar\epsilon_{ijk}\widehat{S}_k$ and $[\sigma_i,\sigma_j] = 2i\epsilon_{ijk}\sigma_k$
A general state of a spin-half system is given by a spinor,
$|\chi\rangle = \alpha|\frac{1}{2},\frac{1}{2}\rangle + \beta|\frac{1}{2},\frac{1}{2}\rangle = \begin{bmatrix}\alpha\\\beta\end{bmatrix}$, where α and β are complex constants.
$a_x = \sin\theta\cos\phi$, $a_y = \sin\theta\sin\phi$, $a_z = \cos\theta$

Magnetic moment of the electron $\vec{\mu} = g\frac{q}{2m}\vec{S}$, gyromagentic factor (distribution of mass != charge). For the electron, $q=-e$, and $\vec{\mu} = -g\frac{e}{2m}\vec{S}$
$\widehat{\vec{\mu}} = -g\frac{e}{2m}\widehat{\vec{S}} = -\frac{g}{2}\frac{e\hbar}{2m}\vec{\sigma} = -\frac{g}{2}\mu_B\vec{\sigma}$, where $\mu_B = \frac{e\hbar}{2m}$ is Bohr magneton.

Electron in a magnetic field Intrinsic spin angular momentum $\to$ intrinsic magnetic moment. Energy from spin & external mag field: $\widehat{H} = \widehat{V} = -\widehat{\vec{\mu}}\cdot\vec{B}$
For a magnetic field along the z-axis, $\vec{B} = B\widehat{z}$, and
$\widehat{H} = -\widehat{\mu}_z B = -(-\frac{g}{2}\frac{e}{m}\vec{S})\dot{B}\widehat{z} = \frac{g}{2}\frac{eB}{m}S_z = \omega_s S_z = \frac{g}{2}\frac{eB\hbar}{2m}\sigma_z$, where $\omega_s = \frac{g}{2}\frac{eB}{m} = \frac{g}{2}\omega_c$ is the spin precession (or Larmor) frequency and $w_c = \frac{eB}{m}$ is cyclotron frequency. $g\approx 2$ but $g\neq 2\to\omega_s\neq\omega_c$.

Rewrite Hamiltonian as $\widehat{H} = \omega_s S_z$. In the bases in which $\widehat{S}$ and $\widehat{S}_z$ are diagonalized, the eigenstates are given by
$\widehat{H}|\frac{1}{2},\frac{1}{2}\rangle = \omega_s\widehat{S}_z|\frac{1}{2},\frac{1}{2}\rangle = \frac{1}{2}\hbar\omega_s|\frac{1}{2},\frac{1}{2}\rangle$,
$\widehat{H}|\frac{1}{2},-\frac{1}{2}\rangle = \omega_s\widehat{S}_z|\frac{1}{2},-\frac{1}{2}\rangle = -\frac{1}{2}\hbar\omega_s|\frac{1}{2},-\frac{1}{2}\rangle$
Interaction of electron spin w external magentic field $\to$ energies $\pm\frac{1}{2}\hbar\omega_s$.
Spin-up $|\frac{1}{2},\frac{1}{2}\rangle$ & spin-down state $|\frac{1}{2},-\frac{1}{2}\rangle$, with a gap of $\hbar\omega_s$ btwn them.

Consider $\vec{B} = B_x\widehat{e}_x + B_y\widehat{e}_y + B_z\widehat{e}_z$.
$\widehat{H} = (\frac{g}{2}\frac{e}{m}\vec{S})\cdot\vec{B} = \frac{g}{2}\frac{e\hbar}{2m}\begin{bmatrix}B_z & B_x - iB_y\\ B_x+iB_y & -B_z\end{bmatrix}$
Eigenvals of matrix $\begin{vmatrix}B_z-\lambda & B_x-iB_y\\ B_x+iB_y & -B_z-\lambda\end{vmatrix} = 0$, which gives $\lambda = \pm B$,
where $B = |\vec{B}|$. Therefore, eigenvals of $\widehat{H}$ are $\pm\frac{g}{2}\frac{e\hbar B}{2m} = \pm\frac{1}{2}\hbar\omega_s$.

The Stern-Gerlach experiment
Force on electron w spin-up: $\vec{F}_1 = -\vec{\nabla}V_1 = \frac{1}{2}\hbar\vec{\nabla}\omega_s = \frac{g}{2}\frac{e\hbar}{2m}\frac{\partial B(z)}{\partial z}$
Force on electron w spin-down: $\vec{F}_2 = -\vec{\nabla}V_2 = -\frac{1}{2}\hbar\vec{\nabla}\omega_s = -\frac{g}{2}\frac{e\hbar}{2m}\frac{\partial B(z)}{\partial z}$
Electrons deflected up/down depending on whether spin-up/spin-down along $\vec{B}$.

Spin precession $|\chi(0)\rangle = \begin{bmatrix}a\\b\end{bmatrix}$, $|a|^2+|b|^2 = 1$ and $a = \cos\frac{\alpha}{2}$, $b = \sin\frac{\alpha}{2}$
$|\chi(0)\rangle = \cos\frac{\alpha}{2}|\frac{1}{2}\frac{1}{2}\rangle + \sin\frac{\alpha}{2}|\frac{1}{2}-\frac{1}{2}\rangle = \begin{bmatrix}\cos\frac{\alpha}{2}\\ \sin\frac{\alpha}{2}\end{bmatrix}$, $|\chi(t)\rangle = \begin{bmatrix}e^{-\frac{i}{2}\omega_s t}\cos\frac{\alpha}{2}\\ e^{\frac{i}{2}\omega_s t}\sin\frac{\alpha}{2}\end{bmatrix}$
$\langle\widehat{S}_z\rangle = |e^{-\frac{i}{2}\omega_s t}\cos\frac{\alpha}{2}|^2\frac{\hbar}{2} - |e^{-\frac{i}{2}\omega_s t}\sin\frac{\alpha}{2}{}^2\frac{\hbar}{2} = (\cos^2\frac{\alpha}{2} - \sin^2\frac{\alpha}{2})\frac{\hbar}{2}$
$\langle\widehat{S}_x\rangle = \frac{\hbar}{2}\sin\alpha\cos\omega_s t$, $\quad\langle\widehat{S}_y\rangle\frac{\hbar}{2}\sin\alpha\sin\omega_s t$, $\langle\widehat{S}_z\rangle = \frac{\hbar}{2}\cos\alpha$
Angle $\alpha\to\pi-\alpha$ for spin-down. Spin-up, $\widehat{S}_z$ eigenval is $\frac{\hbar}{2}$, $|\widehat{S}^2|$ is $\frac{\sqrt{3}\hbar}{2}$.
Space quantization: angular momentum along any fixed direction take only discrete $(2j+1)$ values.

Addition of angular momentum

$\widehat{J}_1$, $|j_1,m_{j1}\rangle$. $\widehat{J}_2$, $|j_2,m_{j2}\rangle$. $\widehat{J} = \widehat{J}_1+\widehat{J}_2$. $\widehat{J}^2$ & $\widehat{J}_z$: sim diag set. $|j,m_j\rangle$

Triplet and singlet states of a system of two spin-halves
$|j_1,m_{j1}\rangle\otimes|j_2,m_{j2}\rangle$
The triplet states ($j=1$ multiplet): $|1,1\rangle = |\frac{1}{2},\frac{1}{2}\rangle\otimes|\frac{1}{2},\frac{1}{2}\rangle$,
$|1,0\rangle = \frac{1}{\sqrt{2}}(|\frac{1}{2},\frac{1}{2}\rangle\otimes|\frac{1}{2},-\frac{1}{2}\rangle + |\frac{1}{2},-\frac{1}{2}\rangle\otimes|\frac{1}{2},\frac{1}{2}\rangle)$,
$|1,-1\rangle = |\frac{1}{2},-\frac{1}{2}\rangle\otimes|\frac{1}{2},-\frac{1}{2}\rangle$
Singlet state ($j=0$): $|0,0\rangle = \frac{1}{\sqrt{2}}(|\frac{1}{2},\frac{1}{2}\rangle\otimes|\frac{1}{2},-\frac{1}{2}\rangle - |\frac{1}{2},-\frac{1}{2}\rangle\otimes|\frac{1}{2},\frac{1}{2}\rangle)$
$s = 1,0$ out of s_1 and s_2 as $\frac{1}{2}\otimes\frac{1}{2} = 1\oplus 0$

$\widehat{J}^2 = \widehat{J}_1^2\otimes 1 + 1\otimes\widehat{J}_2^2 + 2\widehat{J}_{1z}\otimes\widehat{J}_{2z} + \widehat{J}_{1+}\otimes\widehat{J}_{2-} + \widehat{J}_{1-}\otimes\widehat{J}_{2+}$
Spin angular momentum, interchan. use $\widehat{S}$ for $\widehat{J}$, and s and m_s for j and m_j.

Addition of general angular momentum
$|j_1+j_2,j_1+j_2\rangle = |j_1,m_{j1}\rangle\otimes|j_2,m_{j2}\rangle$
$j = j_1\otimes j_2 = j_1+j_2\oplus j_1+j_2-1\oplus j_1+j_2-2\oplus\cdots\oplus|j_1-j_2|$

Clebsch-Gordon coefficients
Complete states: $\sum_{m_{j1},m_{j2}}|j_1,m_{j1};j_2,m_{j2}\rangle\langle j_1,m_{j1};j_2,m_{j2}| = 1$
$|j,m_j\rangle = \sum_{m_j=m_{j1}+m_{j2}}\langle j_1,m_{j1};j_2,m_{j2}|j,m_j\rangle|j_1,m_{j1};j_2,m_{j2}\rangle$
where $\langle j_1,m_{j1};j_2,m_{j2};j,m_j\rangle$ are Clebsch-Gordon coefficients.

5. MANY-PARTICLE SYSTEMS AND PERTURBATION THEORY

5.1 Identical particles

$\Psi(\vec{r}_1,\vec{r}_2,t)$, $H = -\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + V(r_1,r_2,t)$
$\widehat{H} = \widehat{H}(1,2) = \widehat{H}(2,1) = -\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\boldsymbol{\nabla}_2^2 + \widehat{V}(q_1,q_2)$, where
$q_i = \vec{r}_i, s_i$ with $\vec{r}_i$ is the spatial coordinate and s_i denote spin coordinate.
P of finding particle 1 in volume d^3r_1, etc.: $\int|\psi(r_1,r_2,t)|^2d^3r_1d^3r_2 = 1$
$\Psi(\vec{r}_1,\vec{r}_2,t) = \psi(r_1,r_2)e^{-iEt/\hbar}$, $-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2\psi - \frac{\hbar}{2m_2}\boldsymbol{\nabla}_2^2\psi + V\psi = E\psi$
Exchange operator $\widehat{P}_{\text{ex}}: 1\leftrightarrow 2$, which exchanges the two particles.
$\widehat{P}_{\text{ex}}\Psi(q_1,q_2) = \Psi(q_2,q_1)$ and $\widehat{P}_{\text{ex}}^2\Psi(q_1,q_2) = \Psi(q_1,q_2)$
$\widehat{P}_{\text{ex}}$ has two eigenvalues $p_{\text{ex}} = \pm 1$
$[\widehat{P}_{\text{ex}},\widehat{H}] = 0$. Can construct simulataenous eigenstates of $\widehat{P}_{\text{ex}}$ and $\widehat{H}(1,2)$:
$\widehat{H}\Psi_\pm(q_1,q_2) = E\Psi_\pm(q_1,q_2)$, $\widehat{P}_{\text{ex}}\Psi_\pm(q_1,q_2) = \pm\Psi_\pm(q_1,q_2)$
Identical particles in QM come in two and only two classes:
1. Bosons: $\Psi_+(q_2,q_1) = \widehat{P}_{\text{ex}}\Psi_+(q_1,q_2) = +\Psi_+(q_1,q_2)$, $s = 0,1,2,\ldots$
2. Fermions: $\Psi_-(q_2,q_1) = \widehat{P}_{\text{ex}}\Psi_-(q_1,q_2) = -\Psi_-(q_1,q_2)$, $s = \frac{1}{2},\frac{3}{2},\frac{5}{2}$

5.2 Identical noninteracting particles

$\widehat{H}(1,2) = \frac{\widehat{p}_1^2}{2m} + \frac{\widehat{p}_2^2}{2m} + \widehat{V}(\widehat{q}_1) + \widehat{V}(\widehat{q}_2) = \widehat{H}(1) + \widehat{H}(2)$
$\widehat{H}(1)\psi_a(q_1) = E_a\psi_a(q_1)$, $\widehat{H}(2)\psi_a(q_2) = E_a\psi_a(q_2)$
Same set of eigenst, eigenval, and quantum nums: $\{\psi_a(q)\},\{E_a\},\{a\}$
$\Psi_-(q_1,q_2) = \frac{1}{\sqrt{N!}}\det\cdots = \frac{1}{\sqrt{2}}\det\begin{bmatrix}\psi_a(q_1) & \psi_b(q_1)\\ \psi_a(q_2) & \psi_b(q_2)\end{bmatrix}$, Slater det.
Antisymmetrical, for fermions. Bosons: flip all minus signs into plus signs.
Pauli exclusion principle: two identical fermions can't have same quantum nums (or can't occupy the same state). Two bosons can occupy the same state.

Bosons tend to congregate and fermions tend to avoid each other Particle in state $\psi_a(x)$ and another in state $\psi_b(x)$. These two states are orthogonal and normalized.
If distinguishable, $\psi(x_1,x_2) = \psi_a(x_1)\psi_b(x_2)$
If identical bosons, $\psi_+(x_1,x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi)b(x_2) + \psi_b(x_1)\psi_a(x_2)$
If identical fermions, $\psi_-(x_1,x_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]$
Separation of the two particles:
$\langle(\Delta x)^2\rangle = \langle(x_1-x_2)^2\rangle = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1x_2\rangle$
1. Distinguishable particles
$\langle x_1^2\rangle_{\text{dist}} = \int x_1^2|\psi_a(x_1)|^2dx_1\int|\psi_b(x_2)|^2dx_2 = \int x_1^2|\psi_a(x_1)|^2dx_1 = \langle x^2\rangle_a$. Similarly, $\langle x_2^2\rangle_{\text{dist}} = \langle x^2\rangle_b$,
$\langle x_1x_2\rangle_{\text{dist}} = \int x_1|\psi_a(x_1)|^2dx_1\int x_2|\psi_b(x_2)|^2dx_2 = \langle x\rangle_a\langle x\rangle_b$
$\langle(\Delta x)^2\rangle_{\text{dist}} = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b$
2. Identical particles
$|\Psi_\pm(x_1,x_2)|^2 = \frac{1}{2}(|\psi_a(x_1)|^2|\psi_b(x_2)|^2 + |\psi_b(x_1)|^2|\psi_a(x_2)|^2 \pm \psi_a^*(x_1)\psi_b(x_1)\psi_b^*(x_2)\psi_a(x_2) \pm \psi_b^*(x_1)\psi_a(x_1)\psi_a^*(x_2)\psi_b(x_2))$
$\langle x_1^2\rangle_\pm = \langle x_2^2\rangle_\pm = \frac{1}{2}(\langle x^2\rangle_a + \langle x^2\rangle_b)$, $\langle x_1,x_2\rangle = \langle x\rangle_a\langle x\rangle_b \pm |\langle x\rangle_{ab}|^2$
$\langle(x_1-x_2)^2\rangle_\pm = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b \mp 2|\langle x\rangle_{ab}|^2$,
$\langle(\Delta x)^2\rangle\pm = \langle(\Delta x)^2\rangle_{\text{dist}} \mp 2|\langle x\rangle_{ab}|^2$
Id. bosons: spatially closer, id. fermions: apart, compared to distinguishable.
Purely QM effect that follows from sym. or antisym. of the wavefunction.

H_2 molecule and covalent bond Two H atoms each in ground state and spatially far apart.
$\Psi_{\text{tot}-}(q_1,q_2) = \Psi(\vec{r}_1,\vec{r}_2)\chi(1,2)$, where $\Psi(\vec{r}_1,\vec{r}_2)$ is the spatial part of the wavefn and $\chi(1,2)$ is the spin part.
$\Psi_{\text{tot}-} = \Psi(\vec{r}_1,\vec{r}_2)_+\chi(1,2)_-$, sym, produces a covalent bond.
$\Psi_{\text{tot}-} = \Psi(\vec{r}_1,\vec{r}_2)_-\chi(1,2)_+$, antisym, electrons avoid each other spatially.
$\Psi_{\text{tot}-}(q_1,q_2) = \frac{1}{\sqrt{2}}(\psi_{100}(\vec{r}_1-\vec{r}_0)\psi_{100}(\vec{r}_2+\vec{r}_0) + \psi_{100}(\vec{r}_1+\vec{r}_0)\psi_{100}(\vec{r}_2-\vec{r}_0)) = \frac{1}{\sqrt{2}}(|\frac{1}{2}\frac{1}{2}(1)\rangle|\frac{1}{2}-\frac{1}{2}(2)\rangle - |\frac{1}{2}-\frac{1}{2}(1)\rangle|\frac{1}{2}\frac{1}{2}(2)\rangle)$
d-fold degen., energy level occupied by $N>2d$ num of spin-half id fermions $\to$ color.

5.3 Perturbation theory

Time-dependent Hamiltonian $\widehat{H}_0$ with known wavefunctions $|\psi_a^{(0)}\rangle$ and energies $E_a^{(0)}$, $\widehat{H}_0|\phi_a^{(0)}\rangle = E_a^{(0)}|\psi_a^{(0)}\rangle$
SE w new Hamiltonian: $i\hbar\frac{\partial}{\partial t}|\psi_n\rangle = (\widehat{H}_0 + \widehat{H}'(t)|\psi_n\rangle$. We call $\widehat{H}_0$ the unperturbed Hamiltonian and $\widehat{H}'(t)$ the perturbation, which could be time-dep.

Time-independent perturbation theory $\widehat{H}'(t) = \widehat{H}'$. $\widehat{H} = \widehat{H}_0 + \widehat{H}'$ is TI.
$\widehat{H}|\psi_n\rangle = E_n|\psi_n\rangle$, $(E_n - E_a^{(0)})\langle\psi_a^{(0)}\rangle\langle\psi_a^{(0)}|\psi_n\rangle = \sum_b H_{ab}'\langle\psi_b^{(0)}|\psi_n\rangle$,
$H_{ab}' = \langle\psi_a^{(0)}|\widehat{H}'|\psi_n^{(0)}\rangle$: matrix element of perturbation in the unpert. states.
$(E_n^{(0)} - E_a^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots)\langle\phi_a^{(0)}(|\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \ldots) = \sum_b H_{ab}'\langle\phi_b^{(0)}(|\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \ldots)$. SE in a diff form, all exact.
Now suppose $\widehat{H}'$ is small compared to $\widehat{H}_0$. The additional terms should be small. Perturbation theory involves solving above by organizing the corrections s.t. $E_n^{(2)}$ is smaller than $E_n^{(1)}$, $|\psi_n^{(2)}\rangle$ is smaller than $|\psi_n^{(1)}\rangle$, and so on.

Nondegenerate time-independent perturbation theory Nondegenerate: any two unperturbed states $|\psi_a^{(0)}\rangle$ and $|\psi_b^{(0)}\rangle$ with $a\neq b$ have $E_a^{(0)}\neq E_b^{(0)}$

Zeroth order
$(E_n^{(0)} - E_a^{(0)})\langle\psi_a^{(0)}|\psi_n^{(0)}\rangle = 0$. $E_n = E_n^{(0)}$, $|\psi_n\rangle = |\psi_n^{(0)}\rangle$, no corrections.

First order
$(E_n^{(0)} - E_a^{(0)})\langle\psi_a^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_a^{(0)}|\psi_n^{(0)}\rangle = \sum_b H_{ab}'\langle\psi_b^{(0)}|\psi_n^{(0)}\rangle$
$a=n$, $E_n^{(0)} - E_a^{(0)} = 0$, $\delta_{an} = 1$. $a\neq n$, $E_n^{(0)} - E_a^{(0)}\neq 0$, $\delta_{an} = 0$.
$E_n = E_n^{(0)} + H_{nm}'$, $|\psi_n\rangle = |\psi_n^{(0)} - \sum_{m\neq n}\frac{H_{mn}'}{E_m^{(0)} - E_n^{(0)}}|\psi_m^{(0)}\rangle$
$|\frac{H_{mn}'}{E_m^{(0)} - E_n^{(0)}}| << 1$, matrix elements of the perturbation btwn the unperturbed states must be much smaller than the diff btwn corresponding unpert. E's.

Second order: $E_n = E_n^{(0)} + H_{nn}' - \sum_{m\neq n}\frac{|H_{mn}'|^2}{E_m^{(0)} - E_n^{(0)}}$
States of lower energy make pos contribution while states of higher energy make neg contribution.

Degenerate time-independent perturbation theory Ex: unperturbed hydrogen atom where $|\psi^{(0)}_{nlm}\rangle$ w the same n but diff l's and m's are degenerate.
Consider an unperturbed energy level that is d-fold degenerate w d states $|\psi^{(0)}_{n}\rangle, |\psi^{(0)}_{n'}\rangle, \ldots$, having the same energy $E^{(0)}_n = E^{(0)}_{n'} = \ldots$
$(E^{(0)} - E^{(0)}_a)\langle\psi^{(0)}_a|\psi^{(1)}\rangle + E^{(1)}\langle\psi^{(0)}_a|\psi^{(0)}\rangle = \sum_b H'_{ab}\langle\psi^{(0)}_b|\psi^{(0)}\rangle$
Secular equation: $\det|H'_{nn'} - E^{(1)}\delta_{nn'}| = 0$
$|\Psi^0_n\rangle = \sum_{n'} c^{(0)}_{n'}|\psi^{(0)}_{n'}\rangle$
If matrix elements of the pert. Hamiltonian are diagonal, $H'_{nn'} = E^{(1)}_n\delta_{n'n}$, then $\exists$ no cross terms that mix diff states $\rightarrow E^{(1)}_n = H'_{nn}$.

5.4 Fine structure of hydrogen atom

Relativistic kinetic energy correction Relativistic energy of the electron:
$E = mc^2\sqrt{1 + \frac{\vec{p}^2}{m^2c^2}}$
$E = mc^2(1 + \frac{1}{2}\frac{\vec{p}^2}{m^2c^2} - \frac{1}{2}\frac{1}{2}\frac{1}{2}(\frac{\vec{p}^2}{m^2c^2})^2 + \ldots) = mc^2 + \frac{\vec{p}^2}{2m} - \frac{\vec{p}^4}{8m^3c^4} + \ldots$
KE perturbation: $\widehat{H}_k = -\frac{\widehat{\vec{p}}^4}{8m^3c^4}$
Spin-orbit correction $V(r) = -e\Phi(r)$, where $\Phi(r)$ is the corresponding electric potential.
Supposing that the electron sees magnetic field $\vec{B}'$, it has additional energy $\widehat{H}_{\mathrm{SO}} = -\widehat{\vec{\mu}}\cdot\widehat{\vec{B}}'$, where $\widehat{\vec{\mu}} = g\frac{-e}{2mc}\widehat{\vec{S}} = -\frac{e}{mc}\widehat{\vec{S}}$ is the magnetic moment and $g = 2$ is the gyromagnetic ratio of the electron.
Thomas precession: electron is rotating and accelerating around tne nucleus, and it is not an inertial frame. $\vec{B}'_\perp = \vec{B}'$, and $\vec{B}'_\perp = \vec{B} = \frac{1}{2}\frac{\vec{E}\times\vec{v}}{c}$
$\widehat{H}_{\mathrm{SO}} = \frac{1}{2m^2c^2r}\frac{\mathrm{d}\widehat{V}}{\mathrm{d}r}\widehat{\vec{L}}\cdot\widehat{\vec{S}}$. For hydrogenic atoms, $\widehat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}$ and $\frac{\mathrm{d}\widehat{V}}{\mathrm{d}r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \rightarrow \widehat{H}_{\mathrm{SO}} = \frac{Ze^2}{8\pi\epsilon_0 m^2c^2r^3}\widehat{\vec{L}}\cdot\widehat{\vec{S}}$
Darwin correction For states with $l = 0$, no orbital angular momentum, no spin-orbit interaction. $\widehat{H}_D = \frac{\hbar^2 Ze^2}{8m^2c^2\epsilon_0}\delta^3(\vec{r})$