## 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 $\Psi$: $\langle x\rangle = \int x|\Psi|^2 dx$. 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 SE 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 $\rightarrow$ the total probability is constant in time.

### 1.5 Momentum

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

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: $\widehat{r} = \vec{r}$, $\widehat{p} = -i\hbar\vec{\nabla}$

### 1.6: The Uncertainty Principle

The wavelength of $\Psi$ 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:

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

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

$[\widehat{x}_i,\widehat{p}_j] = i\hbar\delta_{ij}$, $[\widehat{x}_i,\widehat{x}_j] = [\widehat{p}_i,\widehat{p}_j] = 0$. $\delta_{ij} = 1$ 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, $V(\vec{r},t) = V(\vec{r})$. Sep of vars: $\Psi(\vec{r},t) = \psi(\vec{r})\varphi(t)$. 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 $\delta_{mn}$ 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 $\int d^3\vec{r'}\psi(\vec{r'},t)\delta^3(\vec{r'}-\vec{r}) = \psi(\vec{r},t)$

**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

Wavefn, mass $m$ 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 $\psi(0) = B = 0 \rightarrow \psi(x) = A\sin(kx)$ at $x = a$ sets $\psi(a) = A\sin(ka) = 0$

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

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: $c_n = \int\psi_n(x)^*f(x)dx$ $c_m = \frac{2}{a}\int_0^a f(x)\sin(\frac{m\pi x}{a})dx$

$|c_n|^2$: 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 $\langle H\rangle = \sum_{n=1}^{\infty}|c_n|^2E_n$

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

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

### 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.

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

$\Psi(x,t) = Ae^{ikx - i\frac{\hbar k^2}{2m}t} + Be^{-ikx - i\frac{\hbar k^2}{2m}t} =$
$Ae^{i(kx-\omega t)} + Be^{-i(kx+\omega t)} = Ae^{ik(x-v_pt)} + Be^{-ik(x+v_pt)}$, 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 $\alpha$ 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: $\psi(x) = Ae^{-\kappa x} + Be^{\kappa x}$. $A = 0$, 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 $\psi(x) = Fe^{-\kappa x}, (x > 0)$.

1st boundary cond: $F = B$. $\psi(x) = \{Be^{\kappa x}, (x \leq 0), Be^{-\kappa x}, (x \geq 0)\}$

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

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

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 $E \rightarrow$ 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

Mass $m$ and energy $E<V_0$ approach from 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,

$T=|\frac{F}{A}|^2=\frac{(2k\kappa)^2}{(k^2+\kappa^2)^2\sinh^2(2\kappa a)+(2k\kappa)^2}$. $T\approx e^{-2\gamma}$, $\gamma=\int_a^b\sqrt{\frac{2m(V(x)-E)}{\hbar^2}}dx$

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

$V(x)=\Big\{-V_0, \quad \text{for } -a<x<a \qquad 0, \quad \text{for } |x|>a$

*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 $\psi_{III}(x)=Fe^{-\kappa x}$

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**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 $\psi$ and $\psi'$ 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 $\kappa$ 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.

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**Wide & deep well**: $z_n\approx\frac{n\pi}{2}, n=1,2,...E_n=-V_0+\frac{\hbar^2\pi^2n^2}{2m(2a)^2}, n=1,2,..$

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 $c^*\langle\psi|$.

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 → 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

$\widehat{\vec r}|\vec r\rangle=\vec r|\vec r\rangle \quad \langle\vec r'|\vec r\rangle=\delta^3(\vec r'-\vec r), \int d^3\vec r|\vec r\rangle\langle\vec r|=1, \langle\vec r'|\widehat{\vec r}|\vec r\rangle=\vec r\delta^3(\vec r'-\vec r)$

$\widehat{\vec p}|\vec p\rangle=\vec p|\vec p\rangle \quad \langle\vec p'|\vec p\rangle=\delta^3(\vec p'-\vec p), \int d^3\vec p|\vec p\rangle\langle\vec p|=1$

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 $\langle\widehat O\rangle=\int d^2\vec r\langle\psi(t)|\vec r\rangle\langle\vec r|\widehat O|\psi(t)\rangle$

$\psi(\vec r,t)=\langle\vec r|\psi(t)\rangle, \qquad \psi(\vec r,t)^*=\langle\vec r|\psi(t)\rangle^*=\langle\psi(t)|\vec r\rangle$,

$\langle\vec r|\widehat O|\psi(t)\rangle=\widehat O(\vec r,-i\hbar\vec\nabla)\psi(\vec r,t), \langle\widehat O\rangle=\int d^3\vec r\psi(\vec r,t)^*\widehat O(\vec r,-i\hbar\vec\nabla)\psi(\vec r,t)$

**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 $\vec p^*=\vec p$. $\widehat O(\widehat{\vec r},\widehat{\vec p})=\widehat O(i\hbar\vec\nabla_{\vec p},\vec p)$.

$\langle\widehat O\rangle=\langle\psi(t)|\widehat O|\psi(t)\rangle\to\langle\widehat O\rangle=\int d^2\vec p\langle\psi(t)|\vec p\rangle\langle\vec p|\widehat O|\psi(t)\rangle$.

$\psi(\vec p,t)=\langle\vec p|\psi(t)\rangle, \qquad \psi(\vec p,t)^*=\langle\vec p\psi(t)\rangle^*=\langle\psi(t)|\vec p\rangle$

$\langle\vec p|\widehat O|\psi(t)\rangle=\widehat O(i\hbar\vec\nabla_{\vec p},\vec p), \langle\widehat O\rangle=\int d^3\vec p\psi(\vec p,t)^*\widehat O(i\hbar\vec\nabla_{\vec p},\vec p)\psi(\vec p,t)$.

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

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

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### 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! → QM contains all of classical mech.

### The simple harmonic oscillator

$\widehat H=\frac{\widehat p^2}{2m}+\frac12 m\omega^2\widehat x^2$

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

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

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

$[\widehat N,\widehat a]=-\widehat a$, $[\widehat N,\widehat a^\dagger]=\widehat a^\dagger$

$\widehat N(\widehat a|n\rangle)=(n-1)(\widehat a|n\rangle)$, $\widehat N(\widehat a^\dagger|n\rangle)=(n+1)(\widehat a^\dagger|n\rangle)$

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

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

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

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

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

**Wavefunctions in position representation** $E_n=(n+\frac12)\hbar\omega, n=0,1,2,...$

The stationary wavefunctions of definite energy: $\psi_n(x)=\langle x|n\rangle$

$\langle x'|\widehat a^\dagger|x''\rangle=\delta(x'-x'')\frac{1}{\sqrt2\sigma}(x''-\sigma^2\frac{\partial}{\partial x''})$, where $\sigma\equiv\sqrt{\frac{\hbar}{m\omega}}$

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

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

**Classical simple harmonic oscillator** Hamiltonian of a simple harmonic is $H=\frac{p^2}{2m}+\frac12m\omega^2x^2. \qquad \dot x=\frac{\partial H}{\partial p}=\frac{p}{m}, \qquad \dot p=-\frac{\partial H}{\partial x}=-m\omega^2x$

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 $|n\rangle$: $|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2}\sum_{n=0}^{\infty}\frac{\alpha^n}{\sqrt{n!}}|n\rangle$

$P(n) = |\langle n|\alpha\rangle|^2 = |\alpha_n|^2 = \frac{\langle n\rangle^n e^{-\langle n\rangle}}{n!}$, 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 $\Delta x\Delta p \geq \frac{\hbar}{2}$ 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 $0 \leq x \leq l_x, \ldots$ while $\psi(x,y,z) = 0$ outside.

Separation of vars: $\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z)$

$\rightarrow$ SE becomes $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_1(x) = E_1\psi_1(x), \ldots$, where $E = E_1 + E_2 + E_3$.

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

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

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

$\widehat{L}_x = \widehat{y}\widehat{p}_z - \widehat{z}\widehat{p}_y, \widehat{L}_y = \widehat{z}\widehat{p}_x - \widehat{x}\widehat{p}_z, \widehat{L}_z = \widehat{x}\widehat{p}_y - \widehat{y}\widehat{p}_x$

$[\widehat{L}_i, \widehat{L}_j] = i\hbar\epsilon_{ijk}\widehat{L}_k$, 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.

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

In pos rep, $\widehat{\vec{L}} = \widehat{\vec{r}} \times \widehat{\vec{p}} = -i\hbar\vec{r} \times \vec{\nabla}$. In sph coords,

$\widehat{\vec{L}} = -i\hbar r\widehat{r} \times (\frac{\partial}{\partial r}\widehat{r} + \frac{1}{r}\frac{\partial}{\partial\theta}\widehat{\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\widehat{\phi} = -i\hbar(\widehat{\phi}\frac{\partial}{\partial\theta} - \widehat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi})$

$\widehat{r} = \sin\theta\cos\psi\widehat{x} + \sin\theta\sin\phi\widehat{y} + \cos\theta\widehat{z}$

$\widehat{\theta} = \cos\theta\cos\phi\widehat{x} + \cos\theta\sin\phi\widehat{y} - \sin\theta\widehat{z}$ $\quad$ $\widehat{\phi} = -\sin\phi\widehat{x} - \cos\phi\widehat{y}$

$\widehat{L}_x = i\hbar(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi})$ $\quad$ $\widehat{L}_y = i\hbar(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi})$

$\widehat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$ $\quad$ $\widehat{\vec{L}}^2 = -\hbar^2[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}]$

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

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

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

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

$\Phi(\phi) = e^{im\phi}$, periodic in $\phi$ w period $2\pi$ 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 $P_l(x) = \frac{1}{2^l l!}(\frac{d}{dx})^l(x^2 - 1)^l$, with $l$ taking values $l = 0, 1, 2, \ldots$ and for each $l$, $m_l$ takes $2l + 1$ values $m_l = -l, -l+1, \ldots, l-1, l$.

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 $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$.

$\widehat{\vec{L}}^2 Y_l^{m_l} = l(l+1)\hbar^2 Y_l^{m_l}$, $\quad$ $\widehat{L}_z Y_l^{m_l} = m\hbar Y_l^{m_l}$

The Legendre polynomials are normalized s.t. they satisfy the ortho relation

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

$P_0^0(\theta) = 1, P_1^1(\theta) = \sin\theta, P_1^1(\theta) = \cos\theta$, 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

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

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

$\widehat{L}_+ = L_x + iL_y$, $\widehat{L}_- L_x - iL_y$, $L_x = \frac{1}{2}(L_- + L_+)$, $\langle L_x^2\rangle = \frac{1}{2}\langle L^2 - L_z^2\rangle$

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

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

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

For the Legendre polynomials, $\widehat{P}P_l^{m_l}(\theta) = (-1)^{l-|m_l|}P_l^{m_l}(\theta)$

$\rightarrow$ even for $l + |m_l|$ even and odd for $l + |m_l|$ odd.

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

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

### The hydrogen atom

Coulomb's law, $\widehat{V} = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$

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

**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 $\rho \rightarrow \infty$, 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 $B = 0 \rightarrow u(\rho) = Ae^{-\rho}$ for large $\rho$.

As $\rho \rightarrow 0$, 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 $\rho^{-l}$ blows up as $\rho \rightarrow 0$, so $D = 0$. Thus, $u(\rho) \approx C\rho^{l+1}$ for small $\rho$.

Peel off the asymptotic behavior, let $u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$

$\frac{du}{d\rho} = \rho^l e^{-\rho}[(l+1-\rho)v + \rho\frac{dv}{d\rho}]$

$\frac{d^2u}{d\rho^2} = \rho^l e^{-\rho}\{[-2l - 2 + \rho + \frac{l(l+1)}{\rho}]v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\}$

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 $\rho$: $v(\rho) = \sum_{j=0}^\infty c_j\rho^j$.

$\frac{dv}{d\rho} = \sum_{j=0}^\infty jc_j\rho^{j-1} = \sum_{j=0}^\infty(j+1)c_{j+1}\rho^j$,

$\frac{d^2v}{d\rho^2} = \sum_{j=0}^\infty j(j+1)c_{j+1}\rho^{j-1}$

$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(l+1)]c_j = 0$

$c_{j+1} = \frac{2(j+l+1)-\rho_0}{(j+1)(j+2l+2)}c_j$

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

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 $\rho$

$\exists c_{j_{\max}+1} = 0$, 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: $E_n = -[\frac{m}{2\hbar^2}(\frac{e^2}{4\pi\epsilon})^2]\frac{1}{n^2} = \frac{E_1}{n^2} = \frac{-13.6\text{ eV}}{n^2}$, $n = 1, 2, 3, \ldots$

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

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

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

$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$, where $L_{q-p}^p(x) \equiv (-1)^p(\frac{d}{dx})^p L_q(x)$ is an associated Laguerre polynomial. $L_q(x) \equiv e^x(\frac{d}{dx})^q(e^{-x}x^q)$ is the $q$th 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: $\frac{1}{\lambda} = R(\frac{1}{n_f^2} - \frac{1}{n_i^2})$, $R \equiv \frac{m}{4\pi c\hbar^3}(\frac{e^2}{4\pi\epsilon_0})^2 = 1.097 \times 10^7\text{ m}^{-1}$

### General angular momentum

$\widehat{\vec{J}} = (\widehat{J}_x, \widehat{J}_y, \widehat{J}_z) = (\widehat{J}_1, \widehat{J}_2, \widehat{J}_3)$ $\qquad$ $\widehat{\vec{J}}^2 = \widehat{\vec{J}}_x^2 + \widehat{\vec{J}}_y^2 + \widehat{\vec{J}}_z^2$

$[\widehat{J}_i, \widehat{J}_j] = i\hbar\epsilon_{ijk}\widehat{J}_k$, $[\widehat{\vec{J}}^2, J_i] = 0$

Take commuting set to be $\widehat{\vec{J}}^2$ and $\widehat{J}_z$. Trade $\widehat{J}_x$ and $\widehat{J}_y$ for $\widehat{J}_\pm = \widehat{J}_x \pm i\widehat{J}_y$

Commutation relations: $[\widehat{J}_+, \widehat{J}_-] = 2\hbar\widehat{J}_z$, $[\widehat{J}_z, \widehat{J}_\pm] = \pm\hbar\widehat{J}_\pm$, $[\widehat{\vec{J}}^2, \widehat{J}_\pm] = 0$

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

$\widehat{\vec{J}}^2(\widehat{J}_\pm|ab\rangle) = a(\widehat{J}_\pm|ab\rangle$ $\qquad$ $\widehat{J}_z(\widehat{J}_\pm|ab\rangle) = (b \pm \hbar)(\widehat{J}_\pm|ab\rangle)$

$\widehat{J}_+$ raises and $\widehat{J}_-$ lowers the eigenvalue $b$ of $\widehat{J}_z$. Assuming $|ab\rangle$ is normalized, $\widehat{J}_\pm|ab\rangle = c_\pm|ab \pm \hbar\rangle$, where $c_\pm$ are normalization constants.

$\widehat{J}_\pm\widehat{J}_\mp = \widehat{\vec{J}}^2 - \widehat{J}_z^2 \pm \hbar\widehat{J}_z$

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

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

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

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

$\langle j'm_j'|\widehat{J}_\pm|jm_j\rangle = \hbar\sqrt{(j \mp m_j)(j \pm m_j + 1)}\langle j'm_j'|jm_j \pm 1\rangle = \hbar\sqrt{(j \mp m_j)(j \pm m_j + 1)}\delta_{j'j}\delta_{m_j'm_j\pm1}$

### 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 $\omega$ 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 $\omega$ 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 $\widehat{\vec{J}} \rightarrow \widehat{\vec{S}}$.

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 $\widehat{\vec{S}}^2$ are diagonal, since simultaneously diagonalized. Matrix elements:

$\langle s'm_s'|\widehat{\vec{S}}^2|sm_s\rangle = s(s+1)\hbar^2\delta_{s's}\delta_{m_s'm_s}$,

$\langle s'm_s'|\widehat{S}_z|sm_s\rangle = m_s\hbar\delta_{s's}\delta_{m_s'm_s}$

$\widehat{\vec{S}}^2 = \frac{3}{4}\hbar^2\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$, $\widehat{S}_z = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$, $\widehat{S}_+ = \hbar\begin{bmatrix}0 & 1\\0 & 0\end{bmatrix}$, $\widehat{S}_- = \frac{\hbar}{2}\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$.

$\widehat{S}_x = \frac{1}{2}(\widehat{S}_+ + \widehat{S}_-)$, $\widehat{S}_y = \frac{1}{2i}(\widehat{S}_+ - \widehat{S}_-)$, $\widehat{S}_x = \frac{\hbar}{2}\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$, $\widehat{S}_y = \frac{\hbar}{2}\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$

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 $\alpha$ and $\beta$ 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 $\rightarrow$ 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 $\widehat{H} = -\widehat{\mu}_z B = -(-\frac{g}{2}\frac{e}{m}\widehat{\vec{S}})\dot{B}\widehat{z} = \frac{g}{2}\frac{eB}{m}S_z = \omega_s S_z = \frac{g}{2}\frac{eB\hbar}{2m}\sigma_z$, 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 the cyclotron frequency. $g \approx 2$ but $g \neq 2 \rightarrow \omega_s \neq \omega_c$.

Rewrite Hamiltonian as $\widehat{H} = \omega_s S_z$. In the bases in which $\widehat{\vec{S}}$ 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 $\rightarrow$ 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 $\vec{B} = B_x\widehat{e}_x + B_y\widehat{e}_y + B_z\widehat{e}_z$.

$\widehat{H} = (\frac{g}{2}\frac{e}{m}\widehat{\vec{S}}) \cdot \vec{B} = \frac{g}{2}\frac{e\hbar}{2m}\begin{bmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{bmatrix}$

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 $\alpha \rightarrow \pi - \alpha$ for spin-down. Spin-up, $\widehat{S}_z$ eigenval is $\frac{\hbar}{2}$, $|\widehat{\vec{S}}^2|$ is $\frac{\sqrt{3}\hbar}{2}$.

Space quantization: angular momentum along any fixed direction take only discrete $(2j+1)$ values.

## Addition of angular momentum

$\widehat{\vec{J}}_1$, $|j_1, m_{j1}\rangle$. $\widehat{\vec{J}}_2$, $|j_2, m_{j2}\rangle$. $\widehat{\vec{J}} = \widehat{\vec{J}}_1 + \widehat{\vec{J}}_2$. $\widehat{\vec{J}}^2$ & $\widehat{J}_z$: 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 $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$

$\widehat{\vec{J}}^2 = \widehat{\vec{J}}_1^2 \otimes 1 + 1 \otimes \widehat{\vec{J}}_2^2 + 2\widehat{J}_{1z} \otimes \widehat{J}_{2z} + \widehat{J}_{1+} \otimes \widehat{J}_{2-} + \widehat{J}_{1-} \otimes \widehat{J}_{2+}$

Spin angular momentum, interchan. use $\widehat{\vec{S}}$ for $\widehat{\vec{J}}$, 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.: $\int|\psi(r_1, r_2, t)|^2 d^3r_1 d^3r_2 = 1$

$\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(r_1, r_2)e^{-iEt/\hbar}$, $-\frac{\hbar^2}{2m_1}\boldsymbol{\nabla}_1^2\psi - \frac{\hbar}{2m_2}\boldsymbol{\nabla}_2^2\psi + V\psi = E\psi$

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:

$\langle(\Delta x)^2\rangle = \langle(x_1 - x_2)^2\rangle = \langle x_1^2\rangle + \langle x_2^2\rangle - 2\langle x_1 x_2\rangle$

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, $\langle x_2^2\rangle_{\text{dist}} = \langle x^2\rangle_b$,

$\langle x_1 x_2\rangle_{\text{dist}} = \int x_1|\psi_a(x_1)|^2dx_1\int x_2|\psi_b(x_2)|^2dx_2 = \langle x\rangle_a\langle x\rangle_b$

$\langle(\Delta x)^2\rangle_{\text{dist}} = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b$

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 $\rightarrow$ 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.

$(E_n^{(0)} - E_a^{(0)} + E_n^{(1)} + E_n^{(2)} + \ldots)\langle\phi_a^{(0)}(|\psi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \ldots) = \sum_b H'_{ab}\langle\phi_b^{(0)}(|\phi_n^{(0)}\rangle + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \ldots)$. 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 $|\psi_{nlm}^{(0)}\rangle$ 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 $|\psi_n^{(0)}\rangle, |\psi_{n'}^{(0)}\rangle, \ldots$, having the same energy $E_n^{(0)} = E_{n'}^{(0)} = \ldots$

$(E^{(0)} - E_a^{(0)})\langle\psi_a^{(0)}|\psi^{(1)}\rangle + E^{(1)}\langle\psi_a^{(0)}|\psi^{(0)}\rangle = \sum_b H'_{ab}\langle\psi_b^{(0)}|\psi^{(0)}\rangle$

Secular equation: $\det|H'_{nn'} - E^{(1)}\delta_{nn'}| = 0$

$|\Psi_n^0\rangle = \sum_{n'}c_{n'}^{(0)}|\psi_{n'}^{(0)}\rangle$

If matrix elements of the pert. Hamiltonian are diagonal, $H'_{nn'} = E_n^{(1)}\delta_{n'n}$, then $\exists$ no cross terms that mix diff states $\rightarrow E_n^{(1)} = H'_{nn}$.

## 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 $\widehat{H}_{\text{SO}} = -\widehat{\vec{\mu}} \cdot \widehat{\vec{B}}'$, 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 $\vec{B}'_\perp = \vec{B} = \frac{1}{2}\frac{\vec{E}\times\vec{v}}{c}$

$\widehat{H}_{\text{SO}} = \frac{1}{2m^2c^2r}\frac{\mathrm{d}\widehat{V}}{\mathrm{d}r}\widehat{\vec{L}} \cdot \widehat{\vec{S}}$. For hydrogenic atoms, $\widehat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}$ and $\frac{\mathrm{d}\widehat{V}}{\mathrm{d}r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \rightarrow \widehat{H}_{\text{SO}} = \frac{Ze^2}{8\pi\epsilon_0 m^2c^2r^3}\widehat{\vec{L}} \cdot \widehat{\vec{S}}$

**Darwin correction** For states with $l = 0$, no orbital angular momentum, no spin-orbit interaction. $\widehat{H}_D = \frac{\hbar^2 Ze^2}{8m^2c^2\epsilon_0}\delta^3(\vec{r})$