

## 1. THE WAVE FUNCTION

### 1.1 The Schrödinger Equation

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

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

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

### 1.3 Probability

Standard deviation:  $\sigma = \sqrt{\langle j^2 \rangle - \langle j \rangle^2}$ . Expectation value of  $x$  given  $\Psi$ :

$$\langle x \rangle = \int x |\Psi|^2 dx. \text{ Probability current: } J(x, t) = \frac{i\hbar}{2m} (\Psi \frac{\partial \Psi^*}{\partial x} - \Psi^* \frac{\partial \Psi}{\partial x})$$

### 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,  $\frac{\partial}{\partial t} \mathcal{P} + \vec{\nabla} \cdot \vec{J} = 0$

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

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

### 1.5 Momentum

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

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

### 1.6: The Uncertainty Principle

The wavelength of  $\Psi$  is related to the momentum of the particle by the de

Brogie 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:

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

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

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

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

## 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:  $-\frac{\hbar^2}{2m} \frac{d^2 \psi(\vec{r})}{dx^2} + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})$

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

$$\langle \hat{H} \rangle = E, \langle \hat{H}^2 \rangle = E^2, \Delta E = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} = 0$$

- 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

$$\psi(\vec{r}, t) = \sum c_n \psi_n(\vec{r}, t) = \sum c_n \psi_n(\vec{r}) e^{-\frac{i}{\hbar} E_n t}$$

where  $c_n$  are complex constants, is a soln the TDSE  $i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \hat{H} \psi(\vec{r}, t)$

- 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

$$\psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}) e^{-\frac{i}{\hbar} E_n t}$$

- Normalization. The constant coefficients are constrained by  $\sum_n |c_n|^2 = 1$
- Completeness. The stationary states form a complete set if  $\sum_n \psi_n(\vec{r})^* \psi_n(\vec{r}, t) = \delta^3(\vec{r} - \vec{r})$ , 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.  $-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x)$

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

### 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

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

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

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

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  $k$ ):  $F = -kx = m \frac{d^2 x}{dt^2}$

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

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

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

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

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

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

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

### 1. Simplify notation with change of variables

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

2. Asymptotic behavior. Working in the large  $\xi^2 \gg K$  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  $K$ :  $a_{j+2} = \frac{-2(n-j)}{(j+1)(j+2)} a_j$

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

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

## 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.

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

$$\Psi(x, t) = A e^{ikx - i\frac{\hbar k^2}{2m} t} + B e^{-ikx - i\frac{\hbar k^2}{2m} t} =$$

$$A e^{i(kx - \omega t)} + B e^{-i(kx + \omega t)} = A e^{ik(x - v_p t)} + B e^{-ik(x + v_p t)}, \text{ where}$$

$\omega = \frac{E}{\hbar} = \frac{\hbar k^2}{2m}$  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,

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

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

$F(k)$  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 1:  $\delta(x) = \{0, \text{ if } x \neq 0; \infty, \text{ if } x = 0\}$

$f(x) \delta(x - a) = f(a) \delta(x - a)$  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.  $-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} - \alpha \delta(x) \psi = E \psi$

Bound states ( $E < 0$ ): To solve for min  $V_0$ , set  $E = 0$

REGION I,  $x < 0$ ,  $V(x) = 0$ ,  $\frac{d^2 \psi_I}{dx^2} - \kappa^2 \psi_I = 0$ , where  $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$ .

General sol:  $\psi(x) = A e^{-\kappa x} + B e^{\kappa x}$ .  $A = 0$ , so  $\psi(x) = B e^{-\kappa x}$ , ( $x < 0$ ).

REGION II,  $x > 0$ ,  $V(x) = 0$   $\psi(x) = F e^{-\kappa x} + G e^{\kappa x}$

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

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

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

$$\begin{aligned} \psi'_{II}(0) - \psi'_{I}(0) &= \lim_{\epsilon \rightarrow 0} \int_{0-\epsilon}^{0+\epsilon} \psi''(x) dx = \lim_{\epsilon \rightarrow 0} \int_{-\epsilon}^{\epsilon} \frac{2m}{\hbar^2} (V(x) - E) \psi(x) dx \\ &= -\frac{2m}{\hbar^2} \int_{-\epsilon}^{\epsilon} \alpha \delta(x - 0) \psi(x) dx = \frac{2m}{\hbar^2} \alpha \psi(0) = -\frac{2m}{\hbar^2} \alpha F \end{aligned}$$

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 1  $E \rightarrow 1$  boundstate.

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

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

General sol is  $\psi(x) = A e^{ikx} + B e^{-ikx}$ . For  $x > 0$ ,

$\psi(x) = F e^{ikx} + G e^{-ikx}$

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

Reflection coefficient:  $R \equiv \frac{|B|^2}{|A|^2}$ , Transmission coefficient:  $T \equiv \frac{|F|^2}{|A|^2}$

$$R + T = 1, R = \frac{1}{1 + (2\hbar^2 E / m\alpha^2)}, T = \frac{1}{1 + m\alpha^2 / 2\hbar^2 E}$$

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  $V(x) = \{0, x < 0; V_0, x > 0\}$ .

Incident and reflected waves in region I, only transmitted wave in region II:

$$\psi_I(x) = A e^{ikx} + B e^{-ikx}, \quad \psi_{II}(x) = C e^{ikx}$$

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  $A$ ,  $B = \frac{k - \kappa}{k + \kappa} A$ ,  $C = \frac{2k}{k + \kappa} A$

Speed of particle is diff in two regions, use probability current.

$$J_{inc} = \frac{\hbar k}{m} |A|^2, \quad J_{ref} = \frac{\hbar k}{m} |B|^2, \quad J_{tra} = \frac{\hbar \kappa}{m} |C|^2$$

$$R = \frac{J_{ref}}{J_{inc}} = \left| \frac{B}{A} \right|^2 = \left( \frac{k - \kappa}{k + \kappa} \right)^2 = \left( \frac{\sqrt{E} - \sqrt{E - V_0}}{\sqrt{E} + \sqrt{E - V_0}} \right)^2$$

$$T = \frac{J_{tra}}{J_{inc}} = \kappa \left| \frac{C}{A} \right|^2 = \frac{4k\kappa}{(k + \kappa)^2} = \frac{4\sqrt{E} \sqrt{E - V_0}}{(\sqrt{E} + \sqrt{E - V_0})^2}$$

$R + T = 1$

## Tunneling

Mass  $m$  and energy  $E < V_0$  approach from left a potential barrier of height  $V_0$ :  
 $V(x) = \{V_0, -a < x < a; \quad 0, |x| > a\}$

$\psi_I(x) = Ae^{ikx} + Be^{-ikx}$ ,  $\psi_{III}(x) = Ce^{\kappa x} + De^{-\kappa x}$ ,  $\psi_{III}(x) = Fe^{ikx}$   
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,

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

Lifetime of a particle of mass  $m$  and energy  $E$ :

Particle has velocity  $v = \sqrt{\frac{2(E-V_0)}{m}}$  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 finite barrier). 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  $\tau \sim Nt = \frac{2a}{\sqrt{\frac{2(E-V_0)}{m}}}e^{2\sqrt{\frac{2m(V_0-E)}{\hbar^2}}(b-a)}$ .

### 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  $\psi''(x) - \kappa^2\psi(x) = 0$ ,  $\kappa \equiv \sqrt{-\frac{2mE}{\hbar}}$

where  $E < 0$  for a bound state. General sol:  $\psi_I(x) = Ae^{-\kappa x} + Be^{\kappa x}$ .

$x = -\infty \rightarrow \psi(x) = 0$ , 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  $\psi'' = -l^2\psi$ ,  $l \equiv \sqrt{\frac{2m(E+V_0)}{\hbar}}$

General sol:  $\psi(x) = C \sin(lx) + D \cos(lx)$ , for  $-a < x < a$

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

**Even bound states:**  $\psi(-x) = \psi(x)$ ,  $\psi_{II}(x) = D \cos(la)$

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**  $\psi_{II}(x) = C \sin(la)$

$x = -a$ ,  $\psi_{II}(-a) = \psi_I(-a)$  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 & 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  $V_0 \rightarrow \infty$ , 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 system in state  $|\psi\rangle$ , measurement will find it in state  $|\phi\rangle$  with prob amplitude  $\langle\phi|\psi\rangle$ .  $P(a_1) = P(a_1|b_1)P(b_1) + P(a_1|b_2)P(b_2)$ .

**Hermitian operator axiom:** Physical observable represented by linear & HO.

**Measurement axiom:** Measurement of a physical observable results in eigenvalue of observable. Observable  $\hat{A}$ , we have  $\hat{A}|a\rangle = a|a\rangle$ , where  $a$  is eigenvalue and  $|a\rangle$  is eigenvector. Measurement of physical quantity represented by  $\hat{A}$  collapses the state  $|\psi\rangle$  before measurement into an eigenstate  $|a\rangle$  of  $\hat{A}$ .

**Time evolution axiom:**  $i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$ , 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  $|0\rangle = \begin{bmatrix} 1 & 0 & \dots \end{bmatrix}, \dots, \langle n| \begin{bmatrix} 0 & \dots & 1 \end{bmatrix}$ .

**Inner product** :  $\langle\phi|\psi\rangle = c$ , where  $c$  is complex.

$\langle\phi|\psi\rangle = \langle\psi|\phi\rangle^* \rightarrow \langle\psi|\psi\rangle$  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  $\hat{A}$  acting on a state vector  $|\psi\rangle$  transforms it into another state vector  $|\phi\rangle$ ,  $\hat{A}|\psi\rangle = |\phi\rangle$ . It is linear.

**Hermitian conjugate (Hermitian adjoint) operator in the dual space**

Hermitian adjoint operator  $\hat{A}^\dagger$  acts on the dual vector  $\langle\psi|$  from the right as  $\langle\psi|\hat{A}^\dagger$ , where  $\hat{A}^\dagger = (\hat{A})^{T*}$ .

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

**Outer product operators** :  $|\psi\rangle\langle\phi|$   $[|\psi\rangle\langle\phi|]\chi = |\psi\rangle\langle\phi|\chi$

**Matrix elements of operators**  $\langle\phi|\hat{A}|\psi\rangle$  (complex num)

Hermitian equiv to complex conj  $\langle\phi|\hat{A}|\psi\rangle^\dagger = \langle\psi|\hat{A}^\dagger|\phi\rangle = \langle\phi|\hat{A}|\psi\rangle^*$

**Hermitian operators** :  $\hat{A}^\dagger = \hat{A}$ , so given  $\hat{A}|\phi\rangle$  in the vector space, we have  $\langle\psi|\hat{A}^\dagger = \langle\phi|\hat{A}$  in the dual vector space.

**Matrix elements of a Hermitian operator**

$\langle\phi|\hat{A}|\psi\rangle^\dagger = \langle\phi|\hat{A}|\psi\rangle^* = \langle\psi|\hat{A}^\dagger|\phi\rangle = \langle\psi|\hat{A}|\phi\rangle$

Hermitian operator, real expectation vals:  $\langle\psi|\hat{A}|\phi\rangle^* = \langle\psi|\hat{A}|\phi\rangle \equiv \langle\hat{A}\rangle$

Same result whether  $\hat{A}$  acts to right or left:  $\langle\phi|\hat{A}|\psi\rangle = \langle\phi|\hat{A}^\dagger|\psi\rangle$

**Eigenvals and eigenvecs of Hermitian operators** :  $\hat{A}|a_n\rangle = a_n|a_n\rangle$

Normalized eigvecs  $\langle a_m|a_n\rangle = \delta_{mn}$ . Gram-Schmidt, degenerate evect.

**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  $\hat{A}$ ,

$\hat{A}|a\rangle = a|a\rangle$ , where  $a$  is continuous.

$\int da' \langle a'|\hat{A}|a\rangle = a \int da' \langle a'|a\rangle = \int da' a' \langle a'|a\rangle \rightarrow \langle a'|a\rangle = \delta(a' - a)$

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  $\rightarrow$  no degeneracy.

1. Normalize each state and define  $\alpha_i = \frac{\alpha_i}{\sqrt{\langle\alpha_i|\alpha_i\rangle}}$ . 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**

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

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

State vector  $|\psi(t)\rangle$  in position space (scalar):  $\langle\vec{r}|\psi(x, t)\rangle \equiv \psi(\vec{r}, t)$

$\langle\psi|\hat{p}|\psi\rangle = \frac{d}{dt} \langle\psi|\hat{r}|\psi\rangle m$

Representation of momentum operator in position space:  $\hat{p} = -i\hbar\vec{\nabla}$ .

$\langle x|\hat{p}|x'\rangle = -i\hbar \frac{\partial}{\partial x} \delta(x - x') = -i\hbar \frac{\partial}{\partial x} \langle x|x'\rangle$ .

$\hat{p} = -i\hbar \frac{\partial}{\partial x}$  is Hermitian,  $\frac{\partial}{\partial x}$  is not.

$\langle x|\hat{p}|p\rangle = p\langle x|p\rangle = -i\hbar \frac{\partial}{\partial x} \langle x|p\rangle$ . 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:  $\hat{r} = \vec{r}$ ,  $\hat{p} = -i\hbar\vec{\nabla}$ .

$\hat{r}$  is Hermitian and  $\langle\phi|\hat{r}^\dagger|\psi\rangle = \langle\phi|\vec{r}|\psi\rangle$ .  $\hat{O}(\vec{r}, \hat{p}) = \hat{O}(\vec{r}, -i\hbar\vec{\nabla})$

The expectation val of the observable should be indep of representation. In state  $\psi(t)$ ,  $\langle\hat{O}\rangle = \langle\psi(t)|\hat{O}|\psi(t)\rangle$ .

Insert  $\int d^2\vec{r}|\vec{r}\rangle\langle\vec{r}| = 1$  to get  $\langle\hat{O}\rangle = \int d^2\vec{r}\langle\psi(t)|\vec{r}\rangle\langle\vec{r}|\hat{O}|\psi(t)\rangle$   
 $\psi(\vec{r}, t) = \langle\vec{r}|\psi(t)\rangle$ ,  $\psi(\vec{r}, t)^* = \langle\vec{r}|\psi(t)\rangle^* = \langle\psi(t)|\vec{r}\rangle$ ,  
 $\frac{\langle\vec{r}|\hat{O}|\psi(t)\rangle}{\bar{q}|q\rangle} = \hat{O}(\vec{r}, -i\hbar\vec{\nabla})\psi(\vec{r}, t)$ ,  $\langle\hat{O}\rangle = \int d^3\vec{r}\psi(\vec{r}, t)^* \hat{O}(\vec{r}, -i\hbar\vec{\nabla})\psi(\vec{r}, t)$   
 $\frac{\langle x|\hat{p}|x\rangle}{\bar{q}|q\rangle} = q|q\rangle \rightarrow \langle x|\bar{q}|q\rangle = q\langle x|q\rangle$ .  $\langle x|\bar{q}|q\rangle = \langle x|c\bar{x} + d\bar{p}|q\rangle = (cx - i\hbar d \frac{d}{dx})\langle x|q\rangle$   
 $(cx - i\hbar d \frac{d}{dx})\langle x|q\rangle > q\langle x|q\rangle > q\langle x|q\rangle$

**Operators and wavefunction in momentum representation**  $\hat{r} = i\hbar\vec{\nabla}_{\vec{p}}$ , or in 1D,  $\hat{x} = i\hbar \frac{\partial}{\partial p}$ ,  $\hat{p} = \vec{p}$ , where  $\vec{p}^* = \vec{p}$ .  $\hat{O}(\vec{r}, \vec{p}) = \hat{O}(i\hbar\vec{\nabla}_{\vec{p}}, \vec{p})$ .

$\langle\hat{O}\rangle = \langle\psi(t)|\hat{O}|\psi(t)\rangle \rightarrow \langle\hat{O}\rangle = \int d^2\vec{p}\langle\psi(t)|\vec{p}\rangle\langle\vec{p}|\hat{O}|\psi(t)\rangle$ .  
 $\psi(\vec{p}, t) = \langle\vec{p}|\psi(t)\rangle$ ,  $\psi(\vec{p}, t)^* = \langle\vec{p}|\psi(t)\rangle^* = \langle\psi(t)|\vec{p}\rangle$   
 $\langle\vec{p}|\hat{O}|\psi(t)\rangle = \hat{O}(i\hbar\vec{\nabla}_{\vec{p}}, \vec{p})\langle\hat{O}\rangle = \int d^3\vec{p}\psi(\vec{p}, t)^* \hat{O}(i\hbar\vec{\nabla}_{\vec{p}}, \vec{p})\psi(\vec{p}, t)$ .

$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$ , where  $\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r}, t)$  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  $[\hat{A}, \hat{B}] = 0$  & states are nondegener,  $|\psi\rangle$  is a simultan. eigenstate of  $\hat{A}$  &  $\hat{B}$ .

$|\psi\rangle = |ab\rangle$ , and  $\hat{A}|ab\rangle = a|ab\rangle$ ,  $\hat{B}|ab\rangle = b|ab\rangle$

**Non-commuting operators and the general uncertainty principle**

$(\Delta A)^2(\Delta B)^2 \geq (\frac{1}{2i} \langle[\hat{A}, \hat{B}]\rangle)^2$ . 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  $\hat{O}$ 's expectation value in state  $|\psi(t)\rangle$  evolves in time,  $\frac{d}{dt} \langle\hat{O}\rangle = \langle \frac{\partial \hat{O}}{\partial t} \rangle + \frac{i}{\hbar} \langle[\hat{H}, \hat{O}]\rangle$ . If operator has no explicit time dep,  $\frac{d}{dt} \langle\hat{O}\rangle = \frac{i}{\hbar} \langle[\hat{O}, \hat{H}]\rangle$ .

For  $\hat{O} = \hat{p}$  and a Hamiltonian that is TI,  $\frac{d}{dt} \langle\hat{p}\rangle = -\langle\vec{\nabla} V(\vec{r})\rangle$ , which is just Newton's Second Law!  $\rightarrow$  QM contains all of classical mech.

**The simple harmonic oscillator**

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

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

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

$\hat{H} = (\hat{N} + \frac{1}{2})\hbar\omega$ , 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  $|n-1\rangle = c_n \hat{a}|n\rangle \rightarrow c_n = \frac{1}{\sqrt{n}} \rightarrow \hat{a}|n\rangle = \sqrt{n}|n-1\rangle$ .

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

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

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

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

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

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  $\sigma \equiv \sqrt{\frac{\hbar}{m\omega}}$

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

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

**Classical simple harmonic oscillator** Hamiltonian of a simple harmonic is

$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$ .  $\dot{x} = \frac{\partial H}{\partial p} = \frac{p}{m}$ ,  $\dot{p} = -\frac{\partial H}{\partial x} = -m\omega^2 x$

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

Rewrite Hamiltonian,  $H = \hbar\omega|\alpha|^2$ ,  $\dot{\alpha} = -i\omega\alpha$ . The sol is  $\alpha = \alpha_0 e^{-i\omega t}$ .

**The quantum simple harmonic oscillator and coherent state** Coherent state, superpos of stat states  $|n\rangle$ :  $|\alpha\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$

$P(n) = |\langle n|\alpha\rangle|^2 = |\alpha_n|^2 = \frac{\langle n|n\rangle e^{-\langle n|}}{n!}$ , where  $\langle n\rangle = \langle \alpha|a^\dagger a|\alpha\rangle = |\alpha|^2$ . Linear superpos. of all quantum numbs 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  $0 \leq x \leq l_x, \dots$

while  $\psi(x,y,z) = 0$  outside.

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

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

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

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

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  $r$ ,  $V(\vec{r}) = V(r)$ .

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

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

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

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

##### 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.

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

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

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

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

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

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

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

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

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

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

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

$\Phi(\phi) = e^{i m \phi}$ , periodic in  $\phi$  w period  $2\pi$  gives constraint  $m = 0, \pm 1, \pm 2, \dots$

$\Theta(\theta)$  can be written in terms of  $x \equiv \cos \theta$  as

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

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  $l = 0, 1, 2, \dots$

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:

$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{i m \phi} P_l^m(\cos \theta)$ , where  $\epsilon = (-1)^m$  for  $m \geq 0$  and  $\epsilon = 1$  for  $m < 0$ .

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

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

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

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

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

Satisfy the orthogonality relation

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

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

$\hat{L}_+ = L_x + iL_y, \hat{L}_- L_x - iL_y, L_x = \frac{1}{2}(L_- + L_+), \langle L_z^2 \rangle = \frac{1}{2}\langle L^2 - L_z^2 \rangle$   
 $L_\pm |lm\rangle = \hbar \sqrt{l(l \mp m)(l \pm m + 1)} |l, m \pm 1\rangle$

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

##### Parity of the spherical harmonics

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

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

→ even for  $l + |m_l|$  even and odd for  $l + |m_l|$  odd.

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

The spherical harmonics are products of two, and  $\hat{P} Y_l^{m_l}(\theta, \phi) =$

$Y_l^{m_l}(\pi - \theta, \phi + \pi) = (-1)^{l-|m_l|+m_l} Y_l^{m_l}(\theta, \phi) = (-1)^l Y_l^{m_l}(\theta, \phi)$

##### The hydrogen atom

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

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

##### The radial wave function

$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$ . Divide by  $\kappa, \frac{1}{\kappa^2} \frac{d^2 u}{dr^2} = [1 - \frac{m e^2}{2\pi\epsilon_0 \hbar^2 \kappa} (\frac{1}{(kr)}) + \frac{l(l+1)}{(\kappa r)^2}] u$

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

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

General sol is  $u(\rho) = A e^{-\rho} + B e^{\rho}$ , but  $B = 0 \rightarrow u(\rho) = A e^{-\rho}$  for large  $\rho$ .

As  $\rho \rightarrow 0$ , centriugal term dominates,  $\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$

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  $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$

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

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

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

Assume  $v(\rho)$  can be expressed as a power series in  $\rho$ :  $v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$ .

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

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

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

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

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,  $c_j = \frac{2^j}{j!} c_0, v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$ , and hence

$u(\rho) = c_0 \rho^{l+1} e^{\rho}$ , which blows up at large  $\rho$

$\sum c_{j\text{max}+1} = 0$ , so  $2(j_{\text{max}} + l + 1) - \rho_0 = 0$ .

Define principle quantum number,  $n \equiv j_{\text{max}} + l + 1$ , so  $\rho_0 = 2n$

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

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

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

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

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  $L_{q-p}^p(x) \equiv (-1)^p (\frac{d}{dx})^p L_q(x)$  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:

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

Wavefunctions are mutually orthogonal.

$\int \psi^*_{n'l'm'_l} \psi_{n l m_l} r^2 \sin \theta dr d\theta d\phi = \delta_{n'n} \delta_{l'l'} \delta_{m'_l m_l}$

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

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

$\hat{J} = (\hat{J}_x, \hat{J}_y, \hat{J}_z) = (\hat{J}_1, \hat{J}_2, \hat{J}_3) \quad \hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$

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

Take commuting set to be  $\hat{J}^2$  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:  $[\hat{J}_+, \hat{J}_-] = 2\hbar \hat{J}_z, [\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm, [\hat{J}^2, \hat{J}_\pm] = 0$

$\hat{J}^2$  and  $\hat{J}_z$  commute → we can simultaneously diagonalize them. Let the

simultaneous eigenstate be  $|ab\rangle$  s.t.  $\hat{J}^2 |ab\rangle = a|ab\rangle, \hat{J}_z |ab\rangle = b|ab\rangle$

$\hat{J}^2 (\hat{J}_\pm |ab\rangle) = a(\hat{J}_\pm |ab\rangle \quad \hat{J}_z (\hat{J}_\pm |ab\rangle) = (b \pm \hbar)(\hat{J}_\pm |ab\rangle)$

$\hat{J}_+$  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.

$\hat{J}_+ \hat{J}_\mp = \hat{J}^2 - \hat{J}_z^2 \pm \hbar \hat{J}_z$

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

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

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

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

$\langle j' m'_j | \hat{J}_\pm | j m_j \rangle = \hbar \sqrt{(j \mp m_j)(j \pm m_j + 1)} \langle j' m'_j | j m_j \pm 1 \rangle =$

$\hbar \sqrt{(j \mp m_j)(j \pm m_j + 1)} \delta_{j' j} \delta_{m'_j m_j \pm 1}$

##### 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  $\omega$

about the  $z$ -axis,  $\vec{L} = I \omega \hat{z} = m \omega r^2 \hat{z}$

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  $\vec{L} = m \omega r^2 \hat{z}, \vec{\mu} = \frac{q}{2} \omega r^2 \hat{z}$ , where we used  $\mu = I \pi r^2$  with current  $I = \frac{q}{2\pi/\omega} = \frac{q}{2\pi}$ . 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  $\hat{J} \rightarrow \hat{S}$ .

Basis vectors are  $|\frac{1}{2}, \frac{1}{2}\rangle \equiv |1\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, |\frac{1}{2}, -\frac{1}{2}\rangle \equiv |2\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

$\hat{S}_z$  and  $\hat{S}^2$  are diagonal, since simultaneously diagonalized. Matrix elements:

$\langle s' m'_s | \hat{S}^2 | s m_s \rangle = s(s+1)\hbar^2 \delta_{s' s} \delta_{m'_s m_s},$

$\langle s' m'_s | \hat{S}_z | s m_s \rangle = m_s \hbar \delta_{s' s} \delta_{m'_s m_s}$

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

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

Spin angular momentum:  $\vec{S} = \frac{\hbar}{2} \vec{\sigma}$ . Pauli m:  $\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

$[\hat{S}_i, \hat{S}_j] = i\hbar \epsilon_{ijk} \hat{S}_k$  and  $[\sigma_i, \sigma_j] = 2i \epsilon_{ijk} \sigma_k$

A general state of a spin-half system is given by a spin



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

Rewrite Hamiltonian as  $\hat{H} = \omega_s S_z$ . In the bases in which  $\hat{S}$  and  $\hat{S}_z$  are diagonalized, the eigenstates are given by  
 $\hat{H}|\frac{1}{2}, \frac{1}{2}\rangle = \omega_s \hat{S}_z |\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{2} \hbar \omega_s |\frac{1}{2}, \frac{1}{2}\rangle$ ,  
 $\hat{H}|\frac{1}{2}, -\frac{1}{2}\rangle = \omega_s \hat{S}_z |\frac{1}{2}, -\frac{1}{2}\rangle = -\frac{1}{2} \hbar \omega_s |\frac{1}{2}, -\frac{1}{2}\rangle$   
Interaction of electron spin w external magnetic 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.  
 $\hat{S}_a = a_x \hat{S}_x + a_y \hat{S}_y + a_z \hat{S}_z$ ,  $|+\rangle = [\cos \frac{\theta}{2}, \sin \frac{\theta}{2} e^{i\phi}]$ ,  
 $|-\rangle = [-\sin \frac{\theta}{2} e^{-i\phi}, \cos \frac{\theta}{2}]$ . — Consider  $\vec{B} = B_x \hat{e}_x + B_y \hat{e}_y + B_z \hat{e}_z$ .  
 $\hat{H} = (\frac{g}{2} \frac{e}{m} \vec{S}) \cdot \vec{B} = \frac{g}{2} \frac{e\hbar}{2m} \begin{bmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{bmatrix}$

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

**Addition of angular momentum**  
 $\hat{J}_1, |j_1, m_{j1}\rangle$ .  $\hat{J}_2, |j_2, m_{j2}\rangle$ .  $\hat{J} = \hat{J}_1 + \hat{J}_2$ .  $\hat{J}^2$  &  $\hat{J}_z$ : 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  $\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$   
 $\hat{J}^2 = \hat{J}_1^2 \otimes 1 + 1 \otimes \hat{J}_2^2 + 2\hat{J}_{1z} \otimes \hat{J}_{2z} + \hat{J}_{1+} \otimes \hat{J}_{2-} + \hat{J}_{1-} \otimes \hat{J}_{2+}$

**Spin angular momentum, interchang.** use  $\hat{S}$  for  $\hat{J}$ , and  $s$  and  $m_s$  for  $j$  and  $m_j$ .  
**Addition of general angular momentum**  
 $|j_1 + j_2, j_1 + j_2\rangle = |j_1, m_{j1}\rangle \otimes |j_2, m_{j2}\rangle$   
 $j = j_1 \otimes j_2 = j_1 + j_2 \oplus j_1 + j_2 - 1 \oplus j_1 + j_2 - 2 \oplus \dots \oplus |j_1 - j_2|$   
**Clebsch-Gordon coefficients**  
Complete states:  $\sum_{m_{j1}, m_{j2}} |j_1, m_{j1}; j_2, m_{j2}\rangle \langle j_1, m_{j1}; j_2, m_{j2}| = 1$   
 $|j, m_j\rangle = \sum_{m_{j1} + m_{j2} = j} \langle j_1, m_{j1}; j_2, m_{j2} | j, m_j \rangle |j_1, m_{j1}; j_2, m_{j2}\rangle$   
where  $\langle j_1, m_{j1}; j_2, m_{j2} | j, m_j \rangle$  are Clebsch-Gordon coefficients.  
State w  $j = \frac{3}{2}$  and  $m_j = -\frac{1}{2}$  made by coupling two states w  $j_1 = 1$  and  $j_2 = \frac{1}{2}$ :  $|1, \frac{1}{2}, \frac{3}{2}, -\frac{1}{2}\rangle = \sqrt{\frac{2}{3}}|1, 0\rangle \otimes |\frac{1}{2}, -\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}|1, -1\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle$ .  
 $j_1 + j_2 = m_j$

## 5. MANY-PARTICLE SYSTEMS AND PERTURBATION THEORY

**5.1 Identical particles**  
 $\Psi(\vec{r}_1, \vec{r}_2, t)$ ,  $H = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(r_1, r_2, t)$   
 $\hat{H} = \hat{H}(1, 2) = \hat{H}(2, 1) = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + \hat{V}(q_1, q_2)$ , 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  $d^3 r_1$ , etc.:  $\int |\psi(r_1, r_2, t)|^2 d^3 r_1 d^3 r_2 = 1$   
 $\Psi(\vec{r}_1, \vec{r}_2, t) = \psi(r_1, r_2) e^{-iEt/\hbar}$ ,  $-\frac{\hbar^2}{2m_1} \nabla_1^2 \psi - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi + V\psi = E\psi$   
Exchange operator  $\hat{P}_{ex} : 1 \leftrightarrow 2$ , which exchanges the two particles.  
 $\hat{P}_{ex} \Psi(q_1, q_2) = \Psi(q_2, q_1)$  and  $\hat{P}_{ex}^2 \Psi(q_1, q_2) = \Psi(q_1, q_2)$   
 $\hat{P}_{ex}$  has two eigenvalues  $p_{ex} = \pm 1$   
 $[\hat{P}_{ex}, \hat{H}] = 0$ . Can construct simultaneous eigenstates of  $\hat{P}_{ex}$  and  $\hat{H}(1, 2)$ :  
 $\hat{H} \Psi_{\pm}(q_1, q_2) = E \Psi_{\pm}(q_1, q_2)$ ,  $\hat{P}_{ex} \Psi_{\pm}(q_1, q_2) = \pm \Psi_{\pm}(q_1, q_2)$

Identical particles in QM come in two and only two classes:  
1. Bosons:  $\Psi_+(q_2, q_1) = \hat{P}_{ex} \Psi_+(q_1, q_2) = +\Psi_+(q_1, q_2)$ ,  $s = 0, 1, 2, \dots$   
2. Fermions:  $\Psi_-(q_2, q_1) = \hat{P}_{ex} \Psi_-(q_1, q_2) = -\Psi_-(q_1, q_2)$ ,  $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$   
**5.2 Identical noninteracting particles**

$\hat{H}(1, 2) = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \hat{V}(\hat{q}_1) + \hat{V}(\hat{q}_2) = \hat{H}(1) + \hat{H}(2)$   
 $\hat{H}(1)\psi_a(q_1) = E_a \psi_a(q_1)$ ,  $\hat{H}(2)\psi_a(q_2) = E_a \psi_a(q_2)$   
Same set of eigen, eigenval, and quantum nums:  $\{\psi_a(q)\}$ ,  $\{E_a\}$ ,  $\{a\}$   
 $\Psi_-(q_1, q_2) = \frac{1}{\sqrt{N!}} \det \dots = \frac{1}{\sqrt{2}} \det \begin{bmatrix} \psi_a(q_1) & \psi_b(q_1) \\ \psi_a(q_2) & \psi_b(q_2) \end{bmatrix}$ , 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  
 $\langle x_1^2 \rangle_{\text{dist}} = \int x_1^2 |\psi_a(x_1)|^2 dx_1 \int |\psi_b(x_2)|^2 dx_2 = \int x_1^2 |\psi_a(x_1)|^2 dx_1 = \langle x^2 \rangle_a$ . Similarly,  $\langle x_2^2 \rangle_{\text{dist}} = \langle x^2 \rangle_b$ ,  
 $\langle x_1 x_2 \rangle_{\text{dist}} = \int x_1 |\psi_a(x_1)|^2 dx_1 \int x_2 |\psi_b(x_2)|^2 dx_2 = \langle x \rangle_a \langle x \rangle_b$   
 $\langle (\Delta x)^2 \rangle_{\text{dist}} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b$   
2. Identical particles  
 $|\Psi_{\pm}(x_1, x_2)|^2 = \frac{1}{2}(|\psi_a(x_1)|^2 |\psi_b(x_2)|^2 + |\psi_b(x_1)|^2 |\psi_a(x_2)|^2 \pm \psi_a^*(x_1)\psi_b(x_1)\psi_b^*(x_2)\psi_a(x_2) \pm \psi_b^*(x_1)\psi_a(x_1)\psi_a^*(x_2)\psi_b(x_2))$   
 $\langle x_1^2 \rangle_{\pm} = \langle x_2^2 \rangle_{\pm} = \frac{1}{2}(\langle x^2 \rangle_a + \langle x^2 \rangle_b)$ ,  $\langle x_1, x_2 \rangle = \langle x \rangle_a \langle x \rangle_b \pm |\langle x \rangle_{ab}|^2$   
 $\langle (x_1 - x_2)^2 \rangle_{\pm} = \langle x^2 \rangle_a + \langle x^2 \rangle_b - 2\langle x \rangle_a \langle x \rangle_b \pm 2|\langle x \rangle_{ab}|^2$   
 $\langle (\Delta x)^2 \rangle_{\pm} = \langle (\Delta x)^2 \rangle_{\text{dist}} \pm 2|\langle x \rangle_{ab}|^2$

Id. bosons: spatially closer, id. fermions: apart, compared to distinguishable.  
**Purely QM effect that follows from sym. or antisym. of the wavefunction.**  
**H<sub>2</sub> 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.  
 $\Psi_{\text{tot}}(q_1, q_2) = \frac{1}{\sqrt{2}}(\psi_{100}(\vec{r}_1 - \vec{r}_0)\psi_{100}(\vec{r}_2 + \vec{r}_0) + \psi_{100}(\vec{r}_1 + \vec{r}_0)\psi_{100}(\vec{r}_2 - \vec{r}_0)) = \frac{1}{\sqrt{2}}(\frac{1}{2}(\frac{1}{2}(1))|\frac{1}{2} - \frac{1}{2}(2) - |\frac{1}{2} - \frac{1}{2}(1))|\frac{1}{2}(\frac{1}{2}(2)))$   
He: electrons are fermions, antisym under exch.  $\psi_{100}(r, \theta, \phi) = \sqrt{\frac{Z^3}{\pi a^3}} e^{-\frac{Zr}{a}}$ ,  $Z = 2$ , where  $a$  is Bohr radius. Slater det,  $\psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) \frac{1}{\sqrt{2}}(\chi(\frac{1}{2}, \frac{1}{2})(1)\chi(\frac{1}{2}, -\frac{1}{2})(2) - \chi(\frac{1}{2}, -\frac{1}{2})(1)\chi(\frac{1}{2}, \frac{1}{2})(2))$   
**d-fold degen., E level occupied by  $N > 2d$  # of spin-half id fermions  $\rightarrow$  color.**  
**5.3 Perturbation theory**

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

**Time-independent perturbation theory**  $\hat{H}'(t) = \hat{H}'$ .  $\hat{H} = \hat{H}_0 + \hat{H}'$  is TI.  
 $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ ,  $(E_n - E_a^{(0)})\langle \psi_a^{(0)} | \psi_n \rangle = \sum_b H'_{ab} \langle \psi_b^{(0)} | \psi_n \rangle$ ,  
 $H'_{ab} = \langle \psi_a^{(0)} | \hat{H}' | \psi_b^{(0)} \rangle$ : matrix element of perturbation in the unpert. states.  
 $(E_n^{(0)} - E_a^{(0)} + E_n^{(1)} + E_n^{(2)} + \dots) \langle \psi_a^{(0)} | (\psi_n^{(0)} + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \dots) = \sum_b H'_{ab} \langle \psi_b^{(0)} | (\psi_n^{(0)} + |\psi_n^{(1)}\rangle + |\psi_n^{(2)}\rangle + \dots)$ . SE in a diff form, all exact.  
Now suppose  $\hat{H}'$  is small compared to  $\hat{H}_0$ . 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**  
 $(E_n^{(0)} - E_a^{(0)})\langle \psi_a^{(0)} | \psi_n^{(1)} \rangle + E_n^{(1)} \langle \psi_a^{(0)} | \psi_n^{(0)} \rangle = \sum_b H'_{ab} \langle \psi_b^{(0)} | \psi_n^{(0)} \rangle$   
 $a = n$ ,  $E_n^{(0)} - E_a^{(0)} = 0$ ,  $\delta_{an} = 1$ .  $a \neq n$ ,  $E_n^{(0)} - E_a^{(0)} \neq 0$ ,  $\delta_{an} = 0$ .  
 $E_n = E_n^{(0)} + H'_{nn}$ ,  $|\psi_n\rangle = |\psi_n^{(0)}\rangle - \sum_{m \neq n} \frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}} |\psi_m^{(0)}\rangle$   
 $|\frac{H'_{mn}}{E_m^{(0)} - E_n^{(0)}}| < 1$ ,  $|\langle m | \hat{H}' | n \rangle| < |E_n^{(0)} - E_m^{(0)}|$ ,  
 $\alpha(\frac{\hbar}{m\omega})^2(n+1)^2 < \hbar\omega$  matrix elements of the perturb. btwn the unpert. 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  $|\psi_{nlm}\rangle$  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  $|\psi_n^{(0)}\rangle, |\psi_{n'}^{(0)}\rangle, \dots$ , having the same energy  $E_n^{(0)} = E_{n'}^{(0)} = \dots$   
 $(E^{(0)} - E_a^{(0)})\langle \psi_a^{(0)} | \psi^{(1)} \rangle + E^{(1)} \langle \psi_a^{(0)} | \psi^{(0)} \rangle = \sum_b H'_{ab} \langle \psi_b^{(0)} | \psi^{(0)} \rangle$   
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:  
 $E = mc^2 \sqrt{1 + \frac{\vec{p}^2}{m^2 c^2}}$   
 $E = mc^2(1 + \frac{1}{2} \frac{\vec{p}^2}{m^2 c^2} - \frac{1}{2} \frac{1}{2} (\frac{\vec{p}^2}{m^2 c^2})^2 + \dots) = mc^2 + \frac{\vec{p}^2}{2m} - \frac{\vec{p}^4}{8m^3 c^4} + \dots$   
KE perturbation:  $\hat{H}_k = -\frac{\vec{p}^4}{8m^3 c^4}$ , all commute bc  $[\vec{p}]$  is invar under rot.

Use  $\hat{H} = E_n = \frac{\hat{p}^2}{2m} + \hat{V}(r) \rightarrow \hat{p}^2 = 2m(E_n - \hat{V}(r))$   
**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  
 $\hat{H}_{SO} = -\hat{\mu} \cdot \vec{B}'$ , where  $\hat{\mu} = g \frac{-e\hbar}{2m} \hat{S} = -\frac{e}{m} \hat{S}$  is the magnetic moment and  $g = 2$  is the gyromagnetic ratio of the electron.  
Thomas precession: electron is rotating and accelerating around the nucleus, and it is not an inertial frame.  $\vec{B}'_{\perp} = \vec{B}$ , and  $\vec{B}'_{\parallel} = \vec{B} = \frac{1}{2} \frac{\vec{E} \times \vec{v}}{c}$   
 $\hat{H}_{SO} = \frac{1}{2m} \frac{1}{c^2} \frac{d\vec{v}}{dr} \hat{L} \cdot \hat{S}$ . For hydrogenic atoms,  $\hat{V} = -\frac{Ze^2}{4\pi\epsilon_0 r}$  and  
 $\frac{d\vec{v}}{dr} = \frac{Ze^2}{4\pi\epsilon_0 r^2} \rightarrow \hat{H}_{SO} = \frac{Ze^2}{8\pi\epsilon_0 m^2 c^2 r^3} \hat{L} \cdot \hat{S}$   
Use  $J = L + S$ ,  $\hat{L} \cdot \hat{S} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$ . Doesn't commute w  $L$ ,  $S$ .  
 $\langle n(l, s), m_j | \dots | n(l, s), j, m_j \rangle$   
 $\frac{1}{4} mc^2 Z^4 \alpha^4 \frac{1}{n^3 j(j+\frac{1}{2})}$  for  $j = l + \frac{1}{2}$ ,  $-\frac{1}{4} mc^2 Z^4 \alpha^4 \frac{1}{n^3(j+\frac{1}{2})(j+1)}$  for  $j = l - \frac{1}{2}$ ,  $l \neq 0$

**Darwin correction** For states with  $l = 0$ , no orbital angular momentum, no spin-orbit interaction.  $\hat{H}_D = \frac{\hbar^2 Ze^2}{8m^2 c^2 \epsilon_0} \delta^3(\vec{r})$   
Invariant under rot and does not contain spin, commutes w all given operators.  
 $E_{n00}^{(1)} = \langle \psi_{n00} | \delta H_D | \psi_{n00} \rangle = \frac{\pi}{2} \frac{e^2 \hbar^2}{m^2 c^2} |\psi_{n00}(0)|^2 = \frac{1}{2} mc^2 Z^4 \alpha^4 \frac{1}{n^3}$