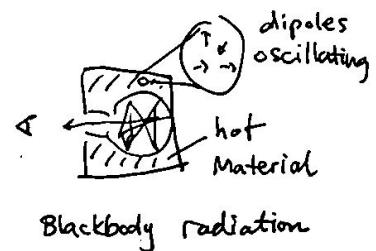
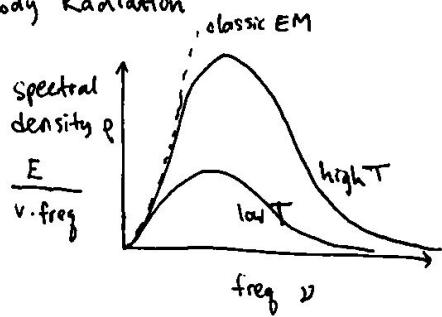


»» Blackbody Radiation



• Classical EM theory

$$\cdot R(\nu, T) = \frac{8\pi\nu^2}{c^3} \langle E_{\text{dip}} \rangle \quad \text{where } \langle E_{\text{dip}} \rangle = k_B T \text{ by equipartition theorem}$$

• incorrect since $\int_0^\infty R(\nu, T) d\nu = \infty$ (ultraviolet catastrophe)

• Planck assumed energy radiated was discretized (quantized)

$$\cdot E = nh\nu, n=1,2,3,\dots$$

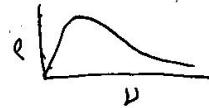
$$\cdot \langle E_{\text{dip}} \rangle = \frac{h\nu}{e^{h\nu/k_B T} - 1} \quad (\text{at high } T, \langle E_{\text{dip}} \rangle = k_B T) \quad (h\nu \ll k_B T)$$

$$(\text{at low } T, \langle E_{\text{dip}} \rangle \rightarrow 0) \quad (h\nu \gg k_B T)$$

• Planck's spectral density

$$\cdot R(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

$$\cdot h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$$



»» Photoelectric Effect

→ Observations

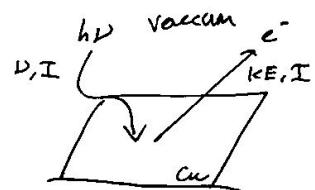
1. # of emitted e^- \propto light intensity, but KE is not

2. No e^- are emitted unless freq is greater than threshold $\nu > \nu_0$, even for high light intensity

3. KE depends on light frequency.

4. e^- are ejected at low intensities, so low that light energy is barely enough to eject e^-

→ photoelectric effect : $KE = h\nu - \Phi$



<< Double Slit Diffraction & Interference

- Davisson & Germer experiment

$$\text{de Broglie wavelength } \lambda = \frac{h}{p} = \frac{h}{mv}$$

<< Emission from hydrogen atom



- only discrete frequency ν observed

$$E_{n_i \rightarrow n_f} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

<< Bohr Model of H Atom

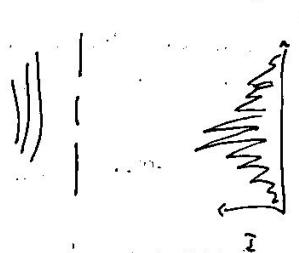
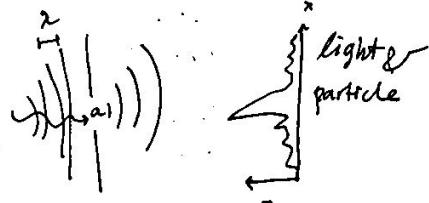


- electron as waves wraps the orbit

$$E_n = -\frac{1}{n^2} R_H$$

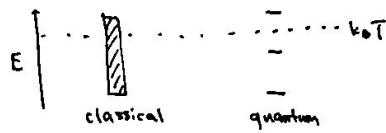
• Rydberg energy for H atom $R_H = 2.18 \times 10^{-18} \text{ J} = 13.6 \text{ eV}$

$$n\lambda = 2\pi R$$



<< Classical & Quantum

- quantum requires discrete energy levels



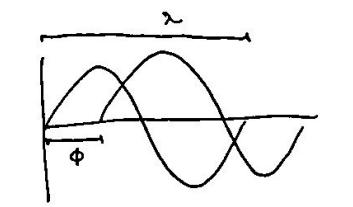
- classically, E levels are accessible by thermal energy
- quantumly, $k_B T \sim \Delta E$
- quantum required when $\lambda \sim L$ problem

<< Wave Equation

> wave equation: $\frac{\partial^2}{\partial x^2} f(x,t) - \frac{1}{v^2} \frac{\partial^2}{\partial t^2} f(x,t) = 0$

$$\text{soln: } f(x,t) = A \sin\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T} + \phi\right)$$

$$= A \sin(kx - \omega t + \phi)$$



$$\text{where } k = \frac{2\pi}{\lambda}, \omega = \frac{2\pi}{T} = 2\pi\nu$$

- wave eqn is linear, its soln is also linear.

- linear combination of soln is also a soln

$$f(x,t) = c_1 f_1(x,t) + c_2 f_2(x,t)$$

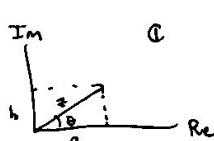
Ex1 $\underbrace{A \sin(kx - \omega t)}_{\text{traveling wave to right}} + \underbrace{A \sin(kx + \omega t)}_{\text{traveling wave to left}} = 2A \sin(kx) \cos(\omega t)$
 $\underbrace{_{\text{standing wave}} = f(x) \cos(\omega t)}$

<< Complex Functions

$$\begin{aligned} f(x,t) &= A \sin(kx - \omega t + \phi) \\ &= A \cos(kx - \omega t + \phi - \frac{\pi}{2}) \\ &= A \cos(kx - \omega t + \phi') \quad \phi' = \phi - \frac{\pi}{2} \\ &= \operatorname{Re}(A e^{i(kx - \omega t + \phi')}) \quad e^{ix} = \cos x + i \sin x \end{aligned}$$

<< Complex Numbers

$$z = a + ib, \text{ where } i = \sqrt{-1}$$



$$\text{complex conjugate} - z^* = a - ib$$

$$\text{magnitude} - |z| = \sqrt{z^* z} = \sqrt{(a - ib)(a + ib)} = \sqrt{a^2 + b^2}$$

$$\text{angle} - \theta = \arctan\left(\frac{b}{a}\right)$$

$$z = |z| e^{i\theta}$$

$$\cdot \text{Addition: } z_1 + z_2 = (a_1 + ib_1) + (a_2 + ib_2) = (a_1 + a_2) + i(b_1 + b_2)$$

$$\cdot \text{Multiplication: } z_1 z_2 = (a_1 + ib_1)(a_2 + ib_2) = (a_1 a_2 - b_1 b_2) + i(a_1 b_2 + b_1 a_2)$$

<< Vectors in 2D

$$\vec{v} = \langle a, b \rangle$$

$$a = |\vec{v}| \cos\theta$$

$$b = |\vec{v}| \sin\theta$$

$$|\vec{v}| = \sqrt{a^2 + b^2} = v = \sqrt{\vec{v} \cdot \vec{v}}$$

$$\vec{v}_1 + \vec{v}_2 = (a_1 \hat{x} + b_1 \hat{y}) + (a_2 \hat{x} + b_2 \hat{y})$$

$$= (a_1 + a_2) \hat{x} + (b_1 + b_2) \hat{y}$$

> dot product - $\vec{v} \cdot \vec{w} = |\vec{v}| |\vec{w}| \cos\phi = \sum_i v_i w_i$

> cross product - $\vec{v} \times \vec{w} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ v_x & v_y & v_z \\ w_x & w_y & w_z \end{vmatrix}$

<< Terminologies

> completeness - a set of vectors $\{x_i\}$ that are linearly independent and span the vector space.

> linearly independent - vectors such that $\sum a_i \vec{x}_i$ is only true for $\vec{a} = \vec{0}$ ($a_i = 0$)

> span - any vector \vec{v} can be expanded as $\vec{v} = \sum_i c_i \vec{x}_i$

> Kronecker delta - $\delta_{ij} = \begin{cases} 1 & i=j \\ 0 & i \neq j \end{cases} = \hat{x}_i \cdot \hat{x}_j = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \mathbb{I}$

> Identity matrix : $\mathbb{I} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \hat{x}\hat{x} + \hat{y}\hat{y} + \hat{z}\hat{z}$ (outer product)

> projections - $\vec{v} = \mathbb{I} \cdot \vec{v} = (\hat{x}\hat{x} + \hat{y}\hat{y} + \hat{z}\hat{z}) \cdot \vec{v} = \underbrace{\hat{x}(\hat{x} \cdot \vec{v})}_{v_x} + \underbrace{\hat{y}(\hat{y} \cdot \vec{v})}_{v_y} + \underbrace{\hat{z}(\hat{z} \cdot \vec{v})}_{v_z}$

> normalization - $\|f(x)\| = \int_D |f(x)|^2 dx = 1$

> orthonormal - orthogonal & normalized

<< Math Review

> normalization - $\int_0^L |f(x)|^2 dx = 1$, where $|f(x)|^2 = f^* f$

$$\boxed{\text{Ex1}} \quad f(x) = N \sin\left(\frac{n\pi x}{L}\right) \quad x \in [0, L]$$

$$1 = \int_0^L N^2 \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$1 = N^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$1 = N^2 \frac{L}{2}$$

$$N = \sqrt{\frac{2}{L}} \quad (\text{Normalization})$$

> orthogonality - $\int_D f^* g dx = 0$

> completeness - $I = \hat{x}\hat{x} + \hat{y}\hat{y} + \hat{z}\hat{z}$

$$I = \sum_n \frac{2}{L} \sin^2\left(\frac{n\pi x}{L}\right)$$

> Dirac delta - $\delta(x-x') = \sum_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x'}{L}\right) = \begin{cases} 0 & x \neq x' \\ \text{undefined} & x = x' \end{cases}$

• We can expand any function on $[0, L]$ in terms of $\left\{ \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) \right\}_{n=1}^{\infty}$ sharing the same boundary conditions ($f(a)=0, f(b)=0$)

$$\cdot \int_a^b \delta(x-c) dx = 1 \quad c \in [a, b]$$

$$\cdot \int_a^b \delta(x-c) f(x) dx = f(c)$$

$$\boxed{\text{Ex1}} \quad f(x) = \int_0^L \delta(x-x') f(x') dx'$$

$$= \int_0^L \sum_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x'}{L}\right) f(x') dx'$$

$$= \sum_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \underbrace{\int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x'}{L}\right) f(x') dx'}_{c_n \text{ projection coeff}}$$

$$= \sum_n \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) c_n$$

<< QM Postulates

1. The state of a QM particle is completely specified by the state vector $|t(t)\rangle$, called an abstract ket.

• $|t\rangle$ can be projected or represented in coordinate basis resulting in wavefn $\psi(x)$.

$$\psi(x) = \langle x | t \rangle$$

• The state vector $|t\rangle$ is representation invariant.

EX3 $\vec{V} = \sum_i c_i \hat{\vec{v}}_i$ or $\sum_i c'_i \hat{\vec{v}}'_i$

• The set of all coordinates is complete according to

$$|t\rangle = "1" |t\rangle = \int dx \underbrace{|x\rangle \langle x|}_{\text{"1"}} |t\rangle = \int dx |x\rangle \psi(x)$$

• Kets can be normalized

$$\langle \psi | \psi \rangle = \langle \psi | \psi | \psi \rangle = \int \langle \psi(x) | \psi(x) \rangle dx = \int \psi^*(x) \psi(x) dx$$

• Bra is adjoint of ket (complex conjugate & transpose)

$$\langle \psi | = |\psi\rangle^\dagger = (|\psi\rangle^*)^\top$$

• $\langle \psi | \phi \rangle$ is projection of ψ to ϕ

$$\langle \psi | \phi \rangle = \langle \psi | \phi | \phi \rangle = \int \langle \psi(x) | \phi(x) \rangle dx = \int \psi^* \phi dx$$

• If $\langle \psi | \phi \rangle = 0$, then $\phi \perp \psi$.

• Superposition $\left\{ \begin{array}{l} |\psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle \\ \langle \psi | = |\psi\rangle^\dagger = c_1^* \langle \psi_1 | + c_2^* \langle \psi_2 | \end{array} \right. , c_1, c_2 \in \mathbb{C}$

• The probability to find particle at time t within interval $(x, x+dx)$ is

$$P(x, x+dx) = \psi^*(x,t) \psi(x,t) dx = |t(x,t)|^2 dx$$

$$\int P(x, x+dx) = \int \psi^* \psi dx = 1 = \langle \psi | \psi \rangle$$

• ψ is twice differentiable and continuous

• probabilistic interpretation of QM (Bohr/ Copenhagen)

<< QM Postulates (cont.)

2. To every observable, there is a corresponding Hermitian operator $\hat{O}^\dagger = \hat{O}$

$$\begin{aligned}\cdot \text{ If } \hat{O} \text{ is Hermitian, } & \int \psi^*(x) (\hat{O} \psi(x)) dx \\ &= \int (\hat{O}^\dagger \psi^*(x)) \psi(x) dx \\ &= \int (\hat{O} \psi^*(x)) \psi(x) dx\end{aligned}$$

• Operators in QM

linear momentum	$\hat{p} \rightarrow$	$\frac{\hbar}{i} \vec{V}$
kinetic energy	$\frac{\hat{p}^2}{2m}$	$-\frac{\hbar^2}{2m} \vec{V}^2$
potential energy	\hat{V}	$V(x)$
total energy (Hamiltonian)	$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}$	$-\frac{\hbar^2}{2m} \vec{V}^2 + V(x)$
angular momentum	$\hat{L} = \hat{x} \times \hat{p}$	$\vec{r} \times \frac{\hbar}{i} \vec{V}$

3. The only results of a measurement are the real valued eigenvalues of the operator \hat{O} corresponding to that observable. The eigenfunctions of \hat{O} form a complete set.

$$\hat{O}f(x) = \lambda f(x) \quad \left\{ \begin{array}{l} \lambda = \text{eigval} \\ f(x) = \text{eigfunc} \end{array} \right.$$

<< QM Postulates (cont.)

4. If many identical and independent quantum state (q.s.) $|\psi(t)\rangle$ are prepared and the observable \hat{O} is measured in each, then the avg value (expectation value) of measurement is

$$\langle \hat{O} \rangle = \langle \psi(t) | \hat{O} | \psi(t) \rangle = \int \psi^*(x) \hat{O} \psi(x) dx = \int (\hat{O} \psi^*(x)) \psi(x) dx$$

assuming $\psi(x)$ is normalized. If $\psi(x)$ is not normalized, then

$$\langle \hat{O} \rangle = \frac{\langle \psi(t) | \hat{O} | \psi(t) \rangle}{\langle \psi(t) | \psi(t) \rangle} = \frac{\int \psi^* \hat{O} \psi dx}{\int \psi^* \psi dx}$$

- If the quantum state $|\phi\rangle$ is an eigenstate of the observable,

$$\hat{A} |\phi\rangle = a |\phi\rangle$$

The expectation value

$$\langle \hat{A} \rangle = \langle \phi | \hat{A} | \phi \rangle = \langle \phi | a | \phi \rangle = a \langle \phi | \phi \rangle = a$$

In this case, the result of every measurement of \hat{A} returns with 100% certainty.

- If $|\phi\rangle$ is NOT an eigenstate of observable \hat{A} , then $|\psi\rangle$ can be expanded to eigenstates $|\phi_n\rangle$ of \hat{A}

$$\hat{A} |\phi_n\rangle = a_n |\phi_n\rangle , \quad |\phi_n\rangle \text{ is complete}$$

$$|\psi\rangle = \sum_n |\phi_n\rangle \underbrace{\langle \phi_n | \psi \rangle}_c = \sum_n |\phi_n\rangle c_n$$

$$\begin{aligned} \langle \hat{A} \rangle &= \langle \psi | \hat{A} | \psi \rangle = \left(\sum_n c_n^* \langle \phi_n | \psi \rangle \right) \hat{A} \left(\sum_n |\phi_n\rangle c_n \right) = \sum_{nn'} c_n^* \langle \phi_n | \hat{A} | \phi_{n'} \rangle c_{n'} \\ &= \sum_{nn'} c_n^* \langle \phi_n | a_{n'} | \phi_{n'} \rangle c_{n'} = \sum_{nn'} c_n^* a_{n'} \langle \phi_n | \phi_{n'} \rangle c_{n'} \\ &= \sum_{nn'} c_n^* a_{n'} \delta_{nn'} c_{n'} = \sum_n c_n^* a_n c_n = \sum_n |c_n|^2 a_n = \sum_n p_n a_n \quad (p_n = |c_n|^2) \end{aligned}$$

$$1 = \langle \psi | \psi \rangle = \langle \psi | \sum_n |\phi_n\rangle \underbrace{\langle \phi_n | \psi \rangle}_c = \sum_n |c_n|^2 = \sum_n p_n$$

** Quantum Mechanical Postulates (cont.)

5. The time evolution of the quantum state $|t(t)\rangle$ is governed by the Schrodinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

or in x -representation

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

\hat{H} =Hamiltonian, total energy operator
 $= KE + PE$

The stationary solutions of the wave equation has form of

$$\begin{aligned} f(x) &= A \sin(kx - \omega t) + A \sin(kx + \omega t) \\ &= 2A \sin(kx) \cos(\omega t) \end{aligned}$$

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{x}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{x})$$

(no time derivative)

Similarly, stationary solution occurs in Schrodinger eqn:

$$\Psi(x,t) = \psi(x) T(t) \quad (\text{ansatz})$$

Substitute into Schrodinger eqn:

$$i\hbar \frac{\partial}{\partial t} \psi(x) T(t) = \hat{H} \psi(x) T(t)$$

$$i\hbar \psi(x) \frac{\partial}{\partial t} T(t) = T(t) \hat{H} \psi(x)$$

$$i\hbar \frac{\frac{\partial \psi(x)}{\partial t} T(t)}{\psi(x) T(t)} = \frac{T(t) \hat{H} \psi(x)}{\psi(x) T(t)}$$

$$i\hbar \frac{\dot{T}(t)}{T(t)} = \frac{\hat{H}(\psi(x))}{\psi(x)} = \text{constant } E$$

LHS: $i\hbar \dot{T}(t) = ET(t)$

$$\int \frac{dT}{T} = \int \left(\frac{E}{i\hbar} \right) dt$$

$$T(t) = C e^{-iEt/\hbar}$$

LHS: $\frac{\hat{H}\psi(x)}{\psi(x)} = E$

$$\hat{H}\psi(x) = E\psi(x)$$

$$\hat{H}|\psi\rangle = E|\psi\rangle \quad \text{Time-independent Schrodinger eqn}$$

Total stationary soln

$$\Psi(x,t) = \psi(x) e^{iEt/\hbar}$$

has constant energy E .

$|\Psi(x,t)\rangle|^2 = (\psi(x) e^{iEt/\hbar})^* (\psi(x) e^{iEt/\hbar}) = |\psi(x)|^2$

$P(x, x+dx) = |\Psi(x,t)\rangle|^2 dx = |\psi(x)|^2 dx \Rightarrow \text{probability density does not change in time, it is stationary.}$

Simple Quantum System

- Classically, with two initial values $x(0) = x_0$, $v(0) = v_0$,

$$F = m\ddot{x} = 0 \quad \text{is solved by} \quad x(t) = x_0 + v_0 t \quad (\text{no external force})$$

- Similarly in QM, a particle with no external forces has a potential energy that is at most a constant

$$F = -\frac{d}{dx} V(x) = 0$$

$$V(x) = \text{const.}$$

- Time-independent S.E. in 1D:

$$H\psi = E\psi \rightarrow \left[\underbrace{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}_{\text{KE}} + \underbrace{V(x)}_{\text{PE}} \right] \psi(x) = E\psi(x)$$

(const.)

- By convention, $V(x) = 0$ (relative)

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x)$$

$$\psi''(x) = -\frac{2mE}{\hbar^2} \psi(x)$$

$$\psi_{\pm}(x) = A_{\pm} e^{\pm ikx}, \quad k = \frac{\sqrt{2mE}}{\hbar} = \frac{2\pi}{\lambda}$$

$$\text{With time, } \Psi_{\pm}(x,t) = A_{\pm} e^{\pm ikt} e^{-iEt/\hbar}$$

$$p = \hbar k$$

$$p = \frac{\hbar k L}{\lambda} = mv$$

$$\Rightarrow \lambda = \frac{\hbar}{p} = \frac{\hbar}{mv}$$

$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\left(\frac{2\pi}{\hbar/mv}\right)^2 = \frac{2mE}{\hbar^2} \Rightarrow E = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

- In perspective of p , $k = \frac{p}{\hbar}$, so

$$\psi_{\pm}(x) = A_{\pm} e^{ipx/\hbar}$$

$$\Psi_{\pm}(x,t) = A_{\pm} e^{ipx/\hbar} e^{-iEt/\hbar}$$

- Probability to find particle in interval dx centered at x at time t is

$$P(x, x+dx) = \frac{\int_x^{x+dx} \psi_{+}^*(x') \psi_{+}(x') dx'}{\int_{-L}^L \psi_{+}^*(x') \psi_{+}(x') dx'} = \frac{|A_{+}|^2 (e^{-ikx} e^{iEt/\hbar}) (e^{ikx} e^{-iEt/\hbar})^*}{|A_{+}|^2 \int_{-L}^L e^{-ikx} e^{iEt/\hbar} e^{ikx} e^{-iEt/\hbar} dx} = \frac{dx}{2L}$$

\Rightarrow independent of x and t

\Rightarrow particle is equally likely to be anywhere

\Rightarrow we know nothing about particle's location

\Rightarrow but we know the momentum exactly $p = \hbar k = mv$

~ Particle in a 1D Box : Wave Function

- Solve time-independent SE: $\hat{H}\psi = E\psi$. Find $\psi(x)$ and E.

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x)$$

$$\psi''(x) = \frac{2m}{\hbar^2} [V(x) - E]\psi(x)$$

- We demand $\psi(x) = 0$ outside the box.

- We demand b.c. $\psi(0) = \psi(L) = 0$ for continuity and twice differentiable.

- Inside the box $x \in [0, L]$, we have a free particle, where $V(x) = 0$.

Its soln is

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

- Impose b.c.

$$\psi(0) = 0 = A_+ + A_- \Rightarrow A_+ = -A_-$$

$$\psi(L) = 0 = A_+ e^{ikL} + A_- e^{-ikL} \quad \leftrightarrow$$

$$0 = A_+ (e^{ikL} - e^{-ikL}) \frac{2i}{2i} \quad (\text{let } A' = 2iA)$$

$$0 = 2iA \sin(kL) \quad (\text{let } A' = 2iA)$$

$$0 = A' \sin(kL)$$

$$0 = \sin(kL)$$

Ignore trivial soln $A' = 0 \Rightarrow$ no particle in box

$$n\pi = kL$$

$$k = \frac{n\pi}{L}$$

$$\psi_n(x) = A' \sin(kx) = A' \sin\left(\frac{n\pi}{L} x\right) \quad n=0 \text{ ignored} \Rightarrow \text{no particle in box}$$

- $n=0$ not physical

- $n < 0$ can map to $n > 0$ since sin is odd func.

- $n > 0$ are physically allowed values.

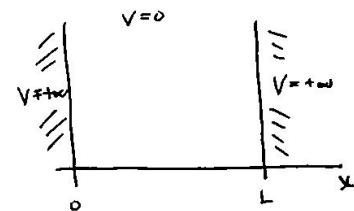
- To find A' , we normalize $\psi_n(x)$ to 1.

$$1 = \int_0^L |\psi_n(x)|^2 dx = A'^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\Rightarrow A' = \sqrt{\frac{2}{L}}$$

- Normalized $\psi_n(x)$ is

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)} \quad n=1, 2, 3, \dots$$



$$V(x) = \begin{cases} 0 & x \in [0, L] \\ \infty & \text{elsewhere} \end{cases}$$

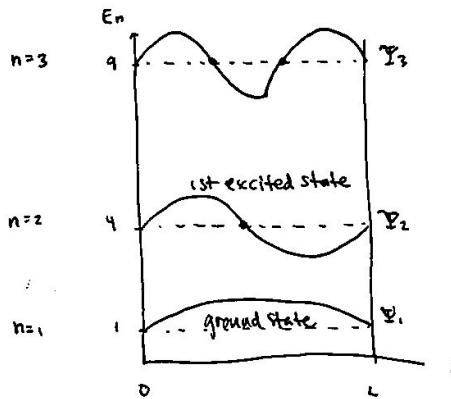
<< Particle in a 1D Box: Energy Eigenvalues

To find energy, substitute $\psi_n(x)$ into S.E.

$$\begin{aligned}\hat{H}\psi_n(x) &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \\ &= -\frac{\hbar^2}{2m} \frac{2}{L} \left(\frac{n\pi}{L}\right)^2 \sin\left(\frac{n\pi x}{L}\right) \\ &= \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2 \underbrace{\sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)}_{E_n}\end{aligned}$$

$$E_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2 = \frac{\hbar^2 n^2 \pi^2}{2m L^2} = \frac{\hbar^2 n^2}{8m L^2} \quad n=1,2,3,\dots$$

(quantum number)



$\Psi_n \perp \Psi_m$, $n \neq m$ orthogonal

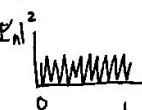
$$\int_0^L \Psi_n^* \Psi_m dx = \begin{cases} 0 & n \neq m \\ 1 & n = m \end{cases} = \delta_{nm} \rightarrow \text{orthonormal}$$

$\{\Psi_n(x)\}_{n=1}^{\infty}$ complete on $x \in [0, L]$

$$\text{zero point energy} - E_1 = \frac{\hbar^2 \pi^2}{2m L^2} \neq 0$$

Time-dependent soln: $\Psi_n(x, t) = \psi_n(x) e^{-iE_n t/\hbar}$

Probability of finding particle in $[a, b]$: Prob(a, b) = $\int_a^b |\Psi_n(x)|^2 dx$

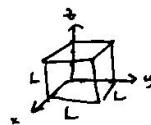


As n grows, probability to find anywhere is equal

As n grows, $\lim_{n \rightarrow \infty} \frac{E_{n+1} - E_n}{n} = \frac{\frac{\hbar^2}{2m L^2} [(n+1)^2 - n^2]}{\frac{\hbar^2}{2m L^2} n^2} = \frac{2n+1}{n^2} \hbar^2 = 0 \rightarrow$ correspondence principle
 $(\Delta E \rightarrow 0)$ - a recovery of classical phys.

<< Particle in a 3D Box

$$\rightarrow 3D S.E. -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) = E \Psi(\vec{r})$$



- Ansatz for 3D SE wavefunction:

$$\Psi(\vec{r}) = \Psi(x, y, z) = X(x) Y(y) Z(z) \quad \text{separation of var., assume } x, y, z \text{ independence}$$

- Substitute in 3D SE:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) XYZ = E XYZ$$

$$= -\frac{\hbar^2}{2m} (YZ X'' + XZ Y'' + XY Z'') = E XYZ$$

- Divide by XYZ :

$$-\frac{\hbar^2}{2m} \left(\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} \right) = E$$

diff var equal, has to be const.

- Separate variable of x (and y, z similarly)

$$\underbrace{-\frac{\hbar^2}{2m} \frac{X''}{X}}_{f(x)} = E - \underbrace{\frac{\hbar^2}{2m} \left(\frac{Y''}{Y} + \frac{Z''}{Z} \right)}_{g(y, z)} \Rightarrow E_x$$

$$\Rightarrow \left\{ \begin{array}{l} -\frac{\hbar^2}{2m} \frac{X''}{X} = E_x \\ -\frac{\hbar^2}{2m} \frac{Y''}{Y} = E_y \\ -\frac{\hbar^2}{2m} \frac{Z''}{Z} = E_z \end{array} \right\} \quad \begin{array}{l} \Psi_e(\vec{r}) = \sqrt{\frac{n_x}{L}} \sin\left(\frac{n_x \pi x}{L}\right) \sqrt{\frac{n_y}{L}} \sin\left(\frac{n_y \pi y}{L}\right) \sqrt{\frac{n_z}{L}} \sin\left(\frac{n_z \pi z}{L}\right) \\ \text{eigenfunc} \\ n_x, n_y, n_z = 1, 2, 3, \dots \end{array}$$

$$\text{Eigenenergy: } E_n = E_{nx} + E_{ny} + E_{nz}$$

$$\begin{aligned} &= \frac{n_x^2 \hbar^2}{8mL^2} + \frac{n_y^2 \hbar^2}{8mL^2} + \frac{n_z^2 \hbar^2}{8mL^2} \\ &= \frac{(n_x^2 + n_y^2 + n_z^2) \hbar^2}{8mL^2} \end{aligned}$$

- Degeneracy - have same energy

$$\text{e.g. } (n_x, n_y, n_z) = (2, 1, 1) = (1, 2, 1) = (1, 1, 2) \quad \text{triply degenerate}$$

- Probability of finding molecule in a cube

$$\text{Prob}(\vec{r}, \vec{r} + d^3x) = |\Psi_n(\vec{r})|^2 d^3x = |\Psi_n(\vec{r})|^2 dx dy dz$$

<< Superposition

$$\psi(x) = a\psi_1 + b\psi_3 = a\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) + b\sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right)$$

$|a|^2 + |b|^2 = 1$ to normalize.

- Is the superposition an eigenstate?

$$\hat{H}\psi(x) = aE_1\psi_1 + bE_3\psi_3 \neq (\text{const}) [\psi(x)]$$

- Superposition states are NOT eigenstates, but they are important to describe physical states

<< Superposition

• Normalization

$$1 = \int_0^L \psi^* \psi dx = \int_0^L (a\psi_1 + b\psi_2)^* (a\psi_1 + b\psi_2) dx$$

$$1 = \int_0^L |a|^2 \psi_1^* \psi_1 + ab \psi_1^* \psi_2 + \cancel{b a \psi_2^* \psi_1} + \cancel{|b|^2 \psi_2^* \psi_2} dx \Rightarrow 1 = |a|^2 + |b|^2$$

• stationary states is expressed as $\Psi(x,t) = f(x)T(t)$

• nonstationary states can't: $\Psi(x,t) \neq f(x)T(t)$

$$\text{The superposition } \psi(x,t) = a\psi_1(x) + b\psi_2(x)$$

$$= Ae^{-iEt/\hbar} \psi_1(x) + Be^{-iEt/\hbar} \psi_2(x)$$

$$\neq f(x)T(t)$$

is NOT stationary. \Rightarrow properties are time dependent

• Particle in a box eigenfunctions: $\{\psi_n(x)\}_{n=1}^{n=\infty}$ are a complete, orthonormal set

• $\psi_n(x)$ are eigenfunction of \hat{H} .

• $\psi_n(x)$ are NOT eigenfunction of position x .

• x isn't constant in $\hat{x}\psi_n(x) = x\psi_n(x)$

• total energy & position of the particle cannot be measured simultaneously.

• We can measure avg position through large number of measurement.

$$\cdot \text{Prob}(x, dx) = |\psi_n(x)|^2 dx$$

$$\cdot \text{Prob}(x_0, x_1) = \int_{x_0}^{x_1} |\psi_n(x)|^2 dx \quad \text{Prob} \in [0, 1]$$

<< Expectation value of position & energy (particle in a box)

$$\cdot \langle \hat{x} \rangle = \int_0^L \text{Prob}(x, x+dx) \times dx = \int_0^L x |\psi_n(x)|^2 dx = \langle \psi_n | \hat{x} | \psi_n \rangle \quad \text{hard way!}$$

$$\cdot \langle \hat{x} \rangle = \underbrace{\langle \psi_n | \hat{x} | \psi_n \rangle}_{= E_n} = \int_0^L \psi_n^*(x) \hat{x} \psi_n(x) dx = \int_0^L \psi_n^*(x) \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} \psi_n(x) dx$$

$$= \int_0^L \psi_n^*(x) E_n \psi_n(x) dx \quad (\text{easy way: } \hat{x} \psi_n = E_n \psi_n)$$

$$= E_n$$

• Each measurement of x may be diff, since \hat{x} is not eigfunc of \hat{H} .

• Every measurement of E returns E_n with 100% certainty since ψ_n is eigfunc of \hat{H} .

\Leftarrow Expectation value of position & energy (superposition)

Consider superposition $\psi(x) = a\psi_1(x) + b\psi_3(x) = a\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) + b\sqrt{\frac{2}{L}} \sin\left(\frac{3\pi x}{L}\right)$

$$\langle \hat{H} \rangle = \int_0^L (a^* \psi_1^*(x) + b^* \psi_3^*(x)) \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} (a\psi_1(x) + b\psi_3(x)) dx$$

$$= \int_0^L (a^* \psi_1^*(x) + b^* \psi_3^*(x)) [aE_1 \psi_1(x) + bE_3 \psi_3(x)] dx$$

$$= \int_0^L |a|^2 E_1 \psi_1^* \psi_1 + a^* b E_3 \psi_3^* \psi_3 + b^* a E_1 \psi_1^* \psi_3 + |b|^2 E_3 \psi_3^* \psi_3 dx$$

$$\langle \hat{H} \rangle = |a|^2 E_1 + |b|^2 E_3 \quad (\text{with } |a|^2 + |b|^2 = 1)$$

Probability in $E_1 = |a|^2$

Probability in $E_3 = |b|^2$

The system is in superposition of ψ_1, ψ_3 , by postulate, only eigenvalues can be measured.

Thus the coeff are probability

$\langle \hat{H} \rangle$ is superposition of E_n

<< Finite Potential Well

$$\text{III} \quad -\frac{\hbar^2}{2m} \psi''(x) = E \psi''_{\text{III}}(x) \quad (V(x)=0)$$

$$\psi''_{\text{III}}(x) = -\frac{2mE}{\hbar^2} \psi_{\text{III}}(x)$$

$$\psi''_{\text{III}}(x) = k^2 \psi_{\text{III}}(x) \quad \text{, where } k = \sqrt{\frac{2mE}{\hbar^2}} > 0$$

$$\psi_{\text{III}}(x) = C e^{ikx} + D e^{-ikx} \quad x \in [0, L]$$

I & III

$$-\frac{\hbar^2}{2m} \psi'' + V_0 \psi'' = E \psi''$$

$$\psi''(x) = -\frac{2m}{\hbar^2} (E - V_0) \psi(x)$$

$$\psi''(x) = -k'^2 \psi(x) \quad \text{, where } k' = \sqrt{\frac{2m}{\hbar^2} (E - V_0)}$$

$$\psi_{\text{I/II}}(x) = \begin{cases} A e^{ik'x} + B e^{-ik'x} & x \leq 0 \\ E e^{ik'x} + F e^{-ik'x} & x \geq L \end{cases}$$

If $E > V_0$ (above potential well), $\psi_{\text{I/II}}$ are oscillatory ($k' > 0$)

If $E < V_0$ (below potential well), then

$$k' = \sqrt{\frac{2m}{\hbar^2} (E - V_0)} = \sqrt{-\frac{2m}{\hbar^2} (V_0 - E)} = i \sqrt{\frac{2m}{\hbar^2} (V_0 - E)} = i k \quad \text{, where } k = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)} > 0$$

Impose continuity at $x=0, x=L$, for $E < V_0$ bound states.

$$\begin{cases} A + B = C + D & \text{I/II} \quad x=0 \\ C e^{ikL} + D e^{-ikL} = E e^{-ikL} + F e^{ikL} & \text{I/II} \quad x=L \end{cases} \quad \textcircled{1} \quad \textcircled{2}$$

Impose continuity of 1st derivative at $x=0, x=L$, for $E < V_0$ bound states.

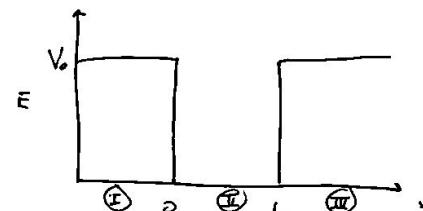
$$\psi''_{\text{I/II}}(x) = \begin{cases} A e^{-kx} + B e^{kx} & x \leq 0 \\ E e^{-kx} + F e^{kx} & x \geq L \end{cases} \quad \text{for } E < V_0$$

$$\psi''_{\text{I/II}}(x) = \begin{cases} -ikA e^{-kx} + ikB e^{kx} & x \leq 0 \\ -ikE e^{-kx} + ikF e^{kx} & x \geq L \end{cases} \quad \psi''_{\text{III}}(x) = C e^{ikx} i k - i k D e^{-ikx}$$

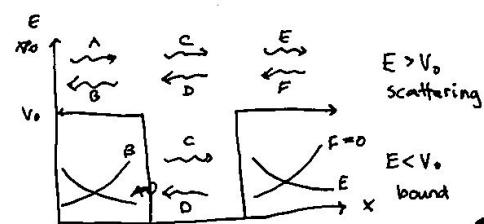
$$\begin{cases} -ikA + ikB = C i k - D i k & x=0 \\ -ikE e^{-ikL} + ikF e^{ikL} = i k C e^{ikL} - i k D e^{-ikL} & x=L \end{cases} \quad \textcircled{3} \quad \textcircled{4}$$

$$\text{Rearrange } \textcircled{3}: A - B = -\frac{i k}{2k} (C - D) \quad \textcircled{5}$$

$$\text{Rearrange } \textcircled{4}: (C e^{ikL} - D e^{-ikL}) = -\frac{i k}{2k} (E e^{-ikL} - F e^{ikL}) \quad \textcircled{6}$$



$$V(x) = \begin{cases} V_0 & \text{elsewhere} \\ 0 & x \in [0, L] \end{cases}$$



$\textcircled{1} \pm \textcircled{3}$:

$$+ : 2A = (1 - i\frac{k}{E})C + (1 + i\frac{k}{E})D$$

$$- : 2B = (1 + i\frac{k}{E})C + (1 - i\frac{k}{E})D$$

$$\begin{bmatrix} A \\ B \end{bmatrix} = \frac{1}{2} \begin{bmatrix} 1 - i\frac{k}{E} & 1 + i\frac{k}{E} \\ 1 + i\frac{k}{E} & 1 - i\frac{k}{E} \end{bmatrix} \begin{bmatrix} C \\ D \end{bmatrix}$$

scattering
matrix

substitute $\Rightarrow \begin{bmatrix} A \\ B \end{bmatrix} = [S] \begin{bmatrix} E \\ F \end{bmatrix}$

 $\textcircled{3} \pm \textcircled{6}$:

+

-

$$\begin{bmatrix} C \\ D \end{bmatrix} = \frac{1}{2} \begin{bmatrix} (1 + i\frac{k}{E})e^{-ikL} e^{-ikL} & (1 - i\frac{k}{E})e^{ikL} e^{-ikL} \\ (1 - i\frac{k}{E})e^{-ikL} e^{ikL} & (1 + i\frac{k}{E})e^{ikL} e^{ikL} \end{bmatrix} \begin{bmatrix} E \\ F \end{bmatrix}$$

- For wave functions to be square normalizable, $\lim_{k \rightarrow \infty} \gamma = 0$, so that $A = 0, F = 0$

- The system becomes

$$\begin{bmatrix} 0 \\ B \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} E \\ 0 \end{bmatrix}$$

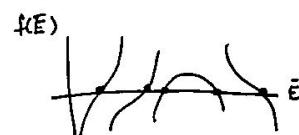
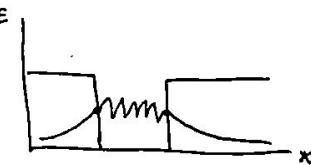
$$\left\{ \begin{array}{l} k = \sqrt{\frac{2mE}{\hbar^2}} \\ E = \frac{2m(V_0 - E)}{\hbar^2} \end{array} \right.$$

$$0 = S_{11}E \Rightarrow S_{11} = 0 = (1 - i\frac{k}{E})(1 + i\frac{E}{k})e^{-ikL}e^{-ikL} + (1 + i\frac{k}{E})(1 - i\frac{E}{k})e^{-ikL}e^{ikL} \dots$$

$$B = S_{21}E \quad \text{solve the transcendental eqn of the form}$$

$$2\sqrt{E} \sqrt{V_0 - E} - (E - (V_0 - E)) \tan \sqrt{E} = 0$$

$$\text{where } \bar{E} = \frac{E}{\hbar^2/2mL^2}, \bar{V}_0 = \frac{V_0}{\hbar^2/2mL^2}$$



$$\text{for } V_0 = 1.2 \times 10^{-18} \text{ J}$$

$$L = 1 \times 10^{-9} \text{ m}$$

<< Barrier Scattering

II Using time-independent SE, we have

$$\psi_{\text{I}}(x) = Ce^{ikx} + De^{-ikx}, \quad k = \sqrt{\frac{2m}{\hbar^2}(E - V_0)}$$

III

$$\psi_{\text{I},\text{II}}(x) = \begin{cases} Ae^{ik'x} + Be^{-ik'x} \\ Ce^{ik'x} + Fe^{-ik'x} \end{cases}, \quad k' = \sqrt{\frac{2mE}{\hbar^2}}$$

Enforce continuity, we have

$$\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} S \\ 0 \end{bmatrix} \begin{bmatrix} E \\ F \end{bmatrix}$$

→ transmission probability $T(E)$ - ratio of the flux of the transmitted wave to that of the incident wave

$$T(E) = \frac{|E|^2}{|A|^2} \xrightarrow{\text{coeff}} = \frac{1}{|S_{11}|^2}$$

• Since nothing left wave reflect from right, $F=0$, so

$$\begin{bmatrix} A \\ B \end{bmatrix} = S \begin{bmatrix} E \\ 0 \end{bmatrix} \Rightarrow A = S_{11}E$$

$$S_{11} = \frac{E}{A}$$

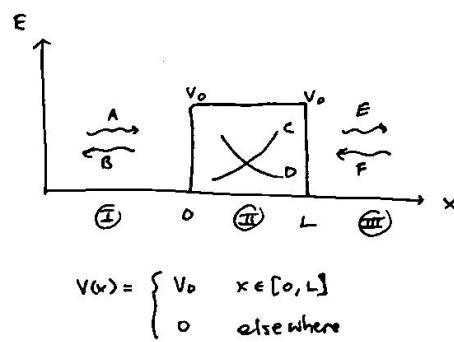
$$\frac{1}{S_{11}} = \left(\frac{E}{A}\right)^2$$

• Effective box length is $2L$.

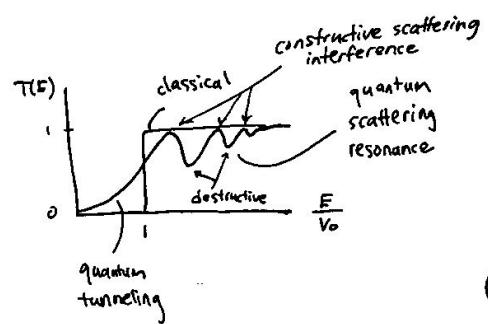
• Resonance condition is $2L = n\lambda = n\frac{\hbar}{p} = n\frac{\hbar}{\tau k} = \frac{2n\pi}{k}$

• e^- does not break up, it stays as one particle

$$T+R=1$$



$$V(x) = \begin{cases} V_0 & x \in [0, L] \\ 0 & \text{elsewhere} \end{cases}$$



see Commutator

- In quantum systems, values of \hat{A} and \hat{B} can only be measured simultaneously if the measurement process doesn't change the state of the system.
- Let ψ_n describe the state of a QM system that we want to measure with \hat{A} and \hat{B} .
- First measure \hat{A} , then \hat{B} : $(\hat{B}(\hat{A}\psi_n))$

if ψ_n is an eigenfunction of \hat{A} , then $\hat{A}\psi_n = a_n\psi_n$

$$\hat{B}(\hat{A}\psi_n) = \hat{B}(a_n\psi_n)$$

if ψ_n is an eigenfunction of \hat{B} , then

$$\hat{B}(\hat{A}\psi_n) = \hat{B}(a_n\psi_n) = a_n(\hat{B}\psi_n) = a_n b_n \psi_n = b_n a_n \psi_n$$

Reversing order does produce the same result

$$\hat{A}(\hat{B}\psi_n) = \hat{B}(\hat{A}\psi_n) \Rightarrow [\hat{A}, \hat{B}]\psi_n = \hat{A}\hat{B}\psi_n - \hat{B}\hat{A}\psi_n = 0$$

commutator $[\hat{A}, \hat{B}]f = \hat{A}\hat{B}f - \hat{B}\hat{A}f$

if $[\hat{A}, \hat{B}] = 0$, they commute, measurement can be performed simultaneously,

if $[\hat{A}, \hat{B}] \neq 0$, they do not commute, cannot be measured simultaneously independent of order.

Position & Momentum

$$\begin{aligned} [\hat{x}, \hat{p}] f(x) &= [x, \frac{\hbar}{i} \frac{d}{dx}] f(x) \\ &= x \frac{\hbar}{i} \frac{d}{dx} f(x) - \frac{\hbar}{i} \frac{d}{dx} (f(x)x) \\ &= \frac{\hbar}{i} x \frac{df}{dx} - \frac{\hbar}{i} \left[\frac{df}{dx} x + f(x) \right] \\ &= -\frac{\hbar}{i} f(x) \end{aligned}$$

$$[\hat{x}, \hat{p}] = i\hbar \Rightarrow \text{do not commute}$$

Momentum & Kinetic Energy

$$[\hat{p}, T] f(x) = \left[\frac{\hbar}{i} \frac{d}{dx}, -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right] f(x) = 0 \Rightarrow \text{commute}$$

Momentum & Total Energy

$$[\hat{p}, \hat{T}] f(x) = \left[\frac{\hbar}{i} \frac{d}{dx}, -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] f(x) = \frac{\hbar}{i} V'(x) f(x) \Rightarrow \text{do not commute.}$$

(unless $V'(x) = 0$; $V(x) = \text{const.}$)

ψ & \hat{H} of Particle in a Box

- Consider particle in a box wave function

$$\psi_n(x) = \frac{1}{\sqrt{L}} \sin\left(\frac{n\pi x}{L}\right)$$

is an eigenfunction of \hat{H} , but not \hat{p} .

Measurement of \hat{H} returns $E_n = \frac{\hbar^2 n^2}{8mL^2}$

Measurements of \hat{p} gives $\langle \hat{p} \rangle = \int_0^L \psi_n^*(x) \frac{i}{\hbar} \frac{d}{dx} \psi_n(x) dx = 0$ (after many measurements)

It's equally likely to measure +/- values of p .

Magnitude and direction of momentum cannot be known precisely.

ψ & \hat{p} of Free particle

In a box of length $2L$, $\psi(x) = Ne^{ikx}$, the prob. of finding particle is

$$\text{Prob}(x, x+dx) = |\psi(x)|^2 dx = \frac{dx}{2L}$$

Let $L \rightarrow \infty$, $\text{Prob}(x, x+dx) \rightarrow 0$

$$\begin{aligned} \langle \hat{p} \rangle &= \frac{\int_{-\infty}^{\infty} \psi^*(x) \frac{i}{\hbar} \frac{d}{dx} \psi(x) dx}{\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx} = \frac{\int_{-\infty}^{\infty} (N e^{-ikx}) \frac{i}{\hbar} \frac{d}{dx} (N e^{ikx}) dx}{\int_{-\infty}^{\infty} (N e^{-ikx}) (N e^{ikx}) dx} = \frac{\frac{i}{\hbar} 2k \int_{-\infty}^{\infty} (N e^{-ikx}) e^{ikx} dx}{\int_{-\infty}^{\infty} (N e^{-ikx}) e^{ikx} dx} \\ &= tk \end{aligned}$$

Standard Deviation

Standard deviation from the mean (of momentum)

$$\sigma_p = \sqrt{\langle (\hat{p} - \langle \hat{p} \rangle)^2 \rangle} = \sqrt{\langle (\hat{p}^2 - 2\hat{p}\langle \hat{p} \rangle + \langle \hat{p} \rangle^2) \rangle} = \sqrt{\langle \hat{p}^2 \rangle - 2\langle \hat{p} \rangle \langle \hat{p} \rangle + \langle \hat{p} \rangle^2}$$

$$\sigma_p = \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2}$$

Uncertainty in the measurement

Uncertainty in momentum is

$$\sigma_p = \sqrt{\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2} = \sqrt{\hbar^2 k^2 - (tk)^2} = 0$$

$$\langle \hat{p}^2 \rangle = \frac{\int_{-\infty}^{\infty} \psi^*(x) \left(\frac{i}{\hbar} \frac{d}{dx}\right)^2 \psi(x) dx}{\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx} = \frac{\int_{-\infty}^{\infty} (N e^{-ikx}) \left(\frac{i}{\hbar} k\right)^2 (N e^{ikx}) dx}{\int_{-\infty}^{\infty} (N e^{-ikx}) (N e^{ikx}) dx} = \hbar^2 k^2$$

Uncertainty in position is

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \infty$$

$$\langle x \rangle = 0 \Rightarrow \langle x \rangle^2 = 0$$

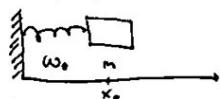
$$\langle x^2 \rangle = \lim_{L \rightarrow \infty} \int_{-L}^L \text{Prob}(x, x+dx) \cdot x^2 dx = \lim_{L \rightarrow \infty} \int_{-L}^L \frac{dx}{2L} x^2 = \lim_{L \rightarrow \infty} \frac{\frac{1}{3} x^3 \Big|_{-L}^L}{2L} = \infty$$

<<Heisenberg Uncertainty Principle

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

$$\sigma_x \sigma_p = \Delta x \Delta p \geq \frac{\hbar}{2}$$

<<Harmonic Oscillator



$$\text{Hooke's law spring constant } k = m\omega_0^2$$

Dynamics of the mass is governed by Newton's eqn

$$F = m\ddot{x} - kx$$

The soln is

$$x(t) = x(0) \cos(\omega_0 t) + \frac{v(0)}{\omega_0} \sin(\omega_0 t) \Rightarrow \text{periodic}$$

The period is $T = \frac{2\pi}{\omega_0}$, so $x(t+nT) = x(t)$.

$$\text{Spring potential } V(x) = \frac{1}{2} kx^2 + C$$

Hamiltonian (total energy) of harmonic oscillator is

$$H = KE + PE$$

$$H = \frac{p^2}{2m} + \frac{1}{2} M \omega_0^2 x^2 \quad \text{, where } k = M \omega_0^2$$

Ex1 Hamiltonian of coupled system



$$H = \left(\frac{p_1^2}{2m_1} + \frac{1}{2} m_1 \omega_1^2 x_1^2 \right) + \left(\frac{p_2^2}{2m_2} + \frac{1}{2} m_2 \omega_2^2 x_2^2 \right) + \underbrace{\frac{g}{2} (x_1 - x_2)^2}_{\text{coupling}}$$

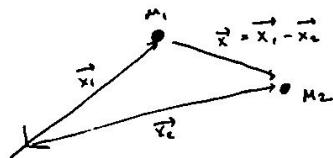
$$\text{normal modes} = \left(\frac{p_+^2}{2M_+} + \frac{1}{2} M_+ \omega_+^2 x_+^2 \right) + \left(\frac{p_-^2}{2M_-} + \frac{1}{2} M_- \omega_-^2 x_-^2 \right)$$

$\rightarrow \rightarrow$
in phase

$\rightarrow \leftarrow$
out of phase

*** Dimer Model

- Consider dimer in lab frame

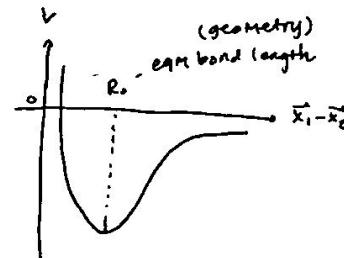


$$H_{\text{dimer}} = \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} + V(|\vec{x}_1 - \vec{x}_2|)$$

KE of particle 1

KE of particle 2

Sum of electronic KE, e-e repulsion, N-N repulsion, e-N attraction



- Center of mass and relative coordinate transformation (COM)

- COM: $\vec{X} = \frac{m_1 \vec{x}_1 + m_2 \vec{x}_2}{M}$, rel. $\vec{x} = \vec{x}_1 - \vec{x}_2$, tot. mass $M = m_1 + m_2$

- COM $\vec{P} = \vec{p}_1 + \vec{p}_2$, rel. $\vec{p} = \frac{M \vec{P} - m_1 \vec{p}_1}{M}$

- Consider dimer in COM/rel coordinate frame

- Equal to H_{dimer} , but with diff form

- $H_{\text{dimer}}^{\text{lab}} = H_{\text{dimer}}^{\text{COM/rel}} = \underbrace{\frac{\vec{P}^2}{2M}}_{\text{COM coord}} + \underbrace{\frac{\vec{p}^2}{2\mu}}_{\text{internal Hamiltonian}} + V(|\vec{x}|)$
- $\mu = \frac{m_1 m_2}{m_1 + m_2}$

COM coord KE - free particle KE
relative coord KE -
total PE + electronic KE

- COM of dimer moves through space as a free particle

- Since Hamiltonian factors into COM & rel pieces that do not couple,
the dimer wave function factors into a product.

$$\Psi_{\text{dimer}}^{\text{lab}}(\vec{x}_1, \vec{x}_2) = \Psi_{\text{dimer}}^{\text{COM/rel}}(\vec{X}, \vec{x}) = \underbrace{\Phi(\vec{X})}_{\text{COM}} \underbrace{\psi(\vec{x})}_{\text{rel.}}$$

and $\Phi(\vec{X}) = e^{\pm i \vec{P} \cdot \vec{X} / \hbar}$

- Internal Hamiltonian

$$H_{\text{int}} \psi(\vec{x}) = \left[\frac{\vec{p}^2}{2\mu} + V(|\vec{x}|) \right] \psi(\vec{x}) = E \psi(\vec{x}) \quad \text{Let } |\vec{x}| \equiv r$$

$$\left[-\frac{\hbar^2}{2M} \nabla_r^2 + V(r) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

- ∇^2 in spherical coord:

$$\nabla^2 = \underbrace{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)}_{\text{radial breathing KE (vibration)}} + \underbrace{\frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right)}_{\text{angular KE (rotational)}} + \underbrace{\frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}}_{\text{KE (rotational)}}$$



$$\theta \in [0, \pi] \\ \phi \in [0, 2\pi]$$

<< Vibration of Quantum Harmonic Oscillator

- Fix angles θ, ϕ (molecule does not rotate), leaving only breathing KE.

Vibrational SE.

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

- Since vibration and rotation are separable, the wavefunction factors as the product

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

- So the vibrational SE becomes

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial^2}{\partial r^2} + V(r) \right] R(r) = E_r R(r)$$

- Substitute $R(r) \approx u(r)/r$

$$R'(r) = u'(r)/r - u(r)/r^2$$

$$\frac{\partial^2}{\partial r^2} r^2 R'(r) = r u''(r)$$

$$\frac{1}{r^2} \frac{\partial^2}{\partial r^2} r^2 R'(r) = u''(r)/r$$

$$\text{We get } -\frac{\hbar^2}{2\mu} \frac{u''(r)}{r} + V(r) \frac{u(r)}{r} = E_r \frac{u(r)}{r}$$

$$-\frac{\hbar^2}{2\mu} u''(r) + V(r) u(r) = E_r u(r)$$

- Approximate $V(r)$ around $r=R_0$ using Taylor expansion

$$V(r) = V(R_0) + V'(R_0)(r-R_0) + \cancel{V''(R_0)(r-R_0)^2} + \dots$$

$$V_{\text{Hooke}} = \frac{1}{2} k x^2$$

- By comparison to Hooke's law $k=m\omega_0^2$,

$$k = V''(R_0) = \mu \omega_0^2 \quad \text{, where } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

and ω_0 being the molecule's natural vibrational frequency.

- Substitute the approximation,

$$-\frac{\hbar^2}{2\mu} u''(r) + [V(R_0) + \frac{1}{2} V''(R_0)(r-R_0)^2 + \dots] u(r) = E_r u(r)$$

- Put $V(R_0)$ to RHS since energy is relative

- Harmonic oscillator approx. take quadratic term.

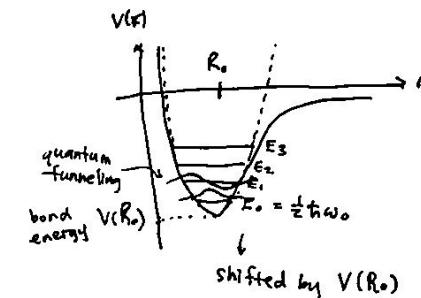
$$-\frac{\hbar^2}{2\mu} u''(r) + \underbrace{\frac{1}{2} V''(R_0)}_{\mu \omega_0^2} (r-R_0)^2 u(r) = [E_r - V(R_0)] u(r)$$

has eigenfunctions

$$u_n(r) = A_n H_n(\sqrt{\alpha} r) \cdot e^{-\alpha(r-R_0)^2/2}$$

with eigenfunctions energy

$$E_n = \hbar \omega_0 (n + \frac{1}{2}), n=0,1,2,\dots$$



$$\alpha = \frac{\hbar \omega_0}{\mu}, \lambda_n = \frac{1}{\sqrt{2^n n!}} \left(\frac{\alpha}{\pi} \right)^{\frac{n}{2}}, n=0,1,2,3,\dots, H_n = \text{Hermite polynomials}$$

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

<< Vibration

- Eigenenergies $E_n = \hbar\omega_0(n + \frac{1}{2})$, $n=0, 1, 2, 3, \dots$

$n=0$ is zero point vibrational energy

<< Rigid Rotor

- internal / relative dimer Hamiltonian has radial and angular parts.

$$\hat{H} = -\frac{\hbar^2}{2\mu} \left[\underbrace{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r)}_{\text{radial}} + \underbrace{\frac{1}{r^2 \sin\theta} \frac{\partial^2}{\partial\theta^2} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial\phi^2}}_{\text{angular}} \right]$$

- freezing $r=R_0$, equilibrium bond length, results in the rigid rotor Hamiltonian ($\frac{\partial}{\partial r}=0$), resulting in

$$-\frac{\hbar^2}{2MR_0^2} \left[\frac{1}{\sin\theta} \frac{\partial^2}{\partial\theta^2} (\sin\theta \frac{\partial}{\partial\theta}) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y(\theta, \phi) = E Y(\theta, \phi)$$

→ Classical Rigid Rotor

- angular momentum - $\vec{L} = \vec{x} \times \vec{p} = I\vec{\omega}$

$$\vec{v} = R_0 \vec{\omega}$$

$$I = mR_0^2$$

- energy - $E = \frac{1}{2}MV^2 = \frac{1}{2}m(R_0\omega^2) \frac{L^2}{I} = \frac{1}{2}I\omega^2 \frac{L^2}{I} = \frac{1}{2}(I\omega)^2 = \frac{L^2}{2I}$

for a freely moving particle of mass m and momentum p , the total energy is $\frac{p^2}{2m}$.

$$E = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$$

With no external force, $F = \frac{dp}{dt} = 0$.

With no external torque, $\tau = \frac{dL}{dt} = 0 \Rightarrow \frac{d}{dt}(I\omega) = 0$

→ Quantum Rigid Rotor

- $\vec{L} = \vec{x} \times \vec{p} \approx$

$$\cdot \vec{L} = \vec{x} \times \vec{p} = \vec{x} \times \left(\frac{\hbar}{i} \vec{v} \right) = \det \begin{bmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ \frac{\hbar}{i} p_x & \frac{\hbar}{i} p_y & \frac{\hbar}{i} p_z \end{bmatrix} = \frac{\hbar}{i} \left\{ \begin{array}{l} \hat{x} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \\ -\hat{y} \left(x \frac{\partial}{\partial z} - z \frac{\partial}{\partial x} \right) \\ +\hat{z} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \end{array} \right\} = L_x \hat{x} + L_y \hat{y} + L_z \hat{z}$$

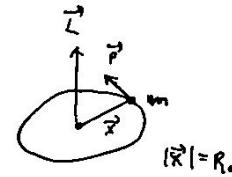
- $L_x = \frac{\hbar}{i} \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] = \frac{\hbar}{i} \left(-\sin\theta \frac{\partial}{\partial\phi} - \cot\theta \cos\phi \frac{\partial}{\partial\theta} \right)$

- $L_y = \frac{\hbar}{i} \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] = \frac{\hbar}{i} \left(\cos\theta \frac{\partial}{\partial\phi} - \cot\theta \sin\phi \frac{\partial}{\partial\theta} \right)$

- $L_z = \frac{\hbar}{i} \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] = \frac{\hbar}{i} \left(\frac{\partial}{\partial\phi} \right)$

- $\vec{L}^2 = \vec{L} \cdot \vec{L} = (L_x^2 + L_y^2 + L_z^2)$

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



10 Nov 2021

L18 Rigid Rotor

CHEM485

<< Rigid Rotor

→ Quantum Rigid Rotor

- commutation relations

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}$$

do not commute
cannot know any two components of \vec{L} simultaneously.
can only know one component of \vec{L} at same time!

$$[\hat{L}^2, \hat{L}_i] = 0 \quad \text{for any component } i$$

- spherical harmonics are eigenfunctions of \hat{L}^2 , with eigenvalue $\hbar^2 l(l+1)$

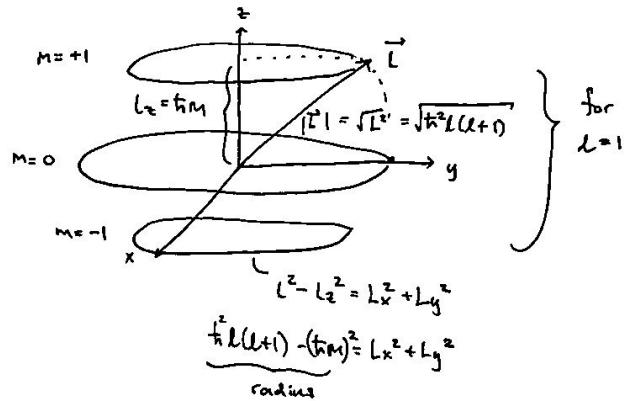
$$\hat{L}^2 Y_{lm} = \hbar^2 l(l+1) Y_{lm}$$

$$l = 0, 1, 2, 3, \dots$$

$$m = -l, \dots, 0, \dots, l$$

- Choose to know \hat{L}_z since it's simple,

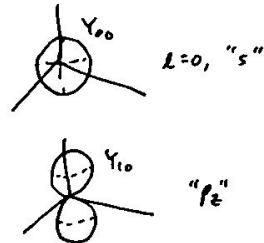
$$\hat{L}_z Y_{lm} = \hbar m Y_{lm}$$



<< Rigid Rotors
→ Spherical Harmonics

$$\cdot Y_{00}(\theta, \phi) = \sqrt{\frac{1}{\pi}}$$

$$\cdot Y_{1m}(\theta, \phi) \begin{cases} m=+1 \\ m=0 \\ m=-1 \end{cases} \quad Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta$$



→ Hamiltonian $\hat{H}_{\text{ang}} = \frac{\hbar^2}{2\mu R_0^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] = \frac{1}{2\mu R_0^2} \frac{\hat{L}^2}{\sin^2\theta} = \frac{\hat{L}^2}{2I} \quad (I = \mu R_0^2)$

• Hamiltonian for rigid rotations

$$\hat{H}_{\text{ang}} = -\frac{\hbar^2}{2\mu R_0^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] = \frac{1}{2\mu R_0^2} \frac{\hat{L}^2}{\sin^2\theta} = \frac{\hat{L}^2}{2I} \quad (I = \mu R_0^2)$$

• Quantum Hamiltonian is analogous to classical ones.

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

• Rigid rotor S.t.

R_0 - eqm bond len.

$$\hat{H}_{\text{ang}} Y_{lm}(\theta, \phi) = E_{\text{ang}} Y_{lm}(\theta, \phi)$$

$$\frac{\hat{L}^2}{2I} Y_{lm}(\theta, \phi) = \frac{\hbar l(l+1)}{2I} Y_{lm}(\theta, \phi) = \frac{\hbar l(l+1)}{2\mu R_0^2} Y_{lm}(\theta, \phi) \quad l = 0, 1, 2, \dots$$

$$\cdot [\hat{H}_{\text{ang}}, \hat{L}^2] = 0 \quad \text{since } \hat{H}_{\text{ang}} \propto \hat{L}^2$$

$$\cdot [\hat{H}_{\text{ang}}, \hat{L}_z] = 0$$

• The rotational quantum numbers l, m are so called "good" quantum labels.

$$\cdot [\frac{\hat{L}^2}{2I}, \hat{H}_{\text{vib}}] = [\hat{H}_{\text{vib}}, \hat{H}_{\text{ang}}] = 0$$

• The collection of labels $\{\vec{r}, n, l, m\}$ completely label the quantum state of molecule

• \vec{r} - global center translational state

• n - vibrational state

• l, m - rotational state

in harmonic oscillation and rigid rotor approximation.

• The dimer energy is thus

$$\cdot \hat{H} = \hat{H}_{\text{com}} + \hat{H}_{\text{res}} + \hat{H}_{\text{vib}} + \hat{H}_{\text{rot}} \Rightarrow \boxed{E_{\text{total}} = \frac{\hat{L}^2}{2M} + \hbar\omega_0(n + \frac{1}{2}) + \frac{\hbar^2 l(l+1)}{2I}}$$

• The dimer wavefunction is

$$\cdot \Psi(\vec{x}_1, \vec{x}_2) = \Psi(\vec{r}, \vec{z}) = \Xi_{\text{com}}(\vec{z}) R_n(r) Y_{lm}(\theta, \phi)$$

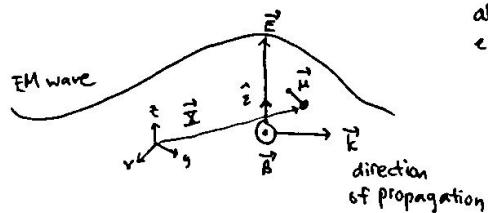
$$= N e^{\pm i(\vec{r} \cdot \vec{z}/\hbar)} \underbrace{\frac{1}{\sqrt{2^n n!}} \frac{1}{r} \left(\frac{\mu \omega_0}{\hbar I} \right)^{\frac{n}{2}} \cdot H_n \left(\frac{\mu \omega_0}{\hbar I} (r - R_0) \right)}_{\text{CoM translation}} \underbrace{e^{-\mu \omega_0 (r - R_0)^2 / 2\hbar}}_{\text{harmonic vibration}} \underbrace{Y_{lm}(\theta, \phi)}_{\text{rigid rotor}}$$

↳ Vibrational Spectroscopy
electromagnetic radiation

$$\cdot c = \lambda \nu$$

$$\cdot 2\pi c = \lambda \omega, \text{ where } \omega = 2\pi\nu$$

$$\Delta E \xrightarrow{\text{absorption}} AE = h\omega = h\nu = \frac{hc}{\lambda}$$



absorption of EM radiation
emission

- Interaction energy between molecular dipole and the applied field is

$$\begin{aligned} A_{int} &= -\vec{\mu} \cdot \vec{E}(\vec{x}) && \text{light-matter electric dipole coupling} \\ &= -\vec{\mu} \cdot E_0 \hat{e} \cos(\vec{k} \cdot \vec{x} - \omega t) \end{aligned}$$

- Both absorption & emission processes involve the transition probability from initial state $|i\rangle$ to final state $|f\rangle$:

$\vec{\mu}_{fi}$ = transition dipole moment

$$|\langle f | A_{int} | i \rangle|^2 = |\langle f | -\vec{\mu} \cdot \vec{E} | i \rangle|^2 = \left| -\overbrace{\langle f | \vec{\mu} | i \rangle}^0 \cdot \vec{E} \right|^2 = |\vec{\mu}_{fi} \cdot \vec{E}|^2$$

- Upon turning on a field, the transition dipole moment becomes

$$\vec{\mu}_{fi} = \langle f | \vec{\mu} | i \rangle = \int_{-\infty}^{\infty} \psi_f^*(x) \vec{\mu}(x_0 + x) \psi_i(x) dx, \quad x \text{ is time-dependent displacement}$$

→ permanent dipole moment $\vec{\mu}(x_0)$ - may exist in the absence of field

→ induced dipole moment $\vec{\mu}(x)$ - induced by field

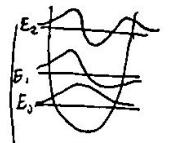
- If x is small compared to x_0 , Taylor expand

$$\vec{\mu}(x_0 + x) = \vec{\mu}(x_0) + x \frac{d\vec{\mu}(x_0)}{dx} + \dots$$

- Keep only linear contributions.

$$\begin{aligned} \vec{\mu}_{fi} &= \int_{-\infty}^{\infty} \psi_f^*(x) \vec{\mu}(x_0 + x) \psi_i(x) dx \\ &\equiv \int_{-\infty}^{\infty} \psi_f^*(x) \left[\vec{\mu}(x_0) + x \frac{d\vec{\mu}(x_0)}{dx} \right] \psi_i(x) dx \\ &= \underbrace{\int_{-\infty}^{\infty} \psi_f^*(x) \vec{\mu}(x_0) \psi_i(x) dx}_{\text{permanent dipole}} + \underbrace{\int_{-\infty}^{\infty} \psi_f^*(x) x \frac{d\vec{\mu}(x_0)}{dx} \psi_i(x) dx}_{\text{induced dipole}} \\ &= \vec{\mu}(x_0) \int_{-\infty}^{\infty} \psi_f^*(x) \psi_i(x) dx + \frac{d\vec{\mu}(x_0)}{dx} \underbrace{\int_{-\infty}^{\infty} \psi_f^*(x) x \psi_i(x) dx}_{\langle f | x | i \rangle} \end{aligned}$$

$$\boxed{\vec{\mu}_{fi} = \frac{d\vec{\mu}(x_0)}{dx} \langle f | x | i \rangle}$$



- For vibrational excitations, $|i\rangle \rightarrow |f\rangle$ ($|n\rangle \rightarrow |n'\rangle$)

$$\cdot \langle n' | x | n \rangle = \int_{-\infty}^{\infty} \psi_{n'}^*(x) x \psi_n(x) dx \quad (\text{for } 0 \rightarrow 0, 0 \rightarrow 2 \text{ gives } 0, \text{ but } 0 \rightarrow 1 \text{ gives finite})$$

- Harmonic oscillator/vibrational selection rule $n' - n = \Delta n = \pm 1$

$\left\{ \begin{array}{l} +1 \text{ absorption} \\ -1 \text{ emission} \end{array} \right.$

<< Vibrational Spectroscopy

→ Degrees of Freedom

- More than 2 atoms molecules ($N = \# \text{molecules}$)

• linear

- 3N total dof

- 3 center of mass translation

- 2 rotation dof

- $3N - 5$ vibrational dof

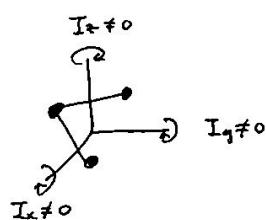
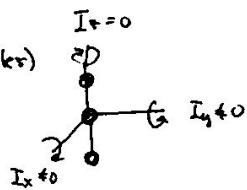
• nonlinear

- 3N total dof

- 3 center of mass translation

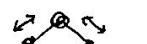
- 3 rotations

- $3N - 6$ vibrational dof



e.g. H₂O

$$3 \times 3 - 6 = 3 \text{ vibrational dof (normal mode)}$$



symmetric stretch

$$\lambda = 2.7 \mu\text{m}$$

$$\tilde{\nu} = 3652 \text{ cm}^{-1}$$



asymmetric stretch

$$\lambda = 2.662 \mu\text{m}$$

$$\tilde{\nu} = 3756 \text{ cm}^{-1}$$



bend

$$\lambda = 5.13 \mu\text{m}$$

$$\tilde{\nu} = 1595 \text{ cm}^{-1}$$

<< Rotational Spectroscopy

- rigid rotor Hamiltonian considers nuclear angular momentum, switch symbol to \vec{J} instead of $\vec{\tau}$.

$$\hat{H} = \frac{\hat{\tau}_z^2}{2I} = \frac{\vec{\tau}^2}{2I}$$

$$\vec{\tau}^2 Y_{JM} = \hbar^2 J(J+1) Y_{JM}$$

$$T_z Y_{JM} = \hbar m Y_{JM}$$

- At fixed bond length (rigid rotor approx), the E-field exerts torque of a molecule

- Probability for a rotational transition between initial and final rotation state is

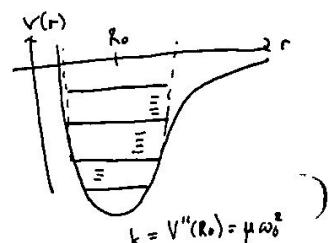
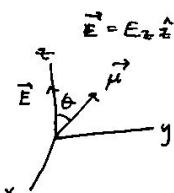
$$P_{fi} = \left| \langle f | -\vec{\mu} \cdot \vec{E} | i \rangle \right|^2 = \left| \langle f | -\mu_z E_z \cos\theta | i \rangle \right|^2$$

- Transition dipole moment is

$$\mu_{fi} \approx \langle f | \mu_z \cos\theta | i \rangle = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta Y_{f,M}^*(\theta, \phi) \mu_z \cos\theta Y_{IM}(\theta, \phi)$$

$$= \mu_z \delta_{M' M} \delta_{J' J \pm 1}$$

- rotational selection rule - $\Delta J = \pm 1$, $\Delta M = 0$ for rotational transition



--> Hydrogen Atom

- In the COM frame, the Hamiltonian becomes

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 + V(|\vec{r}|)$$

- Coulomb potential is a central potential, independent of θ, ϕ .

$$V(|\vec{r}|) = V(r) = \frac{q_1 q_2}{|\vec{r}|} = -\frac{e^2}{r}$$

- proton is 2000x heavier, so approx mass

$$\mu = \frac{m_p m_e}{m_p + m_e} = \frac{m_e}{1 + \frac{m_p}{m_e}} \approx m_e \approx m$$

- Schrodinger eqn for hydrogen

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\vec{r}}^2 + V(|\vec{r}|) \right] \psi(\vec{r}) = E \psi(\vec{r})$$

$$\underbrace{\left[-\frac{\hbar^2}{2m_e} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\vec{l}^2}{2m_e r^2} \right]}_{\text{radial}} \underbrace{-\frac{e^2}{r}}_{\text{radial}} \psi(r) = E \psi(r)$$

- The near-separation of radial & angular energies motivates the ansatz

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

- Substitute ansatz to S.E. gives

$$-\frac{\hbar^2}{2m_e r^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} (R(r) Y(\theta, \phi)) \right) + \frac{\vec{l}^2}{2m_e r^2} R(r) Y(\theta, \phi) - \frac{e^2}{r} R(r) Y(\theta, \phi) = E R(r) Y(\theta, \phi)$$

$$-\frac{\hbar^2}{2m_e r^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} (R(r) Y(\theta, \phi)) \right) - \frac{e^2}{r} R(r) Y(\theta, \phi) + \frac{\vec{l}^2 l(l+1)}{2m_e r^2} R(r) Y(\theta, \phi) = E R(r) Y(\theta, \phi)$$

- Note the competing potential energies

Coulomb potential = $-\frac{e^2}{r}$ (attractive)

Centrifugal potential = $\frac{\vec{l}^2 l(l+1)}{2m_e r^2}$ (repulsive)

adds up to effective potential

$$V_{\text{eff}}(r) = \frac{\vec{l}^2 l(l+1)}{2m_e r^2} - \frac{e^2}{r}$$

- So the Hydrogen S.E. becomes

$$\left[-\frac{\hbar^2}{2m_e r^2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V_{\text{eff}}(r) \right] R Y = E R Y$$

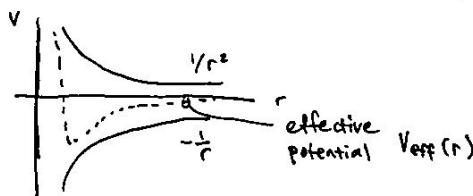
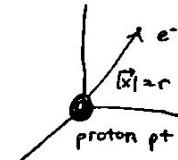
has eigenenergies

$$E_n = -\frac{e^2}{2a_0 n^2} = -\frac{m_e^4}{2\hbar^2 n^2} = \frac{R_H}{n^2}$$

> Rydberg energy - $R_H = 13.6 \text{ eV}$

> principal quantum # - $n = 1, 2, 3, \dots$

> Bohr radius - $a_0 = \frac{\hbar^2}{m_e e^2} \approx 0.529 \text{ \AA}$



- The wavefunctions (eigenfunctions) are

$$\psi(\vec{r}) = \Psi_{nlm}(\vec{r})$$

$$= R_{nl}(r) Y_{lm}(\theta, \phi)$$

- One-electron wavefunction
aka orbitals

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

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

$$m = -l, \dots, 0, \dots, l$$

$\underbrace{\hspace{1cm}}_{2l+1}$

orbitals

$$\begin{array}{ll} l=0 & s \\ l=1 & p \\ l=2 & d \end{array}$$

→ Wavefunctions

- $\psi_{100} = N e^{-r/a_0}$ (1s orbital)

- Normalization: $I = \int |\psi_{100}(r)|^2 dr$

$$I = N^2 \int_0^{2\pi} \int_0^\pi \int_0^\infty e^{-2r/a_0} r^2 \sin\theta dr d\theta d\phi$$

$$I = N^2 \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^\infty e^{-2r/a_0} r^2 dr$$

$$I = N^2 2\pi (2) \int_0^\infty e^{-2r/a_0} r^2 dr$$

$$I = N^2 2\pi (2) \frac{2 a_0^3}{2^3}$$

$$I = N^2 \pi a_0^3$$

$$N = \sqrt{\frac{1}{\pi a_0^3}}$$

- $\psi_{100} = \sqrt{\frac{1}{\pi a_0^3}} e^{-r/a_0}$

- $\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$ (2p_z orbital)

- $\psi_{310} = \frac{1}{8\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{5/2} \left[6\frac{r}{a_0} - \frac{r^2}{a_0^2}\right] e^{-r/3a_0} \cos\theta$ (3p_z orbital)

→ Probability, Expectation Value

- $\text{Prob}(x, x+dx; y, y+dy; z, z+dz) = \text{Prob}(\vec{r}, \vec{r}+d^3\vec{r})$

$$= |\psi_{nlm}(\vec{r})|^2 d^3x$$

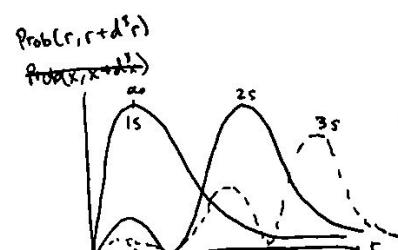
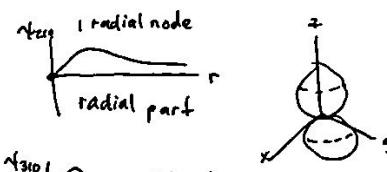
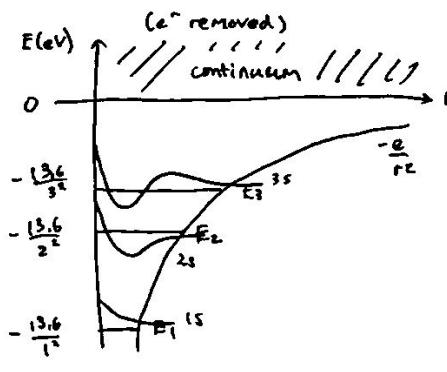
- $\langle r \rangle_{nlm} = \int r \text{Prob}(\vec{r}, \vec{r}+d^3\vec{r})$ is average position of e⁻ in the nlm orbital

$$\langle r \rangle_{nlm} = n^2 a_0 \left[1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right]$$

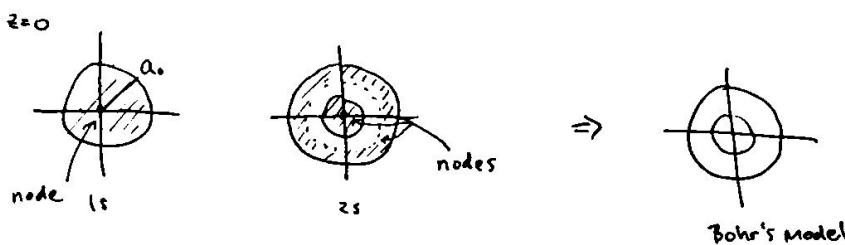
- Most probable e⁻ position independent of θ, φ is in nlm is.

$$\frac{d}{dr} \text{Prob}(r, r+dr) = \frac{d}{dr} \int_{-\infty}^{\infty} \text{Prob}(\vec{r}, \vec{r}+d^3\vec{r}) = 0$$

$$\Rightarrow r_{\text{most prob}} = a_0 \approx 0.529 \text{ Å}$$



<< Orbitals



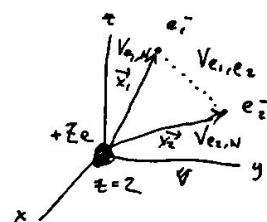
<< Many Electron Atom

- In ${}^2\text{He}$, we have e^-e^- repulsion and e^- -nucleus attraction.

- Coulomb interaction

$$\cdot V_{e_iN} = \frac{(-e)(+2e)}{|\vec{x}_i|} = -\frac{2e^2}{r_i} \quad r_i \equiv |\vec{x}_i| \quad i=1,2$$

$$\cdot V_{e_1e_2} = \frac{(-e)(-e)}{|\vec{x}_1 - \vec{x}_2|} = \frac{e^2}{r_{12}} \quad r_{12} \equiv |\vec{x}_1 - \vec{x}_2|$$



- Helium Schrodinger Equation (nucleus at rest):

$$\left[\underbrace{-\frac{\hbar^2}{2m}\nabla_i^2}_{\text{KE } e_i} + \underbrace{-\frac{\hbar^2}{2m}\nabla_2^2}_{\text{KE } e_2} - \underbrace{\frac{2e^2}{|\vec{x}_1|}}_{e_1-N \text{ attraction}} - \underbrace{\frac{2e^2}{|\vec{x}_2|}}_{e_2-N \text{ attraction}} + \underbrace{\frac{e^2}{|\vec{x}_1 - \vec{x}_2|}}_{e_1-e_2 \text{ repulsion}} \right] \psi(\vec{x}_1, \vec{x}_2) = E \psi(\vec{x}_1, \vec{x}_2)$$

many e^- wavefunction

- Because we know empirically that e^- in different orbitals behave differently, this motivates the orbital approximation of expressing a many- e^- wavefunction as a product of orbitals (single- e^- wavefunction):

$$\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_n) = \phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \dots \phi_n(\vec{x}_n)$$

- The approximation would be exact if without e^-e^- repulsion.

- Correlation energy ~ e^-e^- repulsion term (missed by orbital approx)

- The strategy to determine the orbitals ϕ_i and orbital energies E_i to minimize the atom's energy $E = \langle H \rangle$ with respect to variations in the orbitals subject to the constraint that the orbitals remain orthonormal.

In general, for $\Psi(\vec{x}_1, \dots, \vec{x}_N) = \phi_1(\vec{x}_1) \dots \phi_N(\vec{x}_N) = \prod_{i=1}^N \phi_i(\vec{x}_i)$

The average energy
to be minimized
with constraint

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle - \sum_{ij=1}^N \varepsilon_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij})$$

orthonormal constraint

$$\frac{\partial E}{\partial \phi_i} = 0$$

Lagrange multiplier

$$E[\Psi] = \int \int \phi_1^*(\vec{x}_1) \dots \phi_N^*(\vec{x}_N) \left\{ \sum_{i=1}^N -\frac{\hbar^2 \nabla_i^2}{2m} + \sum_{i=1}^N -\frac{Ze^2}{|\vec{x}_i|} + \frac{1}{2} \sum_{i,j=1}^N \frac{e^2}{|\vec{x}_i - \vec{x}_j|} \right\} \phi_1(\vec{x}_1) \dots \phi_N(\vec{x}_N) d^3x_1 \dots d^3x_N$$

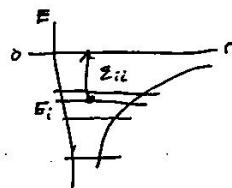
$$- \sum_{ij=1}^N \varepsilon_{ij} \int \phi_i^*(\vec{x}) \phi_j(\vec{x}) - \delta_{ij} d^3x$$

After optimizing $E[\Psi]$, we have Hartree orbital equations

$$\left[-\frac{\hbar^2 \nabla_i^2}{2m} - \frac{Ze^2}{|\vec{x}_i|} + \sum_{j=1, j \neq i}^N \int \frac{e^2 \phi_j^*(\vec{x}') \phi_j(\vec{x}')}{|\vec{x} - \vec{x}'|} d^3x' \right] \phi_i(\vec{x}) = \varepsilon_{ii} \phi_i(\vec{x})$$

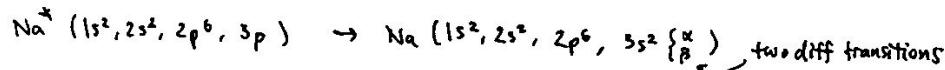
an N-coupled and nonlinear orbital equations that must be solved self-consistently

$\varepsilon_{ii} = \varepsilon_i$ are the ionization energy



<< Spin

- In 1925, Uhlenbeck & Goudsmit conjectured a new "spin" angular momentum to interpret the doubling of spectral lines observed in the emission of light from



- Spin has no classical analog.
- Assume spin is an angular momentum.
- Spin satisfies all the usual angular momentum relations

> Spin vector - $\vec{S} = S_x \hat{x} + S_y \hat{y} + S_z \hat{z}$

- $\vec{S}^2 = \vec{S} \cdot \vec{S} = S^2 = S_x^2 + S_y^2 + S_z^2$

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

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

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

- $[\vec{S}^2, S_i] = 0 \quad i=x, y, z$

- The eigenvalues of \vec{S}^2 and S_z are:

- $\vec{S}^2 \leftrightarrow \hbar^2 s(s+1)$

- $S_z \leftrightarrow \hbar M_s$

- What are images of s and M_s ? Experiments!

- For e^- , $s = \frac{1}{2}$, $M_s = -s, \dots, s$ in integer steps

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

- Eigenfunctions of S_z are α and β

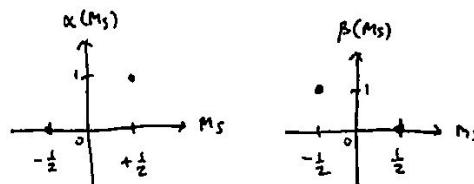
- $S_z \alpha = +\frac{1}{2} \hbar \alpha$

- $S_z \beta = -\frac{1}{2} \hbar \beta$

- α and β are discrete functions of M_s

- $\alpha(M_s) = \begin{cases} 1 & \text{if } M_s = +\frac{1}{2} \\ 0 & \text{if } M_s = -\frac{1}{2} \end{cases}$

- $\beta(M_s) = \begin{cases} 0 & \text{if } M_s = +\frac{1}{2} \\ 1 & \text{if } M_s = -\frac{1}{2} \end{cases}$



- α and β are also eigenv of \vec{S}^2 :

- $\vec{S}^2 \alpha = \hbar^2 \frac{1}{2} (\frac{1}{2}+1) \alpha = \frac{3}{4} \hbar^2 \alpha$

- $\vec{S}^2 \beta = \hbar^2 \frac{1}{2} (\frac{1}{2}+1) \beta = \frac{3}{4} \hbar^2 \beta$

- $M_s = \begin{cases} +\frac{1}{2} & \text{spin up} \\ -\frac{1}{2} & \text{spin down} \end{cases}$

<< Space-spin wavefunctions

• 1 e⁻: $\psi(\vec{x}, m_s) = \psi(x, y, z, m_s) = \psi(\vec{x}) \cdot \begin{cases} \alpha(m_s) \\ \beta(m_s) \end{cases}$

• Normalization: $\int_{m_s=-\frac{1}{2}}^{+\frac{1}{2}} |\psi(\vec{x}, m_s)|^2 d^3x$

$$= \sum_{m_s=-\frac{1}{2}}^{+\frac{1}{2}} \int |\psi(\vec{x})|^2 \cdot \begin{cases} |\alpha(m_s)|^2 \\ |\beta(m_s)|^2 \end{cases} d^3x$$

$$= \underbrace{\int |\psi(\vec{x})|^2 d^3x}_{\text{spatial part}} \sum_{m_s=-\frac{1}{2}}^{+\frac{1}{2}} \underbrace{\begin{cases} |\alpha(m_s)|^2 \\ |\beta(m_s)|^2 \end{cases}}_{\text{spin part}}$$

$$= 1 \checkmark$$

• Here, the total energy is spin independent, but wavefunction is not

- spin-orbit coupling ($\alpha \vec{L} \cdot \vec{s}$) adds spin-dependence to the energy and explains the Goudsmit & Uhlenbeck experiment.

- Without coupling, each level has double degeneracy

- Many e⁻ & the indistinguishability of identical particles

L26 Many e^- & Indistinguishability of Identical Particles

\leftrightarrow Spin-Spin Permutation

\rightarrow Spin-spin permutation (exchange) operator P_{ij}

$$P_{ij} \psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N) = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

where $\vec{r}_i = (\vec{x}_i, m_{s_i})$ is the space-spin coordinate of particle i

• Helium example:

$$\psi_{12} \{ \psi_1(\vec{x}_1) \alpha(m_{s_1}) \psi_2(\vec{x}_2) \beta(m_{s_2}) \} = \psi_1(\vec{x}_2) \alpha(m_{s_2}) \psi_2(\vec{x}_1) \beta(m_{s_1})$$

• Find eigenfunction of P_{ij} and eigenvalues

$$P_{ij} P_{ij} u = P_{ij}^2 u = 1$$

$$P_{ij} u = \lambda u$$

$$P_{ij} P_{ij} u = P_{ij} \lambda u$$

$$u = P_{ij} \lambda u$$

$$u = \lambda P_{ij} u$$

$$u = \lambda^2 u$$

$$P_{ij}^2 = \lambda^2 = 1$$

$$\lambda = \pm 1$$

• 2 eigenval \rightarrow 2 eigfunc

$\lambda = +1$

$$P_{ij} u_+ (\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = u_+ (\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

$$= (+1) u_+ (\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) \xrightarrow{\text{equivalent!}}$$

$\Rightarrow u_+$ is symmetric under interchange of identical particles

$\lambda = -1$

$$P_{ij} u_- (\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = u_- (\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

$$= (-1) u_- (\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) \xrightarrow{\text{equivalent}}$$

$\Rightarrow u_-$ is asymmetric under interchange of identical particles

$>$ Fermions - $\frac{1}{2}$ -integer spin particles (e.g. electrons)

• transform asymmetrically under P_{ij}

$>$ Bosons - integer spin particles

• transform symmetrically under P_{ij}

• Electrons are fermions with $s = \frac{1}{2}$.

<< Pauli Exclusion Principles

- For N electrons (spin $\frac{1}{2}$, so $\lambda = -1$):

$$\psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_{j+1}, \dots, \vec{r}_N) = (-)^j \psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

- When $\vec{r}_i = \vec{r}_j$

$$\underbrace{\psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_i, \dots, \vec{r}_N)}_0 = (-)^j \psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_i, \dots, \vec{r}_N) \Rightarrow \text{Pauli exclusion principle}$$

There is zero probability finding two e^- at the same point in space with same spin.

<< Helium Atom ($2e^-$)

- two possible spin states: $\alpha(1) = \alpha(M_{S1})$, $\alpha(2) = \alpha(M_{S2})$

With conventions $\beta(1) = \beta(M_{S1})$, $\beta(2) = \beta(M_{S2})$

$$\alpha(1)\alpha(2), \alpha(1)\beta(2), \alpha(2)\beta(1), \beta(1)\beta(2)$$

- Apply P_{ij} : $\downarrow \quad \downarrow \quad \downarrow \quad \downarrow$
- | | | | |
|------------------------------------|----------------------------|----------------------------|------------------------------------|
| $\alpha(2)\alpha(1)$ | $\alpha(2)\beta(1)$ | $\alpha(1)\beta(2)$ | $\beta(2)\beta(1)$ |
| symmetric
under $P_{ij}=P_{12}$ | not eigfunc
of P_{12} | not eigfunc
of P_{12} | symmetric
under $P_{ij}=P_{12}$ |

- But the linear combination $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]$ are eigfunc of P_{12}

$$\begin{aligned} & + \text{ combination: } P_{12} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ &= \frac{1}{\sqrt{2}} [\alpha(2)\beta(1) + \beta(2)\alpha(1)] \\ &= \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{aligned} \quad \left. \begin{array}{l} \text{symmetric} \\ \text{under } P_{ij}=P_{12} \end{array} \right\}$$

$$\begin{aligned} & - \text{ combination: } P_{12} \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \frac{1}{\sqrt{2}} [\alpha(2)\beta(1) - \beta(2)\alpha(1)] \\ &= - \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{aligned} \quad \left. \begin{array}{l} \text{asymmetric} \\ \text{under } P_{12} \end{array} \right\}$$

<< Helium Ground State

- Spatial wavefunc - $\Phi_{1s}(\vec{r}_1) \Phi_{1s}(\vec{r}_2)$

• transforms symmetrically under P_{2z}

- space-spin wavefunc - $\Psi_{\text{ground}}(\vec{r}_1, \vec{r}_2) = \underbrace{\Phi_{1s}(\vec{r}_1)}_{\text{antisymmetric}} \underbrace{\Phi_{1s}(\vec{r}_2)}_{\text{symmetric}} \cdot \underbrace{\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]}_{\text{antisymmetric}}$

$$\vec{r}_i = (\vec{r}_i, \frac{\alpha}{\beta})$$

<< Helium 1st Excited state

$$\bullet \Psi_1(\vec{r}_1, \vec{r}_2) = \underbrace{\frac{1}{\sqrt{2}} [\Phi_{1s}(\vec{r}_1) \Phi_{2s}(\vec{r}_2) - \Phi_{2s}(\vec{r}_1) \Phi_{1s}(\vec{r}_2)]}_{\text{antisymmetric}} \cdot \underbrace{\begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\alpha(2) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{cases}}_{\text{symmetric}}$$

> spin multiplicity = 2s+1

$$\begin{array}{c} \alpha\alpha \\ \uparrow\uparrow, \downarrow\downarrow \\ \text{triplets} \\ s = \frac{1}{2} + \frac{1}{2} = 1 \end{array}$$

$$\begin{array}{c} \uparrow\downarrow, \uparrow\uparrow + \downarrow\uparrow \\ \text{singlets} \\ s = \frac{1}{2} - \frac{1}{2} = 0 \end{array}$$

<< Generalization to Many e⁻

- 1929, Slater noticed that many e⁻ wavefunctions can be written as a determinant (in orbital approx)

$$\begin{aligned} \Psi_{\text{ground}}(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} \det \begin{bmatrix} \Phi_{1s}(\vec{r}_1) \alpha(1) & \Phi_{1s}(\vec{r}_2) \beta(2) \\ \Phi_{1s}(\vec{r}_2) \alpha(2) & \Phi_{1s}(\vec{r}_1) \beta(1) \end{bmatrix} \leftarrow e^{-1} \\ &\quad \uparrow \quad \uparrow \\ &\quad \text{orbital 1} \quad \text{orbital 2} \\ &= \frac{1}{\sqrt{2}} [\Phi_{1s}(\vec{r}_1) \alpha(1) \Phi_{1s}(\vec{r}_2) \beta(2) - \Phi_{1s}(\vec{r}_2) \alpha(2) \Phi_{1s}(\vec{r}_1) \beta(1)] \end{aligned}$$

• Li ground state

$$\Psi_{\text{ground}}(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{\sqrt{3!}} \det \begin{bmatrix} \Phi_{1s}(\vec{r}_1) \alpha(1) & \Phi_{1s}(\vec{r}_2) \beta(1) & \Phi_{2s}(\vec{r}_3) \alpha(1) \\ \Phi_{1s}(\vec{r}_2) \alpha(2) & \Phi_{1s}(\vec{r}_3) \beta(2) & \Phi_{2s}(\vec{r}_1) \alpha(2) \\ \Phi_{1s}(\vec{r}_3) \alpha(3) & \Phi_{1s}(\vec{r}_1) \beta(3) & \Phi_{2s}(\vec{r}_2) \alpha(3) \end{bmatrix} \leftarrow e^{-1} \\ \quad \uparrow \quad \uparrow \quad \uparrow \\ \quad \text{orbital 1} \quad \text{orbital 2} \quad \text{orbital 3}$$

> Slater determinant

could choose β too here

Hartree-Fock Orbital Equations

- How do we find new orbitals that result in antisymmetric many-e⁻ wavefunction?

Do what we did before but with spin dependence: $\Phi_i^*(\vec{r}_i) = \Phi_i^*(\vec{x}_i)$. $\downarrow \beta$

$$\frac{\partial}{\partial \Phi_i} \langle \Psi | H | \Psi \rangle = 0 \quad \text{subjected to constraint} \quad \langle \Phi_i | \Phi_j \rangle = \delta_{ij}$$

> Hartree-Fock orbital equations

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + \frac{-Ze^2}{|\vec{r}|} \right] \Phi_i(\vec{r}) + \sum_{j=1}^N \left[\int \frac{e^2 \Phi_j^*(\vec{r}') \Phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \Phi_i(\vec{r}) \right] \rightarrow \text{mean-field Coulomb repulsion } J(\vec{r})$$

$$- \int \frac{e^2 \Phi_j^*(\vec{r}') \Phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \Phi_j(\vec{r}) = \varepsilon_i \Phi_i(\vec{r}) \text{ exchange } K(\vec{r})$$

$$\cdot \int d\vec{r}^3 = \int d^3 x \sum_m$$

$$\cdot \vec{r} = (\vec{x}, m_s)$$

- Since V_{eff} is a function of radius only, the angular solutions are the same as those of Hydrogen (Y_{lm})

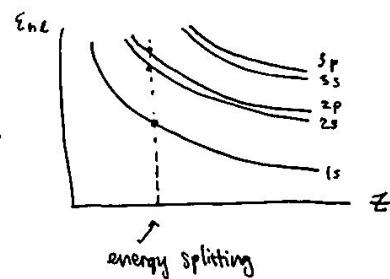
$$V_{eff}(\vec{r})$$

- For $N e^-$ atoms, we still have the usual s, p, d, f, g, ... orbitals
- The most important place where the radial dependence changes the analysis lies in the energy.

Which depends on both n and l : E_{nl} , unlike Hydrogen has $E_n = -\frac{Ry}{n^2}$

- In terms of the wavefunctions $\Phi_i(\vec{r})$, the presence of core e⁻ shields the atomic nucleus
- Effectively lowering V_{eff} and atomic # seen by valence e⁻

> Aufbau principle - fill e⁻ in increasing orbital energy (building up)



Chemical Bonding

- For a general molecule with $N e^-$ and M nuclei, the exact wavefunc is

$$\Psi_{\text{ex}}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M)$$

excited electronic state

$\underbrace{\qquad\qquad\qquad}_{N e^-} \quad \underbrace{\qquad\qquad\qquad}_{M \text{ nuclei}}$

$3(N+M)$ dimension

- Atomic nucleus is $2000\times$ heavier than e^- , so we approximate the wave func as

$$\Psi_{\text{ex}}(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M) \approx \psi_{\text{el}}(\vec{r}_1, \dots, \vec{r}_N; \{\vec{R}_1, \dots, \vec{R}_M\}) \chi(\vec{R}_1, \dots, \vec{R}_M)$$

> Born-Oppenheimer approximation - separate e^- and nucleus wavefunc based on mass diff

- Molecular Hamiltonian

$$H = T_{\text{el}} + T_{\text{nuc}} + V_{\text{ee}} + V_{\text{nn}} + V_{\text{en}} \quad (\text{Let } H_{\text{ex}} = T_{\text{el}} + V_{\text{ee}} + V_{\text{nn}} + V_{\text{en}})$$

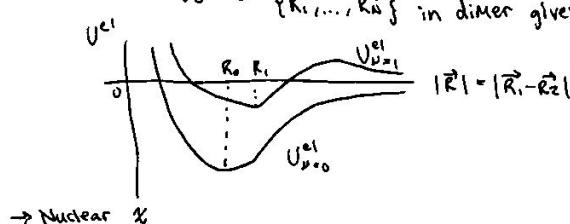
$$= T_{\text{nuc}} + H_{\text{el}}$$

→ Electronic ψ_{el}

- At frozen nuclear geometries

$$H_{\text{el}} \psi_{\text{el}}(\vec{r}_1, \dots, \vec{r}_N; \{\vec{R}_1, \dots, \vec{R}_M\}) = U_{\text{el}}^1(R_1, \dots, R_N) \psi_{\text{el}}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; \{\vec{R}_1, \dots, \vec{R}_M\})$$

- Electronic energy vs $\{\vec{R}_1, \dots, \vec{R}_M\}$ in dimer gives

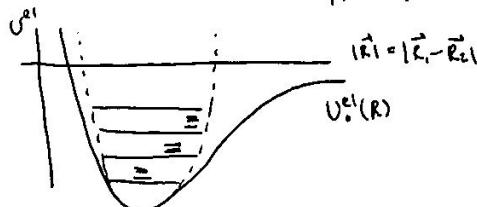


→ Nuclear χ

- Nuclear Schrodinger eqn gives

$$T_{\text{nuc}} \chi_o(\vec{R}_1, \dots, \vec{R}_M) + U_o^1(\vec{R}_1, \dots, \vec{R}_M) \chi_o(\vec{R}_1, \dots, \vec{R}_M) = E \chi_o(\vec{R}_1, \dots, \vec{R}_M)$$

- Harmonic oscillator & rigid rotor approx gives



<< Dimer H_2^+

- Develop molecular orbitals by linear combination of atomic orbitals (MO-LCAO)

- Wavefunction ansatz for MO are

$$\Psi(\vec{r}) = c_1 \phi_1(\vec{r}) + c_2 \phi_2(\vec{r})$$

$$MO = c_1(AO) + c_2(AO)$$

- To find the MOs, invoke the variational principle with Born-Oppenheimer approx.

$$E = \frac{\langle \Psi | H_{\text{eff}} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$\text{where } \Psi(\vec{r}) = c_1 \phi_1(\vec{r}) + c_2 \phi_2(\vec{r})$$

$$E(c_1, c_2) = \frac{|c_1|^2 H_{11} + |c_2|^2 H_{22} + 2c_1 c_2 H_{12}}{|c_1|^2 + |c_2|^2 + 2c_1 c_2 S_{12}}$$

$$\text{where } H_{ij} = \langle \phi_i | H_{\text{eff}} | \phi_j \rangle, H_{11} = E_0, H_{22} = E_0$$

$$S_{12} = \langle \phi_1 | \phi_2 \rangle, \text{ the overlap}$$

- If the orbitals don't overlap ($H_{11} = H_{22} = E_0$),

$$E(c_1, c_2) = \frac{|c_1|^2 E_0 + |c_2|^2 E_0}{|c_1|^2 + |c_2|^2} = E_0 \quad \text{since}$$

$$H_{12} = \langle \phi_1 | H_{\text{eff}} | \phi_2 \rangle = \langle \phi_1 | \phi_2 \rangle E_0 = 0$$

$$S_{12} = \langle \phi_1 | \phi_2 \rangle = 0$$

- Allow ϕ_1, ϕ_2 to overlap, so $S_{12} \neq 0, H_{12} \neq 0$, invoke variation principle

$$\frac{\partial E(c_1, c_2)}{\partial c_1} = 0 \quad \text{and} \quad \frac{\partial E(c_1, c_2)}{\partial c_2} = 0$$

$$(H_{11} - E)c_1 + (H_{12} - ES_{12})c_2 = 0$$

$$(H_{22} - E)c_2 + (H_{12} - ES_{12})c_1 = 0$$

$$\begin{bmatrix} H_{11} - E & H_{12} - ES_{12} \\ H_{22} - ES_{12} & H_{22} - E \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = 0$$

$$E_+ = \frac{E_0 - H_{12}}{1 - S_{12}}$$

$$E_- = \frac{E_0 + H_{12}}{1 - S_{12}}$$

