Chemistry 344 - [redacted]
Summary of Topics

I. Review of basic quantum mechanical principles

A. Scale - correspondence

1) the need for q.m. comes when classical mechanics fails for atomic scale systems - small mass & size

2) Early 20th century problems and solutions you've studied

a) Black body radiation
Planck - energy not continuous

b) Photoelectric effect
Einstein - light had particulate nature
• photon: $E = h\nu$

c) Atomic line spectra
Bohr - energy levels - light emitted by "jump" from one to other: $\Delta E = h\nu$
- angular momentum restricted: $L = n\hbar$

d) DeBroglie - wave nature of particles: $\lambda = h/p$
Proof - electron diffraction - Davisson & Germer

e) Spectroscopic linewidths, excited state life times
Heisenberg uncertainty principle
$\Delta x \Delta p \gtrsim \hbar/2$
$\Delta E \Delta t \gtrsim \hbar$

N.B. ⟶ Opens era of modern quantum mechanics - must get idea straight.

3. Development of Quantúm Mechanics
- generalized formulation contain all of the § 2 "patches" to classical

a) Heisenberg - matrix mechanics - statistical

i) states = vectors
ii) observables = matrices

b) Schröedinger - wave mechanics

i) states = wave functions
ii) observables = operators

Follows classical wave equation approach (in effort to contain duality)

4. Postulates - a set of ground rules from which all else can be derived.

Post. I. Particle described completely by wave function, $\psi(\underset{\sim}{r},t)$, which is:

a) continuous, single valued, integrable square

b) $\psi^*\psi \, d\tau \rightarrow$ probability interpretation

c) Many (n) particles: $\psi(q,t)$ - where $q \rightarrow$ 3n positional coordinates

Post. II. Every observable corresponds to linear, hermetian operator.

a) linear $\hat{\alpha}(f_1 + f_2) = \hat{\alpha}f_1 + \hat{\alpha}f_2$

b) hermitian $\int \psi_n^* \hat{\alpha} \psi_m d\tau = \int \psi_m \hat{\alpha}^* \psi_n^* d\tau$

c) Correspondence with observables

Constant: $a \rightarrow \hat{a}$

position variable: $x \rightarrow \hat{x}$

function of position: $f(x) \rightarrow \widehat{f(x)}$

momentum: $p_x \rightarrow -i\hbar \frac{\partial}{\partial x}$

Post. III. <u>If</u> $\hat{\alpha}$ corresponds to an observable A, ψ_k is an eigenfunction of α with eigenvalue a_k and a set of identical systems are all in a state described by ψ_k; <u>then</u> result of measuring A on any of the systems will be a_k every time.

Post. IV. <u>If</u> the systems in III are <u>not</u> in states described by eigenfunctions of $\hat{\alpha}$, <u>then</u> a measurement of A on each system may be different. The average value of the distribution is:

$$\langle\alpha\rangle = \frac{\int \psi_s^* \hat{\alpha} \psi_s \, d\tau}{\int \psi_s^* \psi_s d\tau}$$

where ψ_s is the wave function that describes each system.

Post. V. Time evolution of $\psi(q,t)$ is given by:

$$i\hbar \frac{\partial}{\partial t} \Psi(q,t) = \mathcal{H} \Psi(q,t)$$

where $\mathcal{H}$ is the hamiltonian (total energy) operator.

-- if $\mathcal{H} \neq \mathcal{H}(t)$ $\quad \Psi(q,t) = \Psi(q) e^{-i Et/\hbar}$

5. Resultant properties of q.m. fct. & op. (fct. = abbreviation for function)

a. Orthonormality of eigenfunction:

normalized: $\int \psi^*_k \psi_k \, d\tau = 1$

orthogonal: $\int \psi^*_k \psi_{k'} \, d\tau = \delta_{kk'}$

b. Completeness: set of n fct ψ_i all orthonormal and spanning n-dimensional space is complete
- any fct ϕ can be expanded in complete set

$\phi = \sum_i c_i \psi_i$ where $c_i = \int \psi_i^* \phi \, d\tau$

c. Average value: $\langle \alpha \rangle = \dfrac{\int \phi^* \hat{\alpha} \phi \, d\tau}{\int \phi^* \phi \, d\tau}$

Contribution of each eigen value a_k weighted by "projection" of ϕ upon "basis set" ψ_k's

d. Commutation: in general $\hat{\alpha}\hat{\beta} \neq \hat{\beta}\hat{\alpha}$

<u>if</u> $[\hat{\alpha}, \hat{\beta}] = \hat{\alpha}\hat{\beta} - \hat{\beta}\hat{\alpha} = 0 \rightarrow$ commute

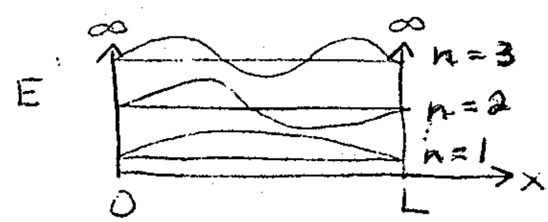
(remember these are operators)

If two operators commute they will have simultaneous eigenfunctions: if $[A,B] = 0$

e. Relationship to Uncertainty Principle, consider $\hat{\alpha}, \hat{\beta}$
- if commute - same eigenfct; can measure observables of both equally accurate
- if do not commute - then system can only be in eigenfct of one or other, i.e. <u>if one precise</u>, <u>other unknown</u>.

B. Model systems

1. Particle in a box



a) $\mathcal{H} = -\hbar^2/2m \; \partial^2/\partial x^2$

b) B.C. $\Psi(L) = \Psi(0) = 0$
↳ Boundary Condition

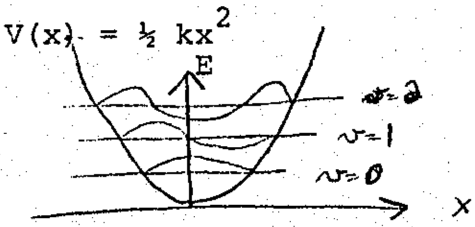
c) $\Psi = A \sin \alpha x$ - eigen function

$\alpha = n\pi/L$ - from B.C.

$A = \sqrt{2/L}$ - from normalization

d) $E_n = \dfrac{\hbar^2}{2m} \dfrac{n^2\pi^2}{L^2}$ -<u>quantized energy</u>

2. Harmonic oscillator $V(x) = \frac{1}{2} kx^2$



a) $\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{1}{2} kx^2$

b) B.C.$\Rightarrow \psi(\pm \infty) = 0$

c) $\psi_v = N_v H_v(y) \exp(\frac{-y^2}{2}) \rightarrow$ solution

where $y = \sqrt{\beta}\, x$, $\beta = \frac{\sqrt{km}}{\hbar}$; N_v-normalization factor

$H_v(y)$ - hermite polynomial

$$H_v(y) = (-1)^v e^{y^2} \frac{d^v}{dy^v}\left(e^{-y^2}\right)$$

d) $E_v = (v + 1/2)\hbar\omega$; $\underline{\omega = 2\pi\nu = \sqrt{k/m}}$ = angular frequency of vibration

Application — Vibrational spectroscopy, isotope effects

3. Rigid Rotor - 2 particle system, change of variable

a) $\mathcal{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2$ (6-dimension)

b) Center of Mass coordinates allow reduction to 3-D:

$$\mathcal{H}_r = -\frac{\hbar^2}{2\mu} \nabla_r^2 , \quad x = x_1 - x_2, \quad y = x_1 - y_2, \quad z = z_1 - z_2 \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

relative coord

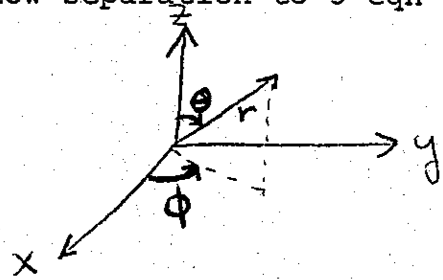
$I = \mu r^2$-moment of inertia

c) Spherical coordinates allow separation to 3 eqn:

$x = r\cos\phi\sin\theta$

$y = r\sin\phi\sin\theta$

$z = r\cos\theta$



Since r - constant (rigid) - 2 equations:

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi$$

$$\frac{d^2\Theta}{d\theta^2} + \frac{\cos\theta}{\sin\theta}\frac{d\Theta}{d\theta} + \left(\frac{2IE}{\hbar^2} - \frac{m^2}{\sin^2\theta}\right)\Theta = 0$$

d) Soln: $\Phi_m(\phi) = e^{im\phi}$ $\quad m = 0, \pm 1, \pm 2 \cdots$ } not normalized

$\Theta_{\ell m}(\theta) = P_\ell^{|m|}(\cos\theta)$ - assoc. Legendre

$$P_\ell^{|m|}(x) = (1-x^2)^{m/2}\frac{d^m}{dx^m}P_\ell(x)$$

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell$$

limits

$\ell = 0,1,2,3$ --- pos. integers

$|m| \leq \ell$ and m = integer $\Rightarrow m = 0, \pm 1, \pm 2 \cdots \pm \ell$

e) $E_\ell = \dfrac{\ell(\ell+1)\hbar^2}{2I}$

i) each level <u>$2\ell + 1$ degerate</u>, $E_\ell \neq f(m)$

ii) ang momentum limited

Application - microwave spectroscopy,

f) Spherical Harmonics $Y_{\ell m} = N_{\ell m}\Theta_{\ell m}\Phi_m$

(here $N_{\ell m}$ = normulization constant)

- eigen function of ang. mom: $\underset{\sim}{L} = \underset{\sim}{r} \times \underset{\sim}{p}$

$$\hat{L}_z Y_{\ell m} = m\hbar Y_{\ell m}$$
$$\hat{L}^2 Y_{\ell m} = \ell(\ell+1)\hbar^2 Y_{\ell m}$$

4) Hydrogen Atom - 2 particles, central potential

a. $\mathcal{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{Ze^2}{r}$

b. Separate variables as for rigid rotor -

note: $V = V(r)$ only

c. θ,ϕ sol'n same as rotor: $Y_{\ell m}(\theta,\phi)$

d. r: $\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \left(\frac{2mE}{\hbar^2} + \frac{2mZe^2}{\hbar^2 r} - \frac{\ell(\ell+1)}{r^2}\right)R = 0$

sol'n: $R_{n\ell} = N x^{\ell} e^{-x/2} L_{n+\ell}^{2\ell+1}(x)$

where $x = \frac{2Zr}{na_o}$

$L_{n+\ell}^{2\ell+1}$ - LaGuerne polynomial

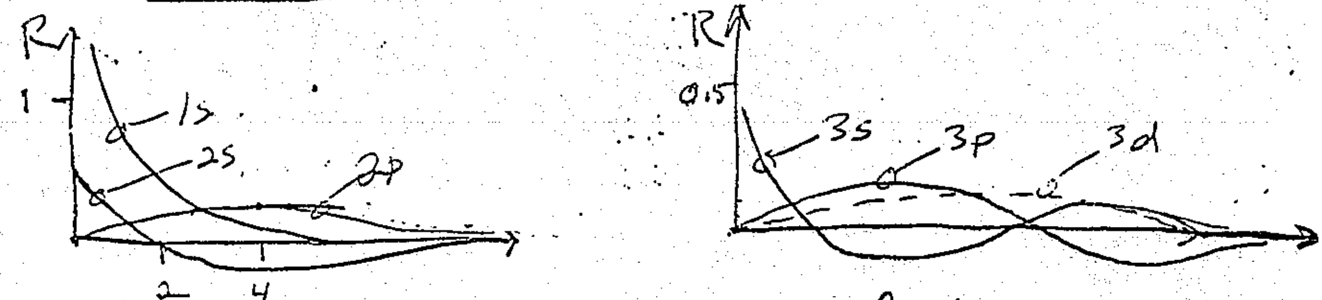
$n = 1,2,3....$ pos. integer

e. total solution:

$$\Psi = R_{n\ell}(r) Y_{\ell m}(\theta,\phi)$$
$$E_n = -\frac{me^4 Z^2}{2n^2\hbar^2}$$

Hydrogen atom <u>fundamental</u> to all of quantum chemistry more difficult problems typically use H-atom w/f as a <u>basis</u> <u>set</u>

Hence important to understand shapes and forms of solutions:



note: nodes # = $n-\ell-1$