

Chem. 1480
12 Mar. '07



Features of Classical Mechanics :

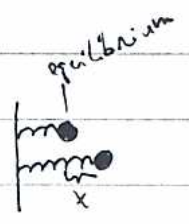
Central purpose : find trajectory $x(t)$

Basic Equation of motion (Newton) $F(x) = m \ddot{x}(t) \equiv m \dot{v}(t) \equiv \dot{p}(t)$

Example (1) Free particle $F=0 \Rightarrow x(t) = \frac{p_0}{m} t + x_0$

(2) $F = \text{const}$; e.g. $\downarrow g$, $F = mg$; now $x(t) = x_0 + \frac{p_0}{m} t + \frac{1}{2} \frac{F}{m} t^2$

(3) Linear restoring force (Harmonic Oscillator) $F(x) = -kx$; Now $m\ddot{x} = -kx$



Or: $\ddot{x}(t) = -\omega^2 x(t)$ where $\omega = \sqrt{k/m}$

Thus: $x(t) = \alpha \cos \omega t + \beta \sin \omega t = x_0 \cos \omega t + \frac{p_0}{m\omega} \sin \omega t$ $\leftarrow (x_0, p_0) \leftrightarrow A, \delta$

$= A \sin(\omega t + \delta) = A [\sin \omega t \cos \delta + \cos \omega t \sin \delta]$

Features of H.O. motion: $A = \text{amplitude (magnitude of maximum displacement)}$

$T = \text{period of oscillation}$; $\omega T = 2\pi$ or $T = \frac{2\pi}{\omega} = \frac{1}{\nu}$ \leftarrow frequency

Principle of Energy Conservation: define potential energy $V(x) = -\int_0^x F(x') dx'$

\uparrow
lower limit is arbitrary

- Thus, for $F=0$, $V(x) = 0$
 $F = \text{const}$, $V(x) = -Fx$
 $F = -kx$, $V(x) = \frac{1}{2} kx^2$

Now consider: $E = \text{"total energy"} = \underbrace{\frac{1}{2} m v(t)^2}_{\text{Kinetic } E} + \underbrace{V(x(t))}_{\text{Potential } E}$

For free particle, $E = \frac{1}{2} \frac{P_0^2}{m} = \frac{1}{2} m v_0^2 = \text{const.}$

For constant force, $E = \frac{1}{2} m \left[\frac{P_0}{m} + \frac{F}{m} t \right]^2 - F \left[x_0 + \frac{P_0}{m} t + \frac{1}{2} \frac{F}{m} t^2 \right] = \frac{P_0^2}{2m} - F x_0 = \text{constant}$

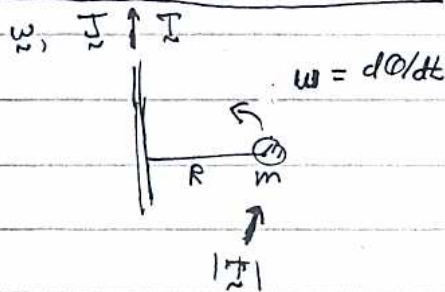
For H.O., $E = \frac{1}{2} m \left[A \omega \cos(\omega t + \phi) \right]^2 + \frac{1}{2} m \omega^2 \left[A \sin(\omega t + \phi) \right]^2 = \frac{1}{2} m \omega^2 A^2 = \frac{1}{2} k A^2$

These are examples of Principle of Conservation of Energy (E)

Some basic characteristics of classical mechanics: ① Arbitrary E 's allowed.

② Trajectories precisely specified

Classical Mechanical description of Rotational Motion.



linear	rotational
m	$I (= m R^2)$, moment of inertia
v	ω , angular velocity
p	J , " momentum
F	τ , torque

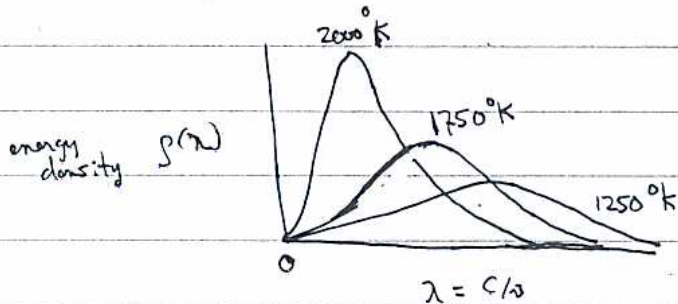
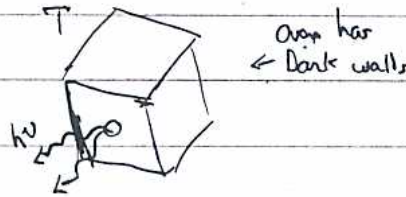
"Newton's Eq" $\dot{J} = \tau$

For constant torque: $\theta(t) = \theta_0 + \omega_0 t + \frac{1}{2} \frac{\tau}{I} t^2$

(rotational) $KE = \frac{1}{2} I \omega^2 = \frac{I \tau^2 t^2}{2I}$ if $\omega_0 = 0$

Failures of Classical Physics [~1900]

(I) Blackbody Radiation



Some

Features: (1) $\lambda_{\text{max}} T = \text{const}$, where λ_{max} = wavelength at which intensity is max. [Wien's Law]

$$(2) \int_0^{\infty} p(\lambda) d\lambda = a T^4 \quad [\text{Stefan's Law}]$$

$$\uparrow$$

$$5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$$

Theories [Rayleigh-Jeans, Planck...]

Aside: Classical Equipartition Thm.: At thermal equilibrium [T = temp, \bar{E}], energy is partitioned into each molecule according to: $\frac{1}{2} k_B T$ in KE for each degree of freedom; and...

$\frac{1}{2} k_B T$ in PE for each vibrational degree of freedom

[Thm, \approx hmo \rightarrow for a 1D H.O., $\bar{E} = k_B T$]

$$\rightarrow k_B = 1.38 \times 10^{-16} \text{ erg/}^\circ\text{K}$$

Now, Rayleigh-Jeans ...

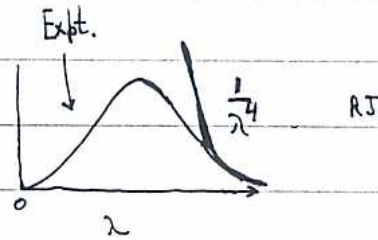
Assumed: (i) electromagnetic field = collection of h.o.'s, one for each possible frequency of light

(ii) classical equipartition thm. [each mode gets kT energy, indep. of frequency]

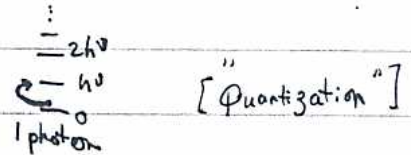
Then: (RJ)
$$p(\lambda) = \frac{8\pi}{\lambda^4} \cdot k_B T$$

energy/mode
or
density of E.M. modes w/ wavelength λ in the cavity

Disaster at high frequencies ["U.V. catastrophe"]:



Planck: for each field oscillator (frequency ν), restrict allowed energies to:



Analysis then shows:
$$\bar{E}(\nu) = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \quad [\nu = \frac{c}{\lambda}]$$

high frequency modes are not excited! [no photons in those modes]

Thus:

(Planck)

$$p(\lambda) = \frac{8\pi h c}{\lambda^5} \frac{1}{[e^{\frac{hc}{\lambda k_B T}} - 1]}$$

; c = speed of light = 3×10^{10} cm/sec

h = Planck's const. = 6.625×10^{-27} erg-sec

Heat Capacity [Quantum Property of Matter]

Einstein Model (of Crystal)



Single frequency, isotropic vibration ν

Molar Internal Energy: $U_m = 3N_A \cdot \overset{\text{energy/mode [classical]}}{kT} \quad (\text{classical}) \Rightarrow C_{v,m} = \frac{\partial U_m}{\partial T} = 3N_A k_B = 3R \quad [\text{Dulong- Petit}]$

↳ vibrational modes / mole atoms

Einstein: followed Planck's analysis, quantizing atomic vibrations $kT \rightarrow \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$

Thus

$$U_m = 3N_A \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \Rightarrow$$

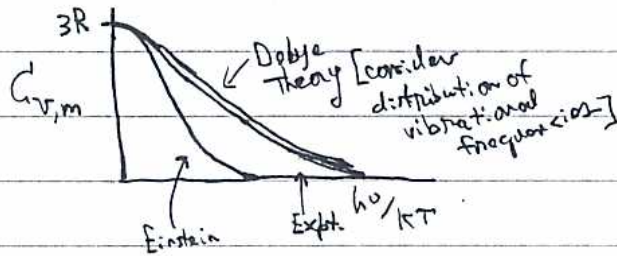
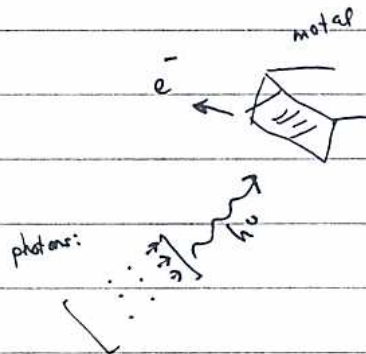


Photo-electron effect [Einstein]



Expt: (1) no e^- for $\nu < \nu_0$

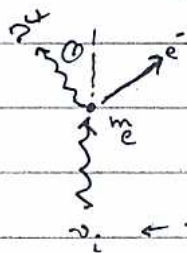
(2) for $\nu > \nu_0$, e^- off w K.E. of $(\nu - \nu_0)$ $\Rightarrow \frac{1}{2}mv^2 = h\nu - h\nu_0$

$\frac{1}{2}mv^2 \leftarrow$ "work functn."

(3) e^- off instantaneously for $\nu > \nu_0$, even at low intensities of metal

Compton scattering:

evidence for corpuscular light

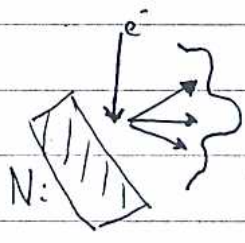


$$\Delta\lambda = \left[\frac{h}{m_e c} \right] [1 - \cos\theta] \quad (\leq \frac{2h}{m_e c})$$

"Compton wavelength"

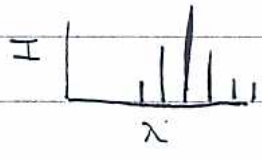
$\nu_i \leftarrow$ treat as particle w $E = h\nu$, $p = \frac{h\nu}{c} = \frac{h}{\lambda}$

Davisson-Germer Expt. [1925] : Interference [Diffraction] in electron-surface scattering \Rightarrow Matter is wavelike



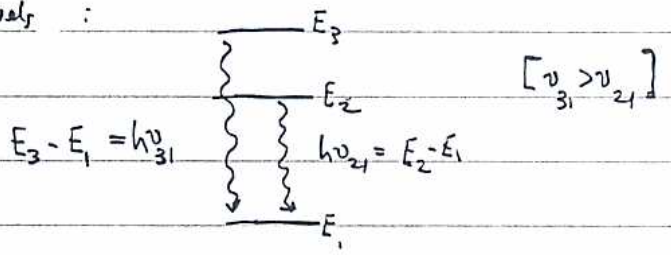
De Broglie : $\lambda = h/p$ for any particle

Atomic + Molecular Spectra - always composed of discrete lines



See Fig. 11.5-11.6 in Atkins

Suggests quantization of atomic/molecular E levels :



Quantum Mechanics : wavelike properties of matter contained in $\psi(x)$

Schrödinger's Eq. [1926] :

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

energy of particle
wavefunction or state function for particle

Study free particle : $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \Rightarrow \psi(x) = e^{\pm ikx} = \cos kx \pm i \sin kx \Rightarrow E = \frac{\hbar^2 k^2}{2m}$ or $k = \frac{\sqrt{2mE}}{\hbar}$

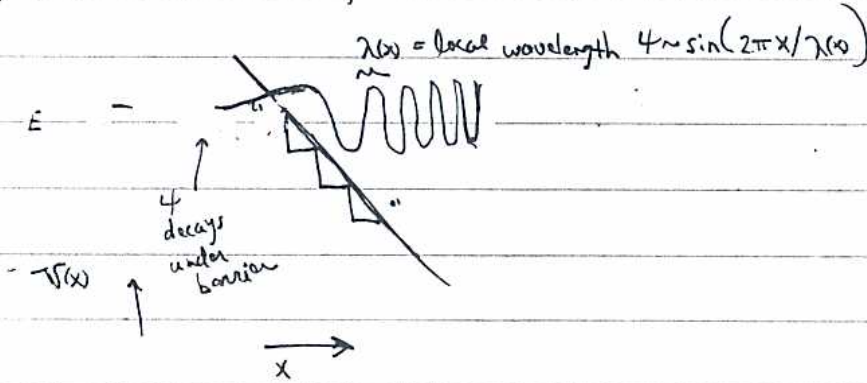
$\cos kx$, since has wavelength $\lambda = \frac{2\pi}{k} = \frac{h}{\sqrt{2mE}} = \frac{h}{p}$ ✓

Next, consider particle moving in const. pot. V : $\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right] \psi(x) = E \psi(x) \Rightarrow k = \frac{\sqrt{2m(E-V)}}{\hbar}$

Thus $E - V = \frac{h^2}{2m\lambda^2} \Rightarrow \lambda = h/\sqrt{2m(E-V)}$ [← faster wiggles \leftrightarrow higher K.E.]

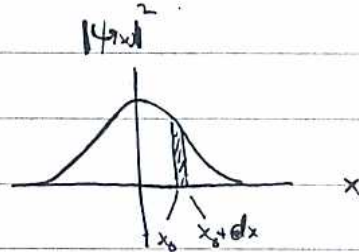


For non-const. pot., no const. λ solns exist, but



Restrictions on the w.f.'s [\leftrightarrow Quantization Conditions]

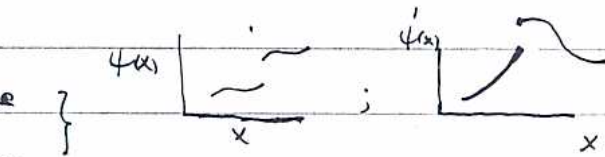
Born Interpretation: $\psi^*(x)\psi(x) = \text{probability density}$



$|\psi_0(x)|^2 dx = \text{prob. of observing between } x_0, x_0 + dx$

Born Interp \Rightarrow Restrictions on w.f.:

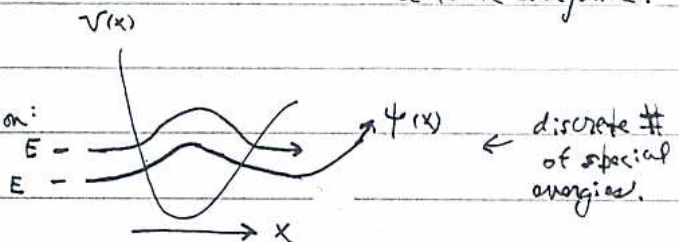
- (1) $\psi(x)$ finite everywhere
- (2) $\psi(x)$ continuous everywhere
- (3) $\psi'(x)$ continuous everywhere
- (4) single-valued everywhere



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

for finite $V(x)$, $\psi''(x)$ must be finite everywhere.

These restrictions provide route to quantization:



A Final Consequence of Born Interp: $I = \int dx \psi^*(x) \psi(x)$; i.e., normalization specified.

Discussion on Probability Concepts: Given an expt. [e.g. roll of dice] w/ n possible outcomes, each w/ probability P_j , then

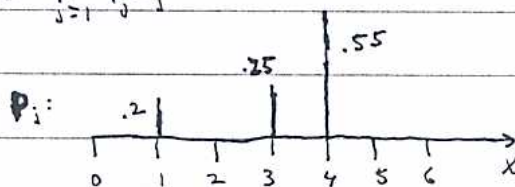
$$P_j \equiv \frac{n_j}{N} \quad \begin{array}{l} \leftarrow \text{\# trials w/ outcome } j \\ \leftarrow \text{total \# trials} \end{array} \quad \text{as } N \rightarrow \infty$$

Note: [1] $1 = \sum_{j=1}^n f_j = \frac{1}{N} \sum_{j=1}^n n_j$

[2] Expectation Values: Let x_j be value of property x associated w/ possible outcome state j ;

then $\langle x \rangle = \sum_{j=1}^n P_j x_j$

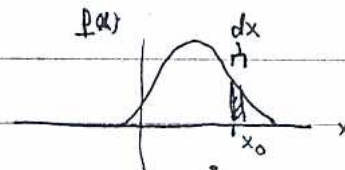
E.g. for discrete mass distribution



Here: $\langle x \rangle = (.2 \times 1) + (.25 \times 3) + (.55 \times 4) = 3.15$

NB: can compute $\langle x^2 \rangle$, etc., analogously.

[3] Generalization to Continuous Probability Distribution, $P(x)$



$P(x) dx =$ probability to find outcome state x in range $x_0 < x < x_0 + dx$

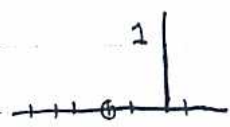
Postulates: (i) $\int_{-\infty}^{\infty} P(x) dx = 1$

(ii) $\langle x^n \rangle = \int_{-\infty}^{\infty} dx P(x) x^n$, etc.

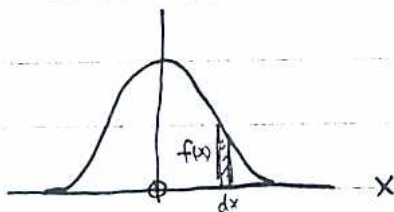
Note $\sigma_x^2 \geq 0$; thus $\sigma_x^2 = \sum_{i=1}^n f_i [x_i^2 - 2x_i \bar{x} + \bar{x}^2] = \langle x^2 \rangle - 2\bar{x} \langle x \rangle + \bar{x}^2$

$$= \langle x^2 \rangle - (\langle x \rangle)^2 \geq 0$$

Thus

$$\langle x^2 \rangle \geq (\langle x \rangle)^2 \quad \left[\text{Equality only when} \right]$$


(iii) Continuous distributions, $f(x)$



probability density [cf. mass density]
 $f(x)dx =$ probability to
 find outcome state
 in range x to $x+dx$

Then, analogously to discrete state case

$$\int_{-\infty}^{\infty} dx f(x) = 1 \quad ; \quad \langle x^n \rangle = \int_{-\infty}^{\infty} dx f(x) x^n \quad ; \quad \sigma_x^2 = \int_{-\infty}^{\infty} dx f(x) [x - \langle x \rangle]^2$$

E.g. for Gaussian normal dist., $f(x) = A e^{-x^2/2a^2}$, find A , $\langle x \rangle$, σ^2

$$1 = A \int_{-\infty}^{\infty} dx e^{-x^2/2a^2} \quad , \text{ so } \quad A = \frac{1}{\sqrt{2\pi a^2}}$$

Then

$$\langle x \rangle = A \int_{-\infty}^{\infty} dx x e^{-x^2/2a^2} = 0 \quad ; \quad \langle x^2 \rangle = \frac{1}{\sqrt{2\pi a^2}} \int_{-\infty}^{\infty} dx x^2 e^{-x^2/2a^2} = a^2$$

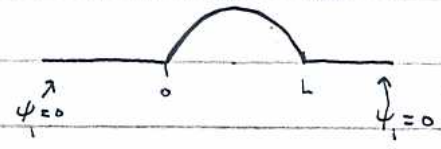
, so $\langle x^2 \rangle = \sigma^2 = a^2$; $\sigma = a =$ "standard deviation"

"Dignosis and Normalization: Examples

Normalization factor

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$$

(i) Particle in 1-d box



$$I = \int_0^L dx \left(\frac{2}{L}\right) \sin^2\left(\frac{\pi x}{L}\right) \quad \checkmark$$

(ii) Hydrogen atom 1s state: $\psi(r) = N e^{-r/a_0}$ [a_0 = Bohr radius]
 ↑
 to be determined

$$I = N^2 \int_0^\infty 4\pi r^2 e^{-2r/a_0} dr = 4\pi N^2 \int_0^\infty r^2 e^{-2r/a_0} dr$$

; Note $\int_0^\infty r^n e^{-\beta r} dr = \frac{n!}{\beta^{n+1}}$

$$= \frac{2!}{(2/a_0)^3} N^2 \Rightarrow N = \sqrt{\frac{1}{\pi a_0^3}}$$

"Principles of Quantum Mechanics

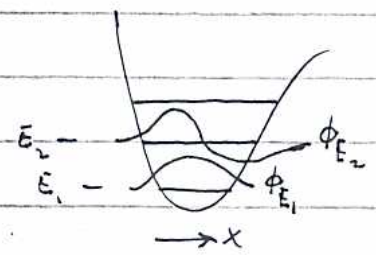
Observable \hat{O} (Linear) Operator \hat{O} st. $\hat{O} \phi_j(x) = O_j \phi_j(x)$ ← Eigenvalue O_j are only measurable values of \hat{O}

$\hat{O} = [p, x, L, \dots]$

↑
eigenfunction of \hat{O}

↑
contains info about system prepared in state j .

For ex, let $\hat{O} = E$; $\hat{O} = \hat{E} = \hat{H}$ = Hamiltonian operator: $\hat{H} \phi_{E_j}(x) = E_j \phi_{E_j}(x)$



Superposition States: Acceptable States other than "pure eigenfnctn." states exist

E.g. $\psi(x) = a_1 \phi_{E_1}(x) + a_2 \phi_{E_2}(x) + a_3 \phi_{E_3}(x) + \dots$ neglect for simplicity

↑
probability amplitude coefficients

↙ measurement of energy yields $E_{1,2,3}$
w/ probability $|a_{1,2,3}|^2$

↘ Or, equivalently, $\langle E \rangle = \sum_{k=1}^3 |a_k|^2 E_k$

holds for eigenfnctns. of any \hat{Q}

To "prove" this, note additional property of the ϕ_{E_j} : Orthonormality $\int_{-\infty}^{\infty} dx \phi_{E_j}^*(x) \phi_{E_k}(x) = \delta_{jk}$

check:

$$1 = \int dx \psi^*(x) \psi(x) = \int dx (a_1^* \phi_{E_1}^* + a_2^* \phi_{E_2}^* + a_3^* \phi_{E_3}^*) (a_1 \phi_{E_1} + a_2 \phi_{E_2} + a_3 \phi_{E_3}) = \sum_{k=1}^3 |a_k|^2$$

Rule for computing Expectation values is then:

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

For an example, check:

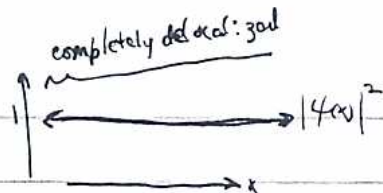
$$\int dx \psi^* \hat{H} \psi = \int dx (a_1^* \phi_{E_1}^* + a_2^* \phi_{E_2}^* + a_3^* \phi_{E_3}^*) \hat{H} (a_1 \phi_{E_1} + a_2 \phi_{E_2} + a_3 \phi_{E_3}) = \sum_{k=1}^3 |a_k|^2 E_k$$

Two more postulates: (1) $\hat{p} = \frac{\hbar}{i} \frac{\partial}{\partial x}$ [Note eigenfnctns $\frac{\hbar}{i} \frac{\partial}{\partial x} e^{ikx} = \hbar k e^{ikx}$]
(2) $\hat{x} = x$

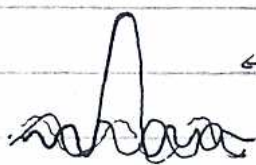
Finally, Uncertainty Principle [Heisenberg]: can't measure position + momentum simultaneously w/ arbitrary precision

↙ [Violates Newtonian world view]

E.g. $\psi(x) = e^{ikx}$ has definite momentum $\hbar k$, but $|\psi(x)|^2 = 1$ everywhere



To build sharply localized function, need ^{to superpose} plane waves of many frequencies ["p's"]



← more wavelengths ^(p's) superposed ⇒ more localization

See Fig. 11.21 Atkins

[Fig. 8.31, Atkins Ed. 8]

Mathematical Statement for Q.M.: $\Delta p \Delta x \geq \hbar/2$

(Note: $\Delta p_x \Delta y = 0$)

"Construction of Common Q.M. Operators [see Albury + Silbey handout.]

Construct \hat{H} ; recovers Schrödinger Eq.

Table 10.1 Classical Mechanical Observables and the Corresponding Quantum Mechanical Operators^a

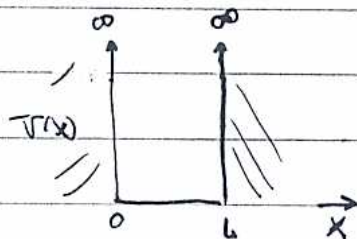
Observables		Operators	
Name	Symbol	Symbol	Operation
For one-dimensional systems			
Position	x	\hat{x}	Multiply by x
Position squared	x^2	\hat{x}^2	Multiply by x^2
Momentum	p_x	\hat{p}_x	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
Momentum squared	p_x^2	\hat{p}_x^2	$-\hbar^2 \frac{\partial^2}{\partial x^2}$
Kinetic energy	$T = \frac{p_x^2}{2m}$	\hat{T}_x	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Potential energy	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
Total energy	$E = T_x + V(x)$	\hat{H}	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$
For three-dimensional systems			
Position	r	\hat{r}	Multiply by r
Momentum	p	\hat{p}	$-i\hbar \left(i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \right)$
Kinetic energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \nabla^2$ $= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$V(x, y, z)$	$\hat{V}(x, y, z)$	Multiply by $V(x, y, z)$
Total energy	$E = T + V$	\hat{H}	$-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$
Angular momentum	$l_x = yp_z - zp_y$	\hat{L}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$l_y = zp_x - xp_z$	\hat{L}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$l_z = xp_y - yp_x$	\hat{L}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

^aAdapted from D. A. McQuarrie, *Quantum Chemistry*. Mill Valley, CA: University Science Books, 1983.

From Alberty + Silbey,
Physical Chemistry

Techniques + Applications

[E] 1-d Particle in a Box



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

General soln is:

$$\psi(x) = A \sin kx + B \cos kx \quad ; \quad k = \sqrt{2mE}/\hbar$$

Impose (physical) B.C.: $\psi(x) = 0$ outside of box $\Rightarrow \psi(0) = \psi(L) = 0$

$\psi(x)$
must be
continuous

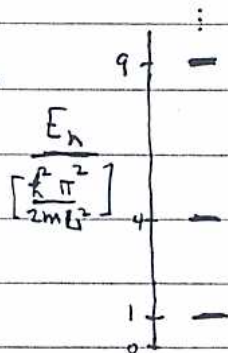
Thus $B=0$; k restricted to values $k_n = \frac{n\pi}{L}$; $n=1,2,3,\dots \Rightarrow \psi_n(x) = A \sin \frac{n\pi x}{L}$ $0 < x < L$

Note corresponding energy eigenvalues $E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{\hbar^2}{8mL^2} n^2$; $n=1,2,3,\dots$

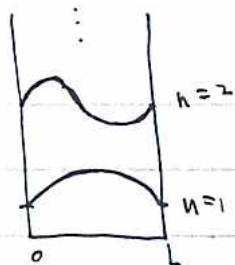
Finally, determine norm const. A : $1 = \int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = A^2 \underbrace{\int_0^L dx \sin^2 \frac{n\pi x}{L}}_{L/2} \Rightarrow A = \sqrt{\frac{2}{L}}$

Final eigenfunction expression is
$$\psi_n(x) = \begin{cases} 0 & x < 0 \\ \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) & 0 < x < L \\ 0 & x > L \end{cases}$$

Study the solution: Energy level diagram



Eigenfunctions



[0] Confinement \Rightarrow Quantization!

Some features: (1) ψ_n are sin waves that "fit into the box" [vanish at $x=0, L$];

nodes in $\psi_n = n-1$

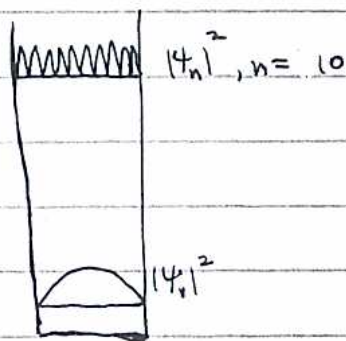
(2) ψ_1 = "ground state" has non-zero K.E = "Zero-point Energy" due to Uncertainty

Principle, namely:

$$\Delta x \sim L \Rightarrow \Delta p \sim \hbar/L \sim \text{typical } p \quad [\leftarrow \text{note } \langle p \rangle = 0]$$

$$\Rightarrow E_{g.s.} \sim \frac{p^2}{2m} \sim \frac{\hbar^2}{2mL^2} \sim E_1$$

(3) For high n , probability distribution becomes essentially uniform [as is case for any classical trajectory of a P in B] \leftrightarrow Bohr correspondence principle



$$[4] E_{n+1} - E_n = \frac{\hbar^2}{8mL^2} (2n+1)$$

\leftarrow Notes: (i) ΔE increases w/n

(ii) for fixed n , ΔE decreases as L or m increase

Example: Free Electron Model (Application to Betadione) \rightarrow to be continued!