Lecture2A--Model QM Problems with Exact Solutions – (1-D)

(Ch 2.2-Levine, 3-3 Atkins, Ch. 2-R&S)

1. Free Particle -- If there is no potential then Schroedinger Equation becomes

$T\ \Psi(x) = E\ \Psi(x)$ ==> $-(\underline{h}^2/2m)\ d^2/dx^2\ \Psi(x) = E\ \Psi(x)$
for this section: let underline "h" be "h-bar": $\underline{h} = h/2\pi$

easiest solution to this has exponential form: **$(d/dx)e^x = e^x$**
but this has only one eigen value 1 and can't well cope with **eigen value**
could use **$\Psi = e^{-kx}$** then **$k = (2mE/\underline{h}^2)^{1/2}$** but would get wrong sign
so need **e^{-ikx}** recall: **$e^{+ikx} = \cos kx + i \sin kx$**

These solutions are plane waves INSERT GRAPH
starting point is due to phase (balance between sin & cos—arbitrary)
but don't measure Ψ just |Ψ Ψ|—thus phase not significant (normally)

This describes motion of a free particle
no potential —> no force (**$F = -dV/dx$**) – continuous motion
[Note these are eigen functions of momentum **$p\Psi_{\pm} = (-i\underline{h})\ d/dx[e^{\pm ikx}] = \pm\underline{h}k\Psi_{\pm}$**]
What is it doing?
$e^{\pm ikx}$ --> motion to the pos x --> $\langle p\rangle = +k\underline{h}$
e^{-ikx} --> motion to the pos x --> $\langle p\rangle = -k\underline{h}$

2 solution: $\Psi_{\pm}$ both solve the problem. These have different eigen values of momentum but different of energy depend on preparation—initial state

cos kx also an eigen function **$T\Psi = T\cos(kx) = -k(-\underline{h}^2/2m)\cos(kx) = E\Psi$**
but **$p \cos(kx) = -k(-i\underline{h})\sin(kx)$** not eigen function

so real component, **cos(kx),** of **$e^{\pm ikx}$** has energy but ill defined momentum
– real wave function—represents motion left (-) and right (+)
--complex wave function—well defined linear momentum (-) or (+)

Note if energy is not well defined – then k varies - means wavelength varies
get wave packet -- super position of these with constructive interference --
if enough waves interfere see particle with some position, finite Δx

Time evolution:

$$\Psi\ (x,t) = Ae^{-ikx}\ e^{-Et/\underline{h}} = Ae^{i[kx\ +\ (k2\underline{h}/\underline{2m})t]}$$

evaluate at different times - point of constructive interference changes – <u>phase shift</u>

*<u>try it</u> with graphing calculator or program

2. Particle in a box with infinite sides—restrict motion - contain with V(x)

$V = 0 \rightarrow 0 < x < L$

$V = \infty \leftarrow$ all else ($x < 0$, $x > L$)

<u>INSERT GRAPH</u>

Region I, III $\quad$ $\mathbf{H\Psi = E\Psi \;\text{-->}\; -(\underline{h}^2/2m)(d^2/dx^2)\Psi = (E - \infty)\Psi}$

so particle of finite energy has <u>no amplitude</u> in this region Ψ (x)=0 (outside box**)**

<u>special result</u> due to $V(x) = \infty$ outside (<u>impenetrable</u>) only need consider <u>Region II</u>

hence <u>locally V = 0</u> – just as above for free particle $\mathbf{Ae^{-ikx}}$

<u>but</u> V(x) provides restrictions on motion (in box) so that leads to quantized behavior

B.C. – boundary conditions, choose : $\mathbf{\Psi = A\cos kx + B\sin kx}$

At wall Ψ**(0) =** Ψ**(L) = 0** – must be a continuous, finite function

$\Psi(0) = A \sin kx$ $\quad$ ($\cos x \neq 0$ at $0 = x$)

$\Psi(L) = 0 \implies k = (n\pi/L)$ where n = 1,2,3. . .integer, (n = 0 not allowed)

Energy is quantized by the B.C. (work it out)

$$\mathbf{k = (2mE/\underline{h}^2)^{1/2} = n\pi/L \implies E_n = n^2\pi^2\underline{h}^2/L^2 2m}$$

Note: still need $Ae^{i\varphi}$, amplitude and phase--

Normalize: $\mathbf{\int\Psi_n{*}\Psi_n dx = 1 \implies A = (2/L)^{1/2} \implies \Psi_n\ (x) = (2/L)^{1/2}\ \sin(n\pi x/L)}$

Important to see what happens as modify B.C.

– as box enlarges Ψ toward free particle, i.e. the <u>energy</u> levels become <u>continuous</u>

– smaller box more energy goes as $\sim 1/L^2$ – note box constrains motion more,

Ψ has more curvature, second derivative is curvature, |T| inc. with curvature

– energy level separation <u>expand</u> with n^2 -- property of <u>steep sides</u>

<u>What are they? H-atom--example</u>

more useful **for smaller masses--eg. electron**

If spectral transition: $\mathbf{h\nu = \Delta E = E_n - E_{n'}}$ **-** change between levels

But—lower mass—electron~*2000 increase Energy over atom

---lower size--1Å (atomic) ~*100 inc Energy over 10Å (molecular) conversely--> bigger box, heavier particle --> near continuous E --> classical corresp

Where is particle? -- $\int_0^L \Psi^*\Psi dx = 1$ ==> it's in the box
Also do region probability, eg. $\int_0^{L/2} \Psi^*\Psi dx = 1/2$ ==> equal distribute by halves
But distribution is peaked ($\sin^2$) and this changes with different excited states

Alternate related Problems--Mess around with your box

2.a.. Translate: Box shift to run from -L/2 to L/2
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Clearly energies must be the same but B.C. change so form of solution changes

$\Psi_1(x) = (2/L)^{1/2} \cos(2\pi x/L)$ --> **sym**
$\Psi_2(x) = (2/L)^{1/2} \sin(4\pi x/L)$ --> **asym**
$\Psi_3(x) = (2/L)^{1/2} \cos(6\pi x/L)$ --> **sym**
$\Psi_4(x) = (2/L)^{1/2} \sin(8\pi x/L)$ --> **asym**

Phase shift, but states now have parity

2.b. Tie the ends together—particle on a ring: -- Looks like 2-D -- But really 1-D because particle can't move off the ring so only variable is θ, R is fixed need transform coordinates**:** $x = R\cos\phi$ and $y = R\sin\phi$

$d^2/dx^2 + d^2/dy^2 = d^2/dR^2 + (1/R)d/dR + (1/R^2)d^2/d\phi^2$

$-\underline{h}^2/2m(d^2/dx^2 + d^2/dy^2)\Psi = E\Psi$ new variables: $\Psi(R,\phi) = K_R\Phi(\phi)$

since R constant only the $d^2/d\varphi^2$ term remains , K_R of the w/f is constant

$-\underline{h}^2/2m(d^2/d\phi^2)\Phi(\phi) = E\Phi(\phi)$ ===> $\Phi(\phi) = A\, e^{ib\phi}$

B.C. – correct $\Phi(0) = \Phi(2\pi)$, ==> $\Phi(\phi) = (1/\sqrt{2\pi})\, e^{im\phi}$

2.c. Particle in 3-D box (Levine 3.5) if we go up to 3-D for one particle:

$H\Psi(xyz) = E\Psi(xyz)$

Now this is the same our simplest problem if we can do one coordinate at a time:
V=0 for 0<x<a, 0<y<b, 0<z<c and V= ∞ outside the box (rectangular)

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Outside the box, it's the same deal: $\Psi(xyz)=0$

Inside must solve

$$\mathbf{H\Psi = -\underline{h}^2/2m(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)\Psi} = \mathbf{-(\underline{h}^2/2m)}\nabla^2 \mathbf{\Psi(xyz) = E\Psi\ (xyz)}$$

Problem needs simplification-- Since $\nabla^2 = \mathbf{(d^2/dx^2 + d^2/dy^2 + d^2/dz^2)}$

This is additive, no cross terms - can separate variables as for time dep. S.E.

$$-2\mathbf{m}E/\underline{\mathbf{h}}^2 = \mathbf{(1/\Psi(xyz))}\nabla^2\ \mathbf{\Psi(xyz)} \text{ -- } \mathbf{Choose\ \Psi(xyz)= X(x)Y(y)Z(z):}$$

$$-2mE/\underline{h}^2 = (1/X(x))\, d^2/dx^2\, X(x) + (1/Y(y))\, d^2/dy^2\, Y(y) + (1/Z(z))\, d^2/dz^2\, Z(z)$$

Each of these is independent set $\mathbf{(1/X(x))\ d^2/dx^2\ X(x) = K_{x},}$ **etc.**

Then $-2\mathbf{m}E/\underline{\mathbf{h}}^2 = K_x + K_y + K_z$

Each one is simple 1-D particle in a box solution

$X(x) = A \sin (K_x x) = A \sin (n_x \pi x/a)$, $\mathbf{E_{nx} = n_x^2\pi^2\underline{h}^2/a^22m}$

Put it together: $\mathbf{E_n = (n_x^2/ a^2 + n_y^2/ b^2 + n_z^2/ c^2)\pi^2\underline{h}^2/2m}$

$$\mathbf{\Psi_{nxnynz}\ (xyz) = (8/abc)^{1/2}\ \sin(n_x\pi x/a)\ \sin(n_y\pi y/b)\ \sin(n_z\pi z/c)}$$

These basically act independently but create a higher density of energy levels
because we can excite modes (states) in 3 different coordinates
with proper (improper?) selection of a, b, c there could be states accidentally
degenerate—e.g. let $b = 2a$, then $E_{411} = E_{271}$

But it is more interesting to have symmetry, e.g. a=b=c now

$E_n = (n_x^2 + n_y^2 + n_z^2)\pi^2\underline{h}^2/2m\, a^2 = (n_x^2 + n_y^2 + n_z^2)E_1$, where E_1 is part. box sol'n

Not important which coordinate is excited, just how many Quanta put in

$E_{111} = 3E_1$ and $E_{211} = E_{121} = E_{112} = 6E_1$ and $E_{121} = E_{221} = E_{212} = 9E_1$ etc.

Degenerate

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2.d. Particle in a finite-well, what happens when V=0 0<x<L, but V=V outside

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Expect the same form but need modify to account for

a) continuity at 0 = x, L = x but $\Psi(0) \neq 0$ since V is finite, thus expect penetration as discussed based on curvature

b) also expect E_n to converge to continuous states as get higher E, higher n