

# Lectures on Quantum Mechanics

## Spring 1962

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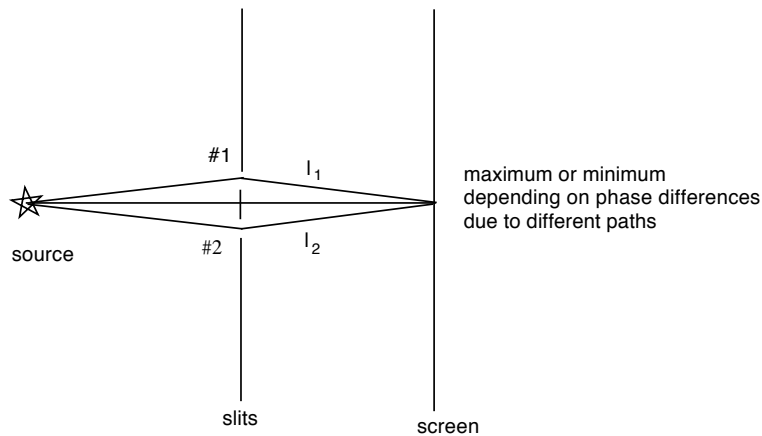
## The Plausibility of Schrödinger's Equation

### Classical Theory

1900 - Planck!

#### (1) Light-waves (Young)

Interference (Fresnel) - absolute proof of wave nature of light



At screen: due to slits #1 and #2

$$A = A_1 e^{ikl_1} + A_2 e^{ikl_2} \quad k = \frac{2\pi}{\lambda}$$

$$\text{Intensity} = I = |A|^2 = A_1^2 + A_2^2 + 2A_1 A_2 \cos k(l_1 - l_2)$$

which  $\rightarrow$  maxima and minima depending on  $l_1 - l_2$ . For any number of slits

$$A = \sum_j A_j e^{ikl_j} \quad (\text{for x-ray diffraction by a crystal})$$

Maxwell - 1864: Theory of electromagnetic waves! Maxwell's equations and wave equation + boundary conditions  $\rightarrow$  complete solution for light-waves.

#### (2) Matter

1897 - electrons - J.J. Thompson

**Newton's equations** -  $m\ddot{x} = F$

$x(t)$  known  $\rightarrow$  accurate knowledge of path, i.e., cloud chamber tracks.

**Hamilton's formulation:**  $q, p$

$$H = \text{total energy} = H(q, p) \rightarrow$$

$$\dot{q} = \frac{\partial H}{\partial p} \quad ; \quad \dot{p} = -\frac{\partial H}{\partial q}$$

and so much for classical theory.

### Quantum Theory of Light

**Photoelectric effect:** 1888 - Hallwachs  $\rightarrow$  electrons can be emitted from a surface by light of sufficiently short wavelength!

For any material

$$\nu > \nu_0 \rightarrow \text{photoelectric effect}$$

$$\nu < \nu_0 \rightarrow \text{no photoelectric effect}$$

Lenard -  $\nu > \nu_0 \rightarrow \Delta I$  of light has no effect  $\rightarrow$  failure of classical concept of light energy storage.

**Explanation:** Einstein - 1905. When light is absorbed by an atom a whole quantum is absorbed!, i.e.,  $E = h\nu - \omega$  where  $E$  = (kinetic energy) of photoelectrons and  $\omega$  is the release energy of electrons - binding, work functions, etc.

**Richardson and Compton:** confirmation of Einstein's relation.

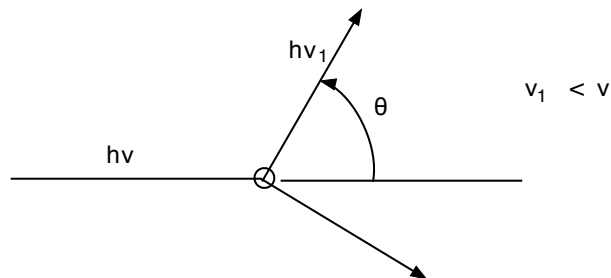
$$\text{light quantum energy} = E = h\nu = \hbar\omega \quad , \quad \hbar = 1.0545 \times 10^{-27} \text{ erg-sec}$$

Converse appears in emission of x-rays, i.e.,

$$h\nu = E_{\text{initial}} - E_{\text{final}}$$

Short  $\lambda$  limit:  $h\nu_{\text{max}} = E_{\text{electron}}$  (Duane-Hunt)

**A.H. Compton:** scattering of x-rays by electrons



Using conservation of energy and momentum

$$\frac{dE}{dp} = \dot{q} = c$$

Therefore,

$$E = pc + A$$

But  $A = 0$  since when  $p = 0 \rightarrow E = 0$ . Therefore for a light quantum

$$p = \frac{E}{c} = \frac{h\nu}{c} \rightarrow \text{explanation of the Compton effect}$$

This is particle-like behavior, i.e., light quanta has

$$E = h\nu \quad , \quad p = \frac{h\nu}{c}$$

But in diffraction  $\rightarrow$  wave-like behavior  $\rightarrow$  duality; *the paradox of waves and particles*.

## Review

- (1) photoelectric effect:  $h\omega$  (quantum)
- (2) short wavelength limit of x-rays  $\rightarrow$  no light whose energy is higher than a quantum is emitted
- (3) Compton effect: light interaction with matter - particle-like behavior
- (4) Planck distribution

## Stationary States in Atoms

- (1) nucleus + electrons
- (2) revolving electrons radiate - (not true for atoms)  $\rightarrow$  ground state with no radiation

**Franck-Hertz Experiment**  $\rightarrow$  energy threshold for radiation.

$$\text{For Na} \quad \begin{cases} 2 \text{ eV} \rightarrow \text{emission of line (yellow)} \\ 4 \text{ eV} \rightarrow \text{another line emitted} \\ 6 \text{ eV} \rightarrow \text{ionization} \end{cases}$$

## Niels Bohr - 1913

Atoms exist in stationary states characterized by certain energies  $E_n$ .  $h\omega = E_{\text{initial}} - E_{\text{final}}$  (of electron)  $\rightarrow$  emission of radiation.

**Rydberg- Ritz Combination Principle** - the frequency of all spectral lines

emitted by an atom can be obtained as the difference of two term values (energy levels of the atom).

**Quantum Theory of Matter** - discrete values of energy.

To get states of Hydrogen atom we postulate electrons in circular orbits with angular momentum  $J = n\hbar$ . Classically we have

$$\text{electric force} \rightarrow \frac{e^2}{r} = m\omega^2 r \text{ and } J = mr^2\omega$$

Heavier atoms  $\rightarrow$  no success.

Molecules: vibration and rotation spectra  $\rightarrow$  some contradictions.

Aperiodic systems  $\rightarrow$  poor.

Periodic table  $\rightarrow$  good, using electron quantum numbers.

Generalized quantum conditions - Sommerfeld and Wilson - 1916.

Stern-Gerlach - 1922.

Heat waves in solids: (specific heats): Einstein 1907; Debye 1912.

**Wave Nature of Matter**

$$\left. \begin{array}{l} 1927 - \text{Davisson and Germer} \\ 1928 - \text{G.P. Thompson} \end{array} \right\} \text{electron diffraction by crystals}$$

$$\text{Experimentally} \rightarrow \lambda_{\text{electron}} = \frac{h}{p} ; p = \text{momentum of electron}$$

deBroglie (1924) postulated

$$\lambda = \frac{h}{p} \quad \text{by analogy with light}$$

i.e.,

$$\lambda_{\text{light}} = \frac{c}{\nu} = \frac{ch}{E} = \frac{h}{p} \quad ; \quad p = \frac{E}{c} = \text{momentum}$$

Surmise that also  $E = h\nu$  for matter.

deBroglie argument:

$$\left. \begin{array}{l} E, \vec{p} \rightarrow \text{4-vector} \\ \omega, \vec{k} \rightarrow \text{4-vector} \end{array} \right\} \text{both invariant under Lorentz transformation}$$

Therefore,  $\rightarrow$  the two quantities should be related by a constant of proportionality  $\rightarrow$  true for light  $\rightarrow$  postulated true for everything!!

$$E = c\sqrt{p^2 + m^2c^2} \quad , \quad \frac{v}{c} = \frac{p}{p^2 + m^2c^2} \quad \text{now } m \neq 0 \text{ or } m = 0$$

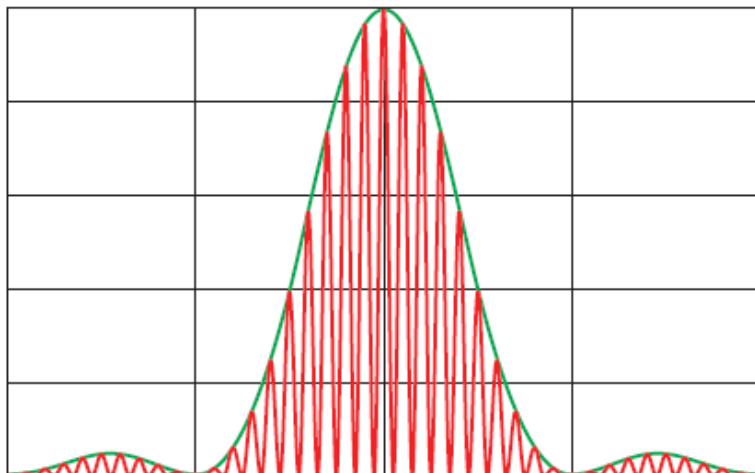
$$m = 0 \quad \frac{v}{c} = 1 \rightarrow v = c \rightarrow E = pc \quad (\text{neutrinos, quanta})$$

$$m \neq 0 \quad \text{no particular values}$$

2nd distinction - particle must either have been created or annihilated in pairs or singly!!

### Critique of the Old Quantum Theory

Most important paradox - particle-wave duality, i.e., a double-slit pattern of the form (green line is one-slit pattern and red line is multi-slit pattern)



can be done with light, electrons, neutrons, etc. For light, replace screen by a photoelectric surface  $\rightarrow$  number of photoelectrons emitted corresponds to diffraction pattern distribution. Therefore light as a wave is diffracted by the slits, but light as particles eject photoelectrons.

If we use counters (of photoelectrons) and reduce the light intensity (1 quanta  $\sim 10^{-6}$  sec) counts registered will not show normal diffraction pattern distribution of light as a wave!

If we reduce intensity to one photon going through the slits we must still expect pattern, but 1 photon will go to only one point. Many experiments with a single photon  $\rightarrow$  approximation to the light diffraction experiment.

Now considering the particle picture: can we tell which slit photon went through? We cover up one slit: wave theory  $\rightarrow$  completely different intensity distribution. With one slit open particles can reach points on screen where two-slit pattern is zero (no particles reach that point). Thus, how can we explain the fact that opening a slit through which the particle doesn't go  $\rightarrow$  that the particle cannot reach a point it has previously reached with one slit open  $\rightarrow$  contradiction of particle theory.

**Uncertainty Principle** - we cannot determine the path of particle to complete accuracy  $\rightarrow$  alleviation of the paradox  $\rightarrow$  this does not tell us what is true.

Quantum mechanics modified particle theory by making less strict the particle path as a function of time  $\rightarrow$  matrix mechanics (Heisenberg 1925). Quantum mechanics modified wave picture  $\rightarrow$  wave mechanics (Schrödinger 1926). Schrödinger showed equivalence of the two theories.

Restriction on wave theory due to particle theory  $\rightarrow$  "Whenever we see or observe a particle, we must see at least *one* particle and no fractions of particles  $\rightarrow$  we must interpret wave intensity as the probability of finding a particle at a given point.

$$\text{prob} \geq 0 \rightarrow \text{probability} \sim |A|^2$$

### The Wave Picture

With definite  $\lambda$  and  $\omega$ , a wave is

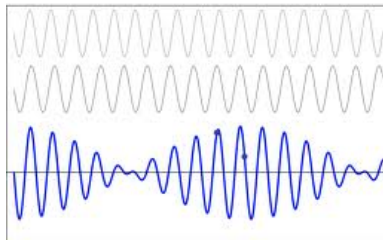
$$\sin(kx - \omega t), \cos(kx - \omega t), e^{i(kx - \omega t)}, e^{-i(kx - \omega t)},$$

For particles (also for light)

$$k = \frac{p}{\hbar}$$

We want to represent a particle by a superposition of these waves  $\rightarrow |A|^2$  is large at one point in space (position of particle) and small everywhere else.

$$\sin k_1 x + \sin k_2 x \rightarrow$$



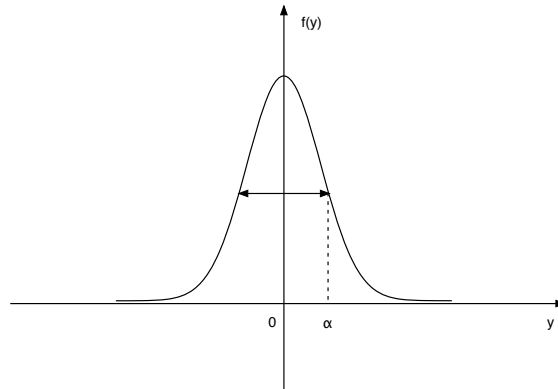


→ particle is most likely to be at places on blue curve where  $A$  is large, but not near zeroes.

Extending this to a continuum of  $k$  values → wave packet!

$$\psi(x) = \int dk f(k - k_0) e^{ikx}$$

We want to choose  $f$  such that  $f$  has a large value (magnitude) only if  $k \approx k_0$



where  $\alpha \approx$  width of the distribution or  $f(y = \alpha) \ll f(y = 0)$ . Let  $y = k - k_0$ . Therefore,

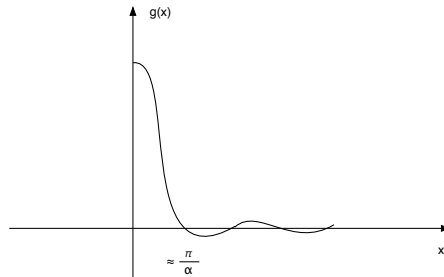
$$\psi(x) = e^{ik_0x} \int dy f(y) e^{iyx} \equiv g(x) \quad f(y) \text{ real, } > 0$$

For  $x = 0$ ,  $g(x)$  very large, all contributions add!!

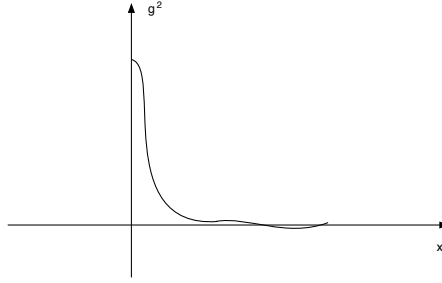
For  $x = \pi/\alpha$

$$\begin{array}{ll} \text{at } y = 0 & yx = 0 \rightarrow e^{iyx} = 1 \\ \text{at } y = \alpha & yx = \pi \rightarrow e^{iyx} = -1 \end{array}$$

→ destructive contributions →  $g(x)$  small, i.e.,



$$|\psi(x)|^2 = \text{probability} = |g(x)|^2$$



→ we have a large probability of finding the particle at  $x = 0$ . Such a “wave packet” → particle is located near  $x_0 \pm \Delta x$  (here  $x_0 = 0$ ,  $\Delta x \approx 1/\alpha$ ) and has wave number near  $k_0 \pm \Delta k$ ,  $\Delta k = \Delta y = \alpha$ .

The best choice of  $f$ :

$$f(y) = C\sqrt{a}e^{-\frac{1}{2}a^2y^2} \quad \text{gaussian form}$$

Therefore

$$\psi(x) = C\sqrt{a} \int_{-\infty}^{\infty} e^{-\frac{1}{2}a^2y^2 + i y x} dy = C\sqrt{\frac{2\pi}{a}} e^{-\frac{1}{2}\frac{x^2}{a^2}} \quad \text{gaussian}$$

i.e., the Fourier transform of a gaussian is a gaussian.

$$f^2(y) = \text{probability of having a given } y \sim e^{-a^2y^2}$$

$$g^2(x) = \text{probability of having a given } x \sim e^{-x^2/a^2}$$

Therefore,

$$\Delta x \sim O(a) \text{ from } g^2(x) \quad , \quad \Delta k \sim O\left(\frac{1}{a}\right) \text{ from } f^2(y)$$

Therefore, the wave packet will represent the particle of approximate position  $x = 0$  and  $k \approx k_0$  with  $\Delta x \sim a$  and  $\Delta k \sim 1/a$ . This fuzziness is inherent in the properties of superposition.

**Uncertainty:** We have

$$\Delta x \Delta k \sim 1 \quad \text{or} \quad \Delta x \Delta p \geq \hbar$$

where the greater than sign is necessary since choice of  $f(y)$  is arbitrary → worse spread in  $y$  and similarly for spread in  $x$ .

Thus we are prevented from measuring position and momentum to any arbitrary degree of accuracy at the *same time*.

If we know  $x$  and  $\dot{x}$  at different times classically, we could determine  $x(t)$ , but in quantum mechanics  $\rightarrow$  subsequent measurement of either  $x$  or  $\dot{x}$  will destroy the results of our prior measurement of other quantities.

**Bohr's Complementarity Principle:** You cannot measure all quantities which are necessary for a classical description!.

Considering non-relativistic mechanics -

$$\Delta x \Delta v = \frac{\hbar}{m} \quad \text{with} \quad \hbar \sim 10^{-27}$$

(1) grain of sand -  $m = 10^{-3} \text{ gm}$

$$\Delta x \Delta v \sim 10^{-24} \quad , \quad \Delta x \sim 10^{-2} \text{ cm} \rightarrow \Delta v \sim 10^{-22} \text{ cm/sec}$$

$\rightarrow$  no restriction on our measurements.

(2) biological cell -  $\Delta x \sim 10^{-4} \text{ cm}$ ,  $m = 10^{-10} \text{ gm} \rightarrow$  still no restrictions.

(3) electron -  $m \sim 9 \times 10^{-27} \text{ gm}$

$$\rightarrow \frac{\hbar}{m} \sim 1$$

Consider an electron gun:

$$\Delta x \sim 10^{-3} \text{ cm} \quad , \quad \Delta v \sim 10^3 \text{ cm/sec}$$

But  $v \sim 10^9 \text{ cm/sec} \rightarrow$  no substantial error.

Consider an electron in an atom:

$$r_0 = a = 10^{-8} \text{ cm} \geq \Delta x \rightarrow \Delta v \geq 10^8 \text{ cm/sec}$$

But  $v \sim 10^8 \text{ cm/sec} \approx$  average velocity of electrons in the atom. Thus,  $\Delta v \sim v$  and the velocity is completely uncertain.

(4) proton in a hydrogen molecule -  $M_p = 1836 m_e$

$$\Delta x \sim 10^{-8} \text{ cm} \quad , \quad \Delta v \sim \frac{1}{2} \times 10^5 \text{ cm/sec} \ll 10^7 = v \text{ in molecule.}$$

$\rightarrow$  we can describe position with considerably greater accuracy than necessary (less than the size of the molecule).

(5) proton in the nucleus

$$\frac{\hbar}{m} = \frac{1}{2} \times 10^{-3} \quad , \quad \Delta x \sim 10^{-12} \text{ cm} \rightarrow \Delta v \sim \frac{1}{2} \times 10^9 \text{ cm/sec} \sim v \text{ in nucleus}$$

$\rightarrow$  no classical path of proton in nucleus.

(6) electron in the nucleus

$$\Delta v < c \rightarrow \Delta x > \frac{\hbar}{mc} \sim \frac{1}{3} \times 10^{-10} \text{ cm} \gg \text{size of nucleus}$$

$\rightarrow$  cannot be in nucleus. [not really correct, i.e., relativistic considerations necessary in argument, but conclusion is correct].

### Time Dependence of the Wave Packet

$$e^{i(kx-\omega t)} \rightarrow \psi(x) = \int dk f(k-k_0) e^{i(kx-\omega t)}$$

Now  $\omega = \omega(k)$ , but since  $f$  is only large for  $k \approx k_0$ , we use a Taylor expansion of  $\omega$  in terms of  $(k-k_0)$  or

$$\omega = \omega(k_0) + \left( \frac{d\omega}{dk} \right)_{k_0} (k-k_0) + \frac{1}{2} (k-k_0)^2 \left( \frac{d^2\omega}{dk^2} \right)_{k_0} + \dots$$

Let  $y = k - k_0 \rightarrow f(y)$  large only for  $y \sim 1/a$ .

We choose  $t$  small enough such that we can neglect 2nd-order and higher order terms!

$$\begin{aligned} \psi(x) &= e^{i(k_0 x - \omega(k_0)t)} \int dy f(y) e^{i y x - i \omega' y t} \\ &= e^{i(k_0 x - \omega(k_0)t)} g(x - \omega' t) \end{aligned}$$

$Prob = |\psi(x)|^2 = g^2(x - \omega' t) \rightarrow$  shape of function is the same at time  $t$  as at  $t = 0$ ; the only change is one of position, i.e., packet moved bodily to new center at  $x = \omega' t$  since wave packet represents a particle

$$\rightarrow v = \omega' = \frac{d\omega}{dk} \rightarrow \frac{d\omega}{dk} = v \rightarrow \text{good representation of the particle}$$

or

$$\frac{v}{\hbar} = \frac{d\omega}{dp}$$

since  $p = \hbar k$  is true for all particles even relativistic - and also for light.

Now in Hamilton's equations, for all cases as before,

$$\frac{dH}{dp} = v \rightarrow \omega = \frac{H}{\hbar} = \frac{E}{\hbar}$$

$\rightarrow$  that the relation must hold for both matter and light.

Our only assumption has been that we can represent particles by wave packets and that the wave packets must move with the classical velocity

$$\frac{d\omega}{dk} = \text{group velocity of wave packet from wave theory}$$

We have used Bohr's complementarity principle here!

Quantum mechanics must go into classical mechanics when in the limit quantum phenomena become unimportant. In classical limit  $\hbar \rightarrow 0 \rightarrow$  width of wave packet  $\rightarrow 0 \rightarrow$  particle is at center and is localized  $\rightarrow$  classical motion.

### Spread of Wave Packet in Later Time

$$\frac{d^2\omega}{dk^2} = \hbar \frac{d^2E}{dp^2}$$

For non-relativistic case

$$E = \frac{p^2}{2m} \rightarrow \frac{d^2\omega}{dk^2} = \frac{\hbar}{m}$$

$\rightarrow$  3rd derivative, et = 0 (only non-relativistically).

$$\Delta x = a \quad , \quad \Delta v = \frac{\hbar}{ma}$$

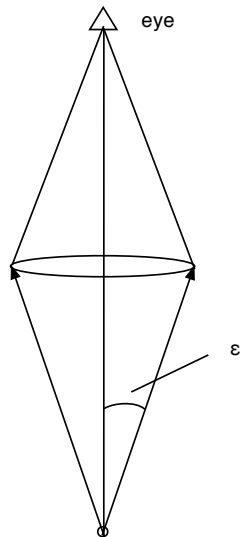
$$\Delta x^2(t) = \Delta x^2(t=0) + \Delta^2 v t^2$$

for a Gaussian  $\rightarrow$  spreading of the wave packet!

“**Postulate**” - all particles are represented by wave functions  $\rightarrow$  no need for thought experiments.

### Thought Experiments

(1) Position Determination: Microscope



$$\Delta x = \frac{\lambda}{\sin \varepsilon} \rightarrow \text{resolving power}$$

Therefore shortest  $\lambda \rightarrow$  smallest  $\Delta x$ . In this thought experiment Heisenberg used  $\gamma$ -rays.

But performing the experiment  $\rightarrow$  interaction between  $\gamma$ -rays and the electron  $\rightarrow$  recoil of the electron.

$$p_\gamma = \frac{h\nu}{c} \text{ after scattering } \rightarrow \text{recoil momentum of electrons}$$

But  $p_\gamma$  can go in range  $\pm\varepsilon$ . Therefore

$$\Delta p_x = \frac{h\nu}{c} \sin \varepsilon$$

We can assume  $p_x, p_\gamma$  are known before the interaction. Therefore

$$\Delta x \Delta p_x = h$$

(2) Momentum Determination: (Doppler effect)

Atom (at rest):

$$\bigcirc \rightarrow f_0 \text{ emitted}$$

Atom (moving):

$$\overset{v \rightarrow}{\bigcirc} \rightarrow f = f_0 \left(1 + \frac{v}{c}\right) \rightarrow \text{velocity of the atom}$$

$$v = c \left( \frac{f}{f_0} - 1 \right)$$

Now if  $\tau$  is the time necessary to measure frequency  $f$ , then

$$\Delta f \sim \frac{1}{\tau}$$

Actually a wave train is emitted

$$e^{-i\omega_0 t} e^{-t/\tau}$$

Fourier analysis  $\rightarrow$  wave packet  $\rightarrow$

$$\omega = \omega_0 \pm \frac{1}{\tau}$$

When the atom emits light it will recoil  $\rightarrow$  change in the velocity of the atom

$$\delta v = \frac{hf}{mc} \text{ exactly known from momentum conservation}$$

→ no trouble in velocity determination.

But we do not know when the emission took place. Therefore

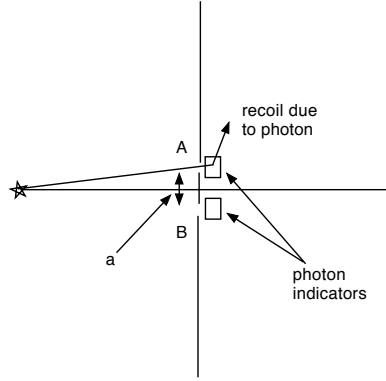
$$\Delta x \sim \delta v \tau = \frac{hf}{mc} \tau$$

$$\Delta p_x = m \Delta v = m \frac{c \Delta f}{f_0} = \frac{m}{\tau} \frac{c}{f_0} = \frac{mc}{\tau f}$$

where  $\Delta v$  = uncertainty and we used  $f \approx f_0$ . Therefore we get

$$\Delta x \Delta p_x = h$$

(3) Diffraction Experiment:



Which slit does the elusive photon go through? There is uncertainty due to indicators! →  $\Delta p_y$  in photon (also  $\Delta p_y$  in the indicators). We do not want this to destroy the diffraction pattern, i.e., since

$$\Delta \theta = (n+1) \frac{\lambda}{a} - n \frac{\lambda}{a} = \frac{\lambda}{a}$$

between maxima and  $\Delta p_y \rightarrow$  deflection due to the indicator equal to

$$\frac{\Delta p_y}{p_{x0}}$$

where we have assumed that the original  $p_y \ll p_{x0}$ . For no destruction of the pattern

$$\frac{\Delta p_y}{p_{x0}} \ll \frac{\lambda}{a}$$

The indicators obey uncertainty relations, such that  $\Delta p_y \Delta y > \hbar$  for the indicators. Therefore

$$\Delta y > \frac{\hbar}{\Delta p_y} > \frac{\hbar a}{p_{x0} \lambda}$$

But

$$p_{x0} = \frac{h}{\lambda} \rightarrow \Delta y \gg a \gg \text{distance between the slits}$$

Thus, the position of the indicator from one slit is so uncertain in position that it could seem to indicate passage through the wrong slit.

Therefore, preservation of the diffraction pattern  $\rightarrow$  destruction of the knowledge of through which slit the photon passed.

### Wave Equation

A plane wave

$$e^{i(kx - \omega t)}$$

describes particles moving in space with a given momentum; in analogy to acoustics  $\rightarrow$  a wave equation!

### Conditions

- (1) linear equation in  $\psi(\vec{r}, t) \rightarrow$  possible superposition of different solutions of the wave equation, i.e., wave packet representation of the particle. Superpositions of solutions of a non-linear equation are not all solutions of original equation.
- (2) wave equation should contain only universal constants, i.e.,  $\hbar, m$ , etc. For example, consider light. We have wave equation

$$\nabla^2 f - \frac{1}{c^2} \frac{\partial^2 f}{\partial t^2} = 0$$

The term

$$\frac{1}{c^2} \text{ can be } \frac{n^2(\vec{r})}{c^2} \rightarrow \text{function of the medium}$$

We want the wave equation to be the same for all media.

- (3) wave equation should conform to deBroglie relation for a free particle
- (4) in the limit the wave equation should  $\rightarrow$  classical motion!

From condition (3) we have

$$k = \frac{p}{\hbar} \quad , \quad \omega = \frac{E}{\hbar}$$

Considering  $e^{i(kx - \omega t)}$  we get

$$\frac{\partial^2 \psi}{\partial t^2} = \frac{\omega^2}{k^2} \frac{\partial^2 \psi}{\partial x^2} = \frac{E^2}{p^2} \frac{\partial^2 \psi}{\partial x^2} = \frac{E}{2m} \frac{\partial^2 \psi}{\partial x^2}$$



But this contradicts condition (2) → each solution is good only for a particular energy → no superposition.

Try

$$\frac{\partial \psi}{\partial t} = \gamma \frac{\partial^2 \psi}{\partial x^2}$$

This implies

$$-i\omega\psi = k^2\gamma\psi$$

Therefore

$$\gamma = \frac{i\omega}{k^2} = \frac{i\hbar E}{p^2} = \frac{i\hbar}{2m}$$

which is a universal constant. Therefore, we have a satisfactory wave equation which is

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}$$

and only the exponential solution  $e^{i(kx-\omega t)}$  is a solution.

In 3 dimensions

$$\psi = e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

where

$$\vec{k} = \text{wave vector} = \frac{\vec{p}}{\hbar}$$

These conditions force us to reject all solutions not going in the direction of  $\vec{p}$ .

Now

$$\frac{\partial^2 \psi}{\partial x^2} = -k_x^2 \psi$$

and similarly for  $y$  and  $z$ . Therefore, for  $k^2 = k_x^2 + k_y^2 + k_z^2$  we have

$$\nabla^2 \psi = -k^2 \psi$$

$$\frac{\partial \psi}{\partial t} = -i\omega\psi = +\frac{i\omega}{k^2} \nabla^2 \psi$$

Therefore

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi$$

Now

$$E\psi = \hbar\omega\psi = i\hbar \frac{\partial \psi}{\partial t}$$

for any  $\omega$ . For any arbitrary wave packet of different frequencies → analysis of  $\frac{\partial \psi}{\partial t}$  by splitting, Fourier analysis and recombination. But we can get this immediately from the original relation, since this relation is true for any component of  $\omega$ , and the relation is linear → it is true for any superposition of solutions.

$$p_x\psi = \hbar k_x\psi = -i\hbar \frac{\partial \psi}{\partial x}$$

$$\vec{p}\psi = \hbar\vec{k}\psi = -i\hbar\nabla\psi$$

Therefore, since these are linear relations, we can consider these relations as giving meaning to the statement  $K\psi = M\psi$  as  $K$  operates on  $\psi$  and  $K \equiv M$ . Therefore, the operators are

$$E = i\hbar \frac{\partial\psi}{\partial t} \quad , \quad p = -i\hbar\nabla$$

$$E\psi = \frac{p^2}{2m}\psi$$

or

$$i\hbar \frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi \rightarrow \text{wave equation}$$

**Particle in External Force Field:**  $\vec{F} = -\nabla V$  (a conservative force)

$$E = \frac{p^2}{2m} + V \quad (\text{classical})$$

The operator equation in quantum mechanics is

$$E\psi = \frac{p^2}{2m}\psi + V\psi$$

***This is an assumption!!***

We will prove that in the limit, this equation gives the classical result for the equation of motions, thus proving the assumptions are correct. We note that  $V$  is not an operator; only a multiplier. Therefore

$$i\hbar \frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

Interpretation of the wave equation gives certain solutions - depending on the potential  $V$ . In interpreting this equation we must take into account the particle picture.  $\psi$  can give only statistical information  $\rightarrow$  probability.

### Statistical Interpretation due to Born

He postulated that  $|\psi|^2 d\tau$  gives the probability of finding the particle in  $d\tau$ . Why shall we take  $|\psi|^2$  for the probability and not something else?

- (1)  $P$  (probability) must be positive definite. But we know that  $\psi$  is necessarily complex, so that we could get an equation which was 1st-order in time.  $|\psi|^2$  is the simplest, smooth, positive definite function derivable from  $\psi$ .

- (2) Total probability

$$\int P d\tau = 1$$

must be conserved. Consider

$$\frac{\partial}{\partial t} \int |\psi|^2 d\tau$$

We have

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{\partial}{\partial t}\psi^*\psi = \psi^*\frac{\partial\psi}{\partial t} + \frac{\partial\psi^*}{\partial t}\psi$$

Using

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

and

$$-i\hbar\frac{\partial\psi^*}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi^* + V\psi^*$$

which is a much used procedure in quantum mechanics, we get

$$i\hbar\left(\psi^*\frac{\partial\psi}{\partial t} + \frac{\partial\psi^*}{\partial t}\psi\right) = -\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + \frac{\hbar^2}{2m}(\nabla^2\psi^*)\psi = -\frac{\hbar^2}{2m}\nabla\cdot\vec{S}$$

where  $\vec{S} = \psi^*\nabla\psi - (\nabla\psi^*)\psi$ . Therefore

$$\frac{\partial}{\partial t}|\psi|^2 = \frac{i\hbar}{2m}\nabla\cdot\vec{S}$$

This finally gives (using Gauss' theorem)

$$\frac{\partial}{\partial t} \int |\psi|^2 d\tau = \frac{i\hbar}{2m} \int \nabla\cdot\vec{S} d\tau = \frac{i\hbar}{2m} \int \vec{S}\cdot d\vec{A}$$

We have encountered the following types of  $\psi$ :

- (1)  $\psi$  decreases at large distances
  - (a) wave packet -  $\psi = 0$  on surface  $A$  if  $A$  is sufficiently far away from the wave packet.
  - (b) bound electron - the probability of finding the electron far away from the nucleus is small; when the surface  $A$  is far away from the nucleus  $\psi = 0$ .
- (2)  $\psi$  remains constant at large distances, i.e.,  $e^{i(kx-\omega t)}$ . In this case the surface  $A$  and the conditions on  $\psi$  can be suitably chosen so that  $\int_A = 0$ .

The  $\int P d\tau$  is independent of time. We then choose the constants such that  $\int P d\tau = 1$ .

Normalizing conditions on wave function must be imposed before we can consider the wave function as well-defined. The wave function is always arbitrary by a phase factor  $e^{i\alpha}$ . This phase factor makes no difference in  $|\psi|^2$  or in  $\vec{S}$ :

$$\underbrace{\frac{\partial}{\partial t}|\psi|^2}_{\frac{\partial P}{\partial t}} + \underbrace{\frac{\hbar}{2mi}\nabla\cdot\vec{S}}_{\nabla\cdot\vec{S}'} = 0$$

or

$$\frac{\partial P}{\partial t} + \nabla \cdot \vec{S}' = 0$$

Thus, we have a continuity equation and  $S'$  is a probability current density. (compare to electricity where we have  $\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0$ ). The continuity equation represents conservation of probability in a small volume, i.e.,

$$\frac{\partial}{\partial t} \int_V P d\tau + \int_A \vec{S}' \cdot d\vec{A} = 0$$

so that if we take a sufficiently large volume and use  $|\psi|^2$  as the probability density, Schrödinger's equation  $\rightarrow \int |\psi|^2 d\tau = 1$ .

**Definition of Expectation Value:** We can calculate the average value of  $x$  as

$$\begin{aligned} \langle x \rangle &= \int |\psi|^2 x d\tau \\ \langle f(\vec{r}) \rangle &= \int |\psi|^2 f(\vec{r}) d\tau \end{aligned}$$

This is the definition of a statistical average called the expectation value; in general

$$\langle x^2 \rangle \neq \langle x \rangle^2$$

The expectation value of  $x \rightarrow$  classical position by the correspondence principle.

How do we get  $\langle p_x \rangle$  or  $\langle E \rangle$  ? Use correspondence principle and require that in the classical limit the results are valid, i.e., we want to define  $\langle p^2 \rangle \rightarrow$  classical  $p^2$ . It is reasonable to define the expectation values such that

$$\langle E \rangle = \frac{1}{2m} \langle p^2 \rangle + \langle V \rangle$$

It is necessary and sufficient to define  $\langle A \rangle$  in such a way that

$$\langle A \rangle = \int \psi^* A \psi d\tau \quad (A = \text{operator})$$

Once we postulate  $\langle A \rangle = \int \psi^* A \psi d\tau$ , then

$$\langle E \rangle = \frac{1}{2m} \langle p^2 \rangle + \langle V \rangle$$

follows from the Schrödinger equation.

We have

$$\begin{aligned} \langle E \rangle &= i\hbar \int \psi^* \frac{\partial \psi}{\partial t} d\tau \\ \langle p^2 \rangle &= -\hbar^2 \int \psi^* \nabla^2 \psi d\tau \\ \langle p_x \rangle &= -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} d\tau \end{aligned}$$

Then Schrödinger equation  $\rightarrow$

$$\int \psi^* \left( -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi \right) d\tau = \langle E \rangle$$

**Ehrenfest Theorem**

$$\frac{d}{dt} \langle x \rangle = \int x \frac{\partial}{\partial t} |\psi|^2 d\tau = -\frac{\hbar}{2im} \int x \nabla \cdot \vec{S} d\tau$$

Now from vector analysis

$$\nabla \cdot (j \vec{S}) = j \nabla \cdot \vec{S} + (\nabla j) \cdot \vec{S}$$

Therefore

$$\begin{aligned} \frac{d}{dt} \langle x \rangle &= -\frac{\hbar}{2im} \underbrace{\int_V \nabla \cdot (x \vec{S}) d\tau}_{=0 \text{ since } \int_A = 0; \psi \rightarrow 0 \text{ on } A} + \frac{\hbar}{2im} \int_V \underbrace{\overbrace{(\nabla x)}^{\vec{1}_x}}_{S_x} \cdot \vec{S} d\tau \\ &= \frac{\hbar}{2im} \int_V S_x d\tau = \frac{\hbar}{2im} \int_V \left( \psi^* \frac{\partial \psi}{\partial x} - \frac{\partial \psi^*}{\partial x} \psi \right) d\tau \\ &= \frac{\hbar}{2im} \int_V \left( 2\psi^* \frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x} (\psi^* \psi) \right) d\tau \quad (\text{integrating by parts}) \\ &= \frac{\hbar}{im} \int_V \psi^* \frac{\partial \psi}{\partial x} d\tau \quad (\text{using } \int_V \frac{\partial}{\partial x} (\psi^* \psi) d\tau = \frac{\partial}{\partial x} \int_V \psi^* \psi d\tau = \frac{\partial}{\partial x} (1) = 0) \\ &= \frac{\langle p_x \rangle}{m} \end{aligned}$$

The relation obtained for expectation values is precisely that obtained classically for the corresponding values. The correspondence principle requires that classical mechanics holds in the limit, but Ehrenfest's theorem gives

$$\frac{d}{dt} \langle x \rangle = \frac{\langle p_x \rangle}{m}$$

The center of the wave packet moves with the classical velocity. This is an exact relation - true for all time. This is true for all wave packets, no matter how the shape of the wave packet may change.

Now

$$\begin{aligned} \frac{d\langle p_x \rangle}{dt} &= -i\hbar \int \left[ \frac{\partial \psi^*}{\partial t} \frac{\partial \psi}{\partial x} - \psi^* \frac{\partial}{\partial t} \frac{\partial \psi}{\partial x} \right] d\tau \\ &= \int \left( -\frac{\hbar^2}{2m} \nabla^2 \psi^* + V \psi^* \right) \frac{\partial \psi}{\partial x} d\tau - \int \frac{\partial}{\partial x} \left( -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi \right) d\tau \\ &= - \int \psi^* \psi \frac{\partial V}{\partial x} d\tau = \left\langle -\frac{\partial V}{\partial x} \right\rangle \end{aligned}$$

as expected! We now have

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}, t) + V(\vec{r}, t) \psi(\vec{r}, t)$$

$$\rho(\vec{r}, t) = |\psi(\vec{r}, t)|^2$$

**Properties of the Solutions of Schrödinger's Equation** (time-independent, i.e.,  $V = V(r)$ )

Is separation of variables possible, i.e.,

$$\text{general solution} \rightarrow \psi(\vec{r}, t) = \sum_n c_n(f_n(t)u(\vec{r}))$$

For now let  $\psi(\vec{r}, t) = f(t)u(\vec{r})$  which implies that

$$i\hbar u(\vec{r}) \frac{\partial f}{\partial t} = -\frac{\hbar^2}{2m} f(t) \nabla^2 u(\vec{r}) + V(r) u(\vec{r}) f(t)$$

or

$$\underbrace{i\hbar u(\vec{r}) \frac{1}{f} \frac{\partial f}{\partial t}}_{g(t) \text{ only}} = \underbrace{-\frac{\hbar^2}{2m} \frac{1}{u(\vec{r})} \nabla^2 u(\vec{r}) + V(r)}_{k(r) \text{ only}} = \text{constant} = E$$

Therefore

$$i\hbar \frac{\partial f}{\partial t} = E f$$

and

$$-\frac{\hbar^2}{2m} \nabla^2 u(\vec{r}) + V(r) u(\vec{r}) = E u(\vec{r})$$

For the  $t$  equation

$$f(t) = A e^{-i \frac{Et}{\hbar}}$$

Therefore

$$\psi(\vec{r}, t) = u(\vec{r}) e^{-i \frac{Et}{\hbar}}$$

$\rightarrow |\psi|^2 = |u(r)|^2 \rightarrow$  stationary or eigenstate solution, i.e.,  $|\psi|^2 \neq m(t)$  or probability density is independent of time!

The  $r$  equation is a 2nd-order differential equation  $\rightarrow$  need for two boundary conditions, i.e.,  $(r, \nabla r)_{t=t_0}$ .

We want only physically useful solutions!

**Physical requirements on  $u(\vec{r})$**

- (1) wave packet -  $|\psi|^2 \rightarrow 0$  as  $r \rightarrow \infty$ . For wave packets we can set  $\int |\psi|^2 d\tau = 1$  by normalization  $\rightarrow$  localization of particle!

(2) traveling wave - say a plane wave

$$\phi(\vec{r}, t) = e^{i(\vec{k} \cdot \vec{r} - \omega t)}$$

$\rightarrow |\psi|^2 = 1$  at large  $r \rightarrow$  equal distribution of particles everywhere!

Therefore, **1st requirement**  $\rightarrow$  bounded everywhere (at large distances).

(3) Continuity requirements, i.e.,  $u(r)$ ,  $\frac{du}{dr}$  are continuous,  $\rightarrow \psi$  is uniquely given by the boundary conditions!

These should also be single valued and finite

(a) single-valued  $\rightarrow$  uniquely defined probability

(b) infinite  $\rightarrow$  a local probability becomes infinite at a point  $\rightarrow$  absolute localization!

$\psi$  for localized particle: there is a discrete spectrum of allowed  $E$  values, i.e.,  $E_1, E_2, \dots$   $\left. \vphantom{\begin{matrix} \psi \\ \psi \end{matrix}} \right\}$  not yet shown  
 $\psi$  for traveling wave: there is a continuous spectrum of all energy eigenvalues!

### Schrödinger's Equation in One Dimension

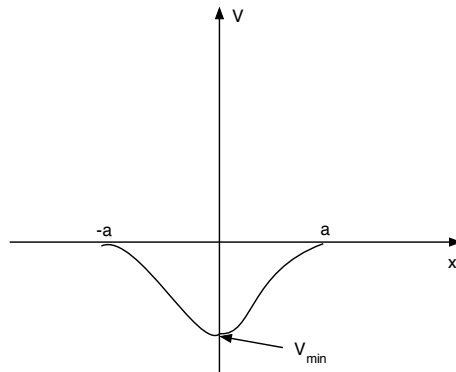
$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + V(x)u(x) = Eu(x) \quad \text{or} \quad \frac{d^2 u}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))u(x) = 0$$

**For localized particles:**

$$V(x) \rightarrow \text{constant} \quad |x| \rightarrow \infty$$

$V = \text{constant} \rightarrow$  no forces; this is reasonable for localized particles since if forces existed at large distances  $\rightarrow$  some particles at  $\infty \rightarrow$  no real validity to the idea of localization!

Since  $V$  scale is arbitrary, let  $V = \text{constant} = 0$  as  $|x| \rightarrow \infty$ . Let us put the further restriction that for  $|x| > a$ ,  $V = 0$ . Therefore we have



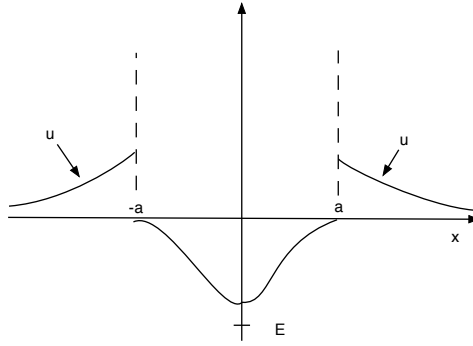
Suppose  $E < 0$ ;  $|x| > a \rightarrow V = 0$ . Therefore

$$\frac{d^2u}{dx^2} + \frac{2m}{\hbar^2}Eu = 0 \quad \beta^2 = -\frac{2mE}{\hbar^2} > 0 \rightarrow u = e^{\pm\beta x}$$

Now from physical requirements,  $x \rightarrow \pm\infty \rightarrow$  bounded  $\rightarrow$

$$u = e^{-\beta|x|} \quad , \quad |x| > a$$

This gives



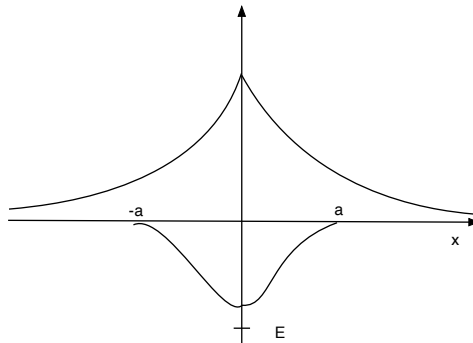
Now for  $|x| < a$ , if  $E < V_{min}$ , then

$$\frac{2m}{\hbar^2}(E - V(x)) < 0 \quad \text{everywhere}$$

Now if  $\frac{1}{u} \frac{d^2u}{dx^2} > 0 \rightarrow$  concave upwards function. Since we have

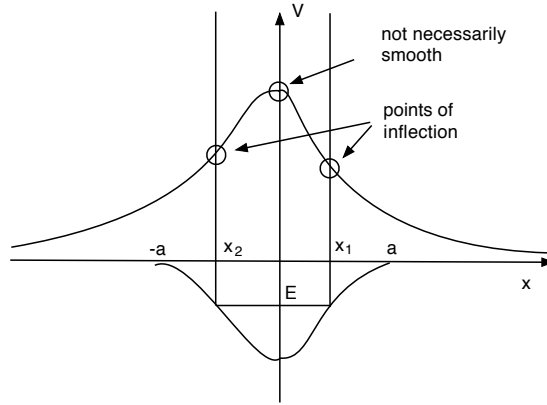
$$\frac{1}{u} \frac{d^2u}{dx^2} > 0 \quad \text{for all } x$$

$\rightarrow$  wave function is concave away from axis for all  $x$  (as shown).



Note that at  $x = 0$ ,  $\frac{du}{dx}$  is not continuous  $\rightarrow$  we cannot get meaningful functions.





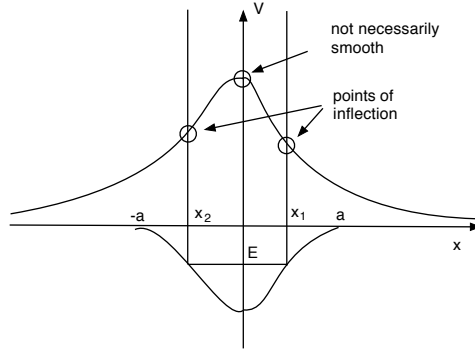
Therefore we can now conclude that  $o > E > V_{min}$ . then two points exist where  $E = V(x)$ , say  $x_1$  and  $x_2$ ; between these two points  $(E - V(x)) > 0$  (as shown) Note that at  $x_1$  and  $x_2$  we have  $\frac{d^2u}{dx^2} = 0$ . In general, it seems as though we will obtain a continuous derivative. Let us choose  $V$  to be symmetric, i.e.,  $V(x) = V(-x)$ . Then

$$\frac{d^2u}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))u = 0 \rightarrow u(x) = u(-x)$$

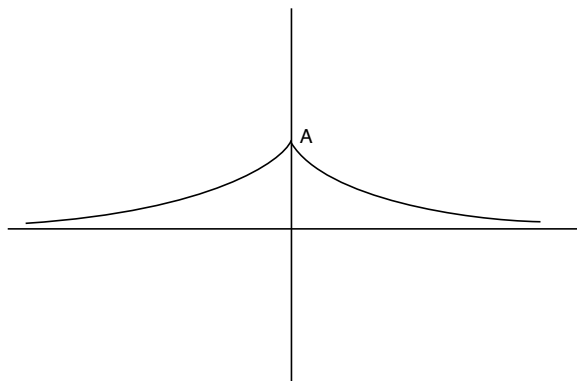
We note that

$$\left. \frac{du}{dx} \right|_{x=0} = 0 \rightarrow \text{solution} \rightarrow \text{continuous derivative}$$

Thus, in general, under these conditions we will have:

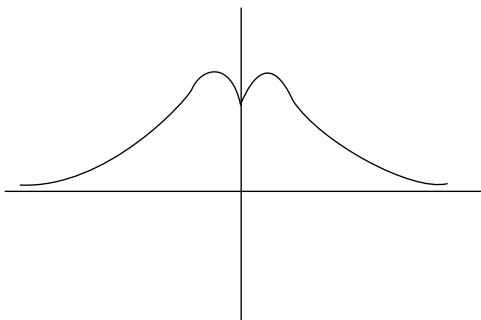


For  $E = V_{min}$ , all curvature is upwards (concave) except at  $x = 0 \rightarrow$  no curvature  $\rightarrow$  continuous derivative.

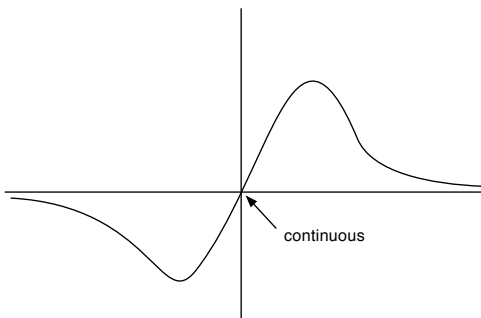


We note that, in this case,  $V > E$  except at  $x = 0$  where  $V = E$ . At point A, we have  $\frac{d^2 u}{dx^2} = 0 \rightarrow \frac{du}{dx}$  is continuous (i.e., it exists).

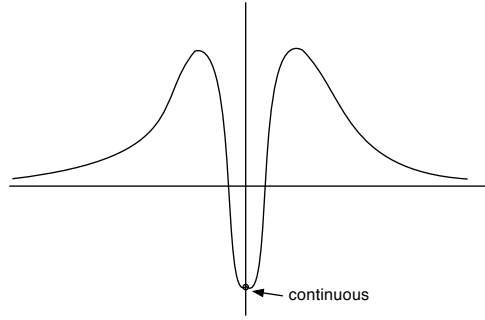
But as  $E$  increases, curvature increases  $\rightarrow$  eventual discontinuous derivative; i.e., increasing  $E \rightarrow$



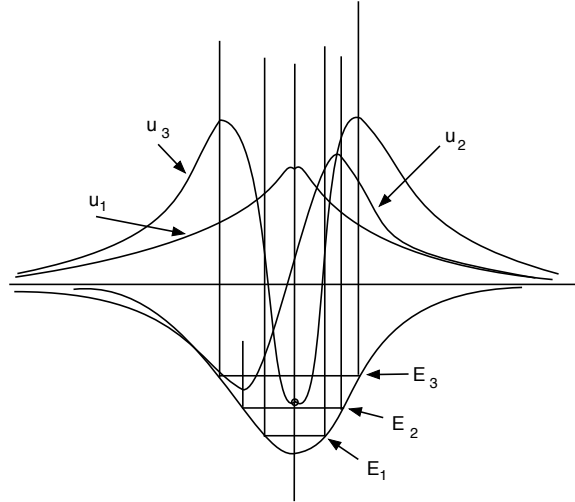
This corresponds to no continuous derivatives. Still increasing  $E$  (choosing  $u(x) = -u(-x)$  until



Note that it is continuous at  $x = 0$ . Continue to increase  $E$  until (choosing  $u(x) = u(-x)$ ).



All this  $\rightarrow$  only discrete values of  $E \rightarrow$  continuous  $u$  and  $\frac{du}{dx} \rightarrow$  only discrete values of  $E$  give meaningful solutions. Thus we have



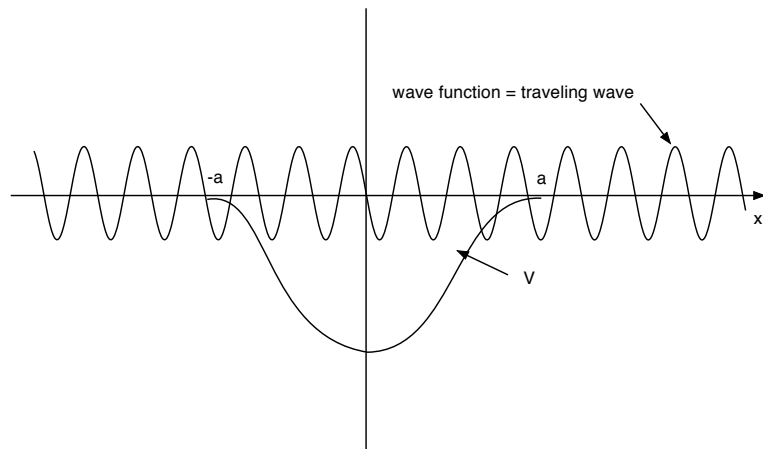
Now for  $E > V_{max} = 0$  and  $|x| > a$  we have

$$\frac{d^2 u}{dx^2} + \frac{2m}{\hbar^2} E u = 0 \quad E > 0$$

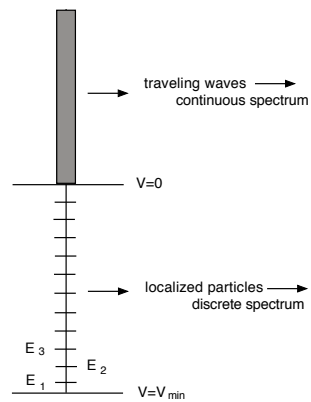
For

$$\alpha^2 = \frac{2mE}{\hbar^2} \rightarrow u \sim e^{\pm i\alpha x} \quad , \quad |u|^2 = 1$$

or all  $E$  values are allowed since the wave function is bounded at  $\infty$  for all  $E$ .  
(see below).

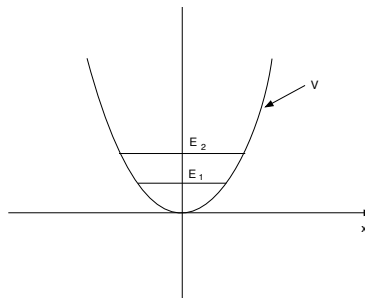


The energy spectrum becomes



### Removal of Restrictions

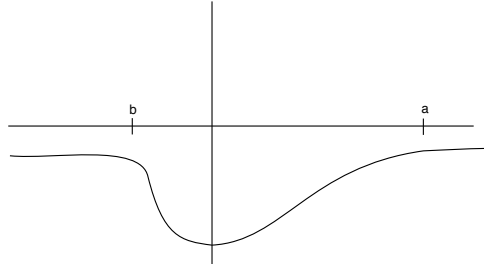
(1)  $V$  does not  $\rightarrow$  constant at  $\infty$ , i.e., harmonic oscillator  $V = \frac{1}{2}kx^2$



$E < V \rightarrow$  continuous upward curvature  $\rightarrow$  no continuity of  $\frac{du}{dx}$  at  $x = 0 \rightarrow$  no meaningful functions.

We get an infinite number of  $E$  levels, therefore restriction of limit at infinity is really not a restriction!

- (2) Restriction of symmetry potential; consider the asymmetric potential (shown below)



we have

$$V = \text{constant} = V_1; x < b$$

$$\frac{d^2u}{dx^2} + \frac{2m}{\hbar^2}(E - V_1)u = 0$$

$$\frac{d^2u}{dx^2} - \beta^2 u = 0 \quad -\beta^2 = \frac{2m}{\hbar^2}(E - V_1)$$

$$E < V_1 \rightarrow u \approx e^{-\beta x} + e^{\beta x}$$

and

$$V = \text{constant} = V_0; x > a$$

$$\frac{d^2u}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)u = 0$$

$$\frac{d^2u}{dx^2} - \alpha^2 u = 0 \quad -\alpha^2 = \frac{2m}{\hbar^2}(E - V_0)$$

$$E < V_0 \rightarrow u \approx e^{-\alpha x} + e^{\alpha x}$$

Start at point  $b$  and solve going towards  $a \rightarrow$  when we reach  $a$ ,  $\frac{du}{dx}$  and  $u$  must be continuous at  $a \rightarrow$  restriction

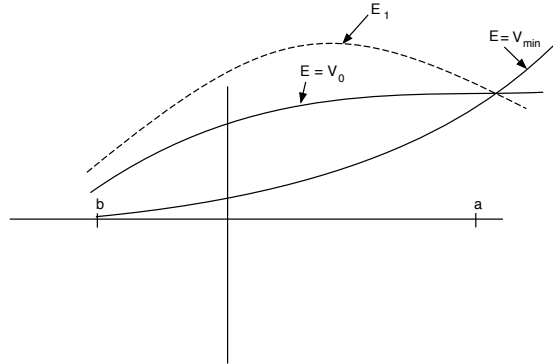
$$u(a) = Ae^{\alpha a} + Be^{-\alpha a}$$

$$u'(a) = \alpha Ae^{\alpha a} - \alpha Be^{-\alpha a}$$

$$A = \frac{1}{2}e^{-\alpha a}(\alpha u(a) + u'(a))$$

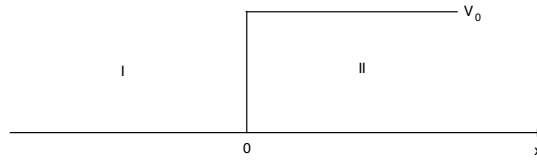
$$B = \frac{1}{2}e^{\alpha a}(\alpha u(a) - u'(a))$$

But  $A$  must be zero or we will have  $u \sim e^x \rightarrow$  unbounded at  $\infty$ .



This implies there will be some energy value ( $E_1$  where the solution will lead to the decreasing exponential and thus lead to a meaningful solution (dotted solution)!!

### (3) Infinite Potential Jump



Consider the two regions I and II:

Region I:

$$\frac{d^2 u}{dx^2} - k^2 u = 0 \quad , \quad k^2 = \frac{2mE}{\hbar^2}$$

$$u = A \sin kx + B \cos kx$$

Region II: (for  $V_0$  large)

$$\frac{d^2 u}{dx^2} - \beta^2 u = 0 \quad , \quad \beta^2 = \frac{2m(E - V_0)}{\hbar^2}$$

$$u = C e^{-\beta x}$$

For a match at  $x = 0$  we must have

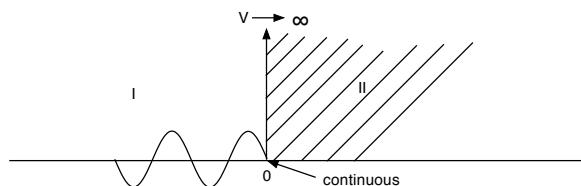
$$B = C \quad , \quad kA = -\beta C$$

As  $\beta \rightarrow \infty$ , we may bet  $A \rightarrow \infty$  or an infinite normalization constant, which is of no value to us. Therefore, we must have

$$C = 0 \rightarrow B = 0$$

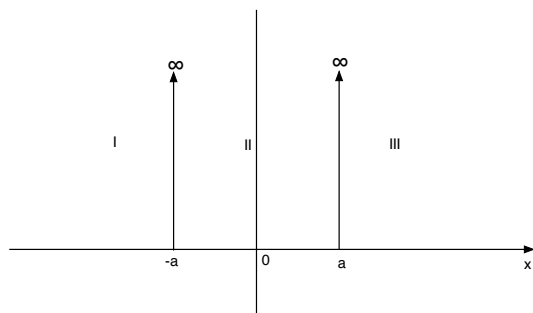
Therefore

$$u(x) = \begin{cases} A \sin kx & x < 0 \\ 0 & x > 0 \end{cases}$$



$u$  is continuous;  $u'$  is discontinuous (due to  $\infty$  jump). Also  $P(y)$  and  $S(x)$  are continuous.  $u'$  will be continuous for non-infinite jumps!

**Example:** Consider the infinite square well (shown below)



We must have  $u = 0$  in regions I and III. In region II:

$$\frac{d^2 u}{dx^2} + \beta^2 u = 0 \quad , \quad \beta^2 = \frac{2mE}{\hbar^2}$$

$E < 0 \rightarrow$  curvature always upwards  $\rightarrow$  no meaning!

$E > 0 \rightarrow u(x) = A \sin \beta x + B \cos \beta x$

Matching at  $\pm a \rightarrow$

$$0 = A \sin \beta a + B \cos \beta a \quad , \quad 0 = -A \sin \beta a + B \cos \beta a$$

which implies that

$$A \sin \beta a = B \cos \beta a = 0$$

1st solution:  $A = B = u = 0 \rightarrow$  no wave function!

2nd solution:  $A = 0$  and  $\cos \beta a = 0 \rightarrow u = B \cos \beta x$  and

$$\beta a = (2n + 1) \frac{\pi}{2} \quad n = 0, 1, 2, 3 \dots$$

Therefore,

$$\beta^2 = (2n + 1)^2 \frac{\pi^2}{4a^2} = \frac{2m}{\hbar^2} E \rightarrow E_{2n+1} = \frac{\hbar^2}{2m} (2n + 1)^2 \frac{\pi^2}{4a^2}$$

3rd solution:  $B = 0$  and  $\sin \beta a = 0 \rightarrow u = A \sin \beta x$  and  $\beta = 2n \frac{\pi}{2} \quad n = 1, 2, 3, \dots$  ;  
note that case  $n = 0$  is just the 1st solution (trivial case).

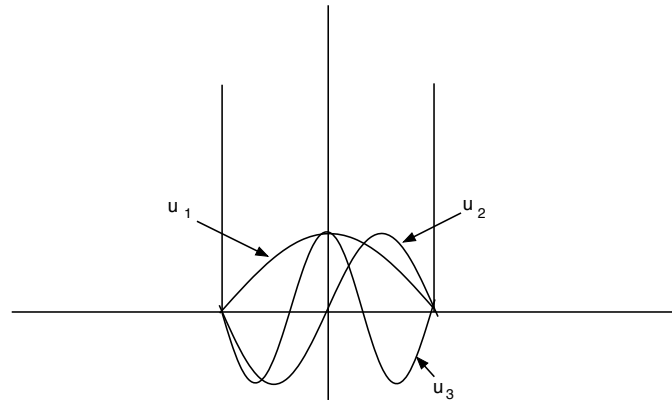
Therefore,

$$E_{2n} = \frac{\hbar^2}{2m} (2n)^2 \frac{\pi^2}{4a^2}$$

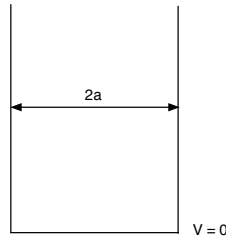
we have

$$u_1 = B \cos \frac{\pi}{2a} x \text{ with } E_1 = \frac{\hbar^2 \pi^2}{8ma^2}$$

etc. The first three wave functions are shown below:



We also have



with corresponding quantities

$$\Delta x \sim a, \quad \Delta p \sim \frac{\hbar}{a}, \quad \langle p^2 \rangle > \frac{\hbar^2}{a^2}$$

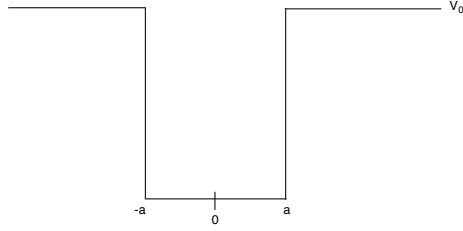


which implies that

$$E_{lowest\ state} > \frac{\hbar^2}{2ma^2} \quad \text{this is only an estimate}$$

But, solution of problem  $\rightarrow E_1 = \frac{\hbar^2}{ma^2} \frac{\pi^2}{8} > E_{lowest\ state} \rightarrow$  O.K. Only a Gaussian will give minimum uncertainty  $\rightarrow$  zero point energy.

### Finite Potential Well



We have

$$\frac{d^2u}{dx^2} + \frac{2m}{\hbar^2}(E - V)u = 0$$

where

$$V = \begin{cases} 0 & |x| < a \\ V_0 & |x| > a \end{cases}$$

$$|x| < a \rightarrow u = A \sin \alpha x + B \cos \alpha x \quad , \quad \alpha^2 = \frac{2mE}{\hbar^2}$$

$$|x| > a \rightarrow u = C e^{-\beta x} + D e^{\beta x} \quad , \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

$$\left. \begin{array}{l} x > a \rightarrow u = C e^{-\beta x} \quad D = 0 \\ x < -a \rightarrow u = D e^{\beta x} \quad C = 0 \end{array} \right\} \text{ so that } u \rightarrow \text{finite as } |x| \rightarrow \infty$$

For continuity at  $|x| = a$ :

$$\left. \begin{array}{l} A \sin \alpha a + B \cos \alpha a = C e^{-\beta a} \\ -A \sin \alpha a + B \cos \alpha a = D e^{-\beta a} \end{array} \right\} \text{ continuity of } u$$

This implies

$$2A \sin \alpha a = (C - D) e^{-\beta a} \quad (1)$$

$$2B \cos \alpha a = (C + D) e^{-\beta a} \quad (2)$$

Continuity of  $\frac{du}{dx}$ :

$$\begin{aligned} A \alpha \cos \alpha a - B \alpha \sin \alpha a &= -C \beta e^{-\beta a} \\ A \alpha \cos \alpha a + B \alpha \sin \alpha a &= D \beta e^{-\beta a} \end{aligned}$$

$$2A \alpha \cos \alpha a = -(C - D) \beta e^{-\beta a} \quad (3)$$

$$2B\alpha \sin \alpha a = (C + D)\beta e^{-\beta a} \quad (4)$$

From (1) and (3)

$$\text{either } A = C - D = 0 \quad (5)$$

$$\text{or } \alpha \cot \alpha a = -\beta \quad (6)$$

From (2) and (4)

$$\text{either } B = C + D = 0 \quad (7)$$

$$\text{or } \alpha \tan \alpha a = \beta \quad (8)$$

(5) and (7)  $\rightarrow$  trivial solution

(6) and (8) cannot be used simultaneously.

**Class I Solutions:**

$$\alpha a \tan \alpha a = \beta a$$

$$A = C - D = 0$$

$$B \neq 0$$

$$C + D \neq 0$$

$\rightarrow$  only  $\cos \alpha x$  occurs.

**Class II Solutions:**

$$\alpha a \cot \alpha a = -\beta a$$

$$A \neq 0$$

$$C - D \neq 0$$

$$B = C + D = 0$$

$\rightarrow$  only  $\sin \alpha x$  occurs.

Now let  $\alpha a = \xi$  and  $\beta a = \eta$ , then we have

$$\xi^2 + \eta^2 = \frac{2m}{\hbar^2} V_0 a^2 \quad (9)$$

Now for Class I

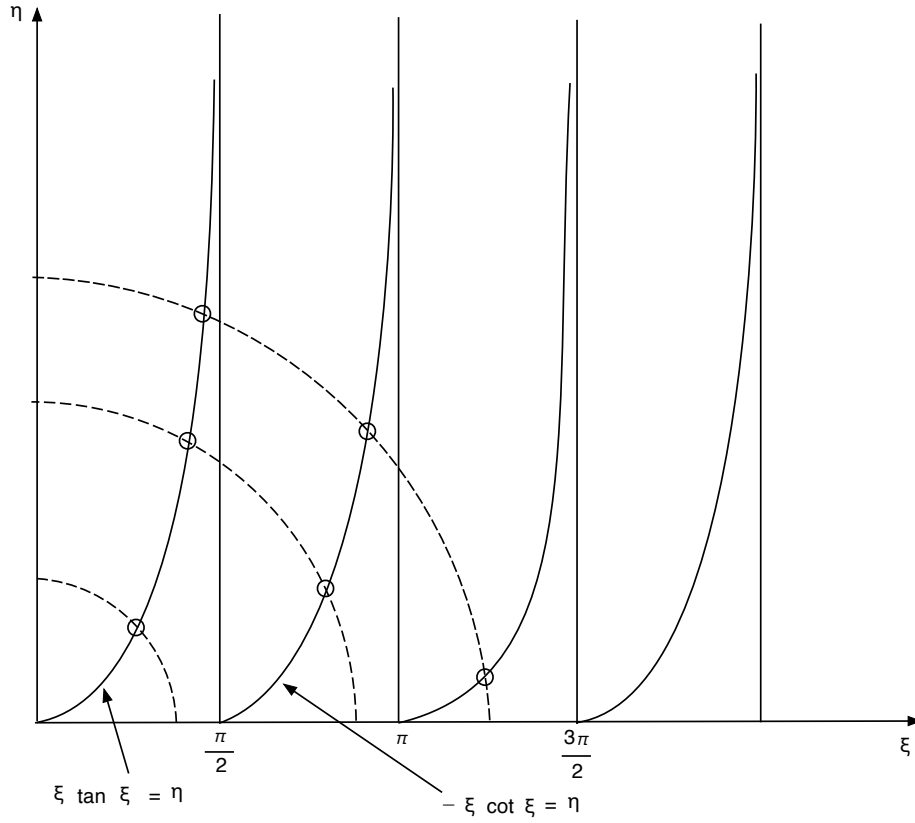
$$\xi \tan \xi = \eta \quad (10)$$

and for Class II

$$-\xi \cot \xi = \eta \quad (11)$$

Equations (9), (10), and (11)  $\rightarrow$  solutions;  $\xi$  values  $\rightarrow$  energy eigenvalues!

A graphical solution is shown below:



Note that curve in 2nd quadrant is inconsistent.

We have

$$\xi^2 + \eta^2 = r^2 = \frac{2m}{\hbar^2} V_0 a^2 \quad (\text{dotted circles (radius} = r) \text{ on diagram)}$$

→ number of intersections → number of solutions.

$$\begin{aligned} \xi_1 &= \text{lowest } \xi & 0 < \xi_1 < \frac{\pi}{2} \\ \xi_3 &= \text{2nd } \xi & \pi < \xi_1 < \frac{3\pi}{2} \end{aligned}$$

Class II solutions → similar intersections. Discrete intersections → discrete values of  $\xi$  → discrete  $E$  values (all depending on  $r$ ). We have the result

$$\frac{n-1}{2}\pi < r < \frac{n\pi}{2} \rightarrow \text{exactly } n \text{ solutions.}$$

## Parity

We make *assumption*:  $V(-x) = V(x) \rightarrow$  symmetric potential. Then we have

$$\frac{d^2 u(x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] u(x) = 0$$

$$\frac{d^2 u(-x)}{d(-x)^2} + \frac{2m}{\hbar^2} [E - V(-x)] u(-x) = 0$$

or

$$\frac{d^2 u(-x)}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] u(-x) = 0$$

$\rightarrow$  same differential equation as for  $u(x)$ .

Assume only one solution  $u$  for given energy  $E$

$$\rightarrow u(-x) = \varepsilon u(x)$$

$$x \rightarrow -x \rightarrow u(x) = \varepsilon u(-x) = \varepsilon^2 u(x) \rightarrow \varepsilon = \pm 1$$

Therefore

$$\begin{array}{ll} u(-x) = u(x) & \text{I} \rightarrow \text{symmetric function - EVEN function} \\ \text{or } u(-x) = -u(x) & \text{II} \rightarrow \text{antisymmetric function - ODD function} \end{array}$$

$$\left. \begin{array}{l} \text{II } u(0) = 0 \\ \text{I } \left. \frac{du}{dx} \right|_0 = 0 \end{array} \right\} \text{ solutions for successive values of discrete } E\text{'s} \rightarrow \text{EVEN, ODD alternation}$$

## Elimination of Restriction of Unique Solutions

Assume several solutions for a given  $E$ !  $u(x)$  is a solution...where we can write

$$\begin{aligned} u(x) &= u_e(x) + u_o(x) \\ u(-x) &= u_e(x) - u_o(x) \end{aligned}$$

Substituting in Schrödinger's equation  $\rightarrow$

$$\frac{d^2 u_e}{dx^2} + \frac{2m}{\hbar^2} [E - V] u_e + \frac{d^2 u_o}{dx^2} + \frac{2m}{\hbar^2} [E - V] u_o = 0$$

Letting  $x \rightarrow -x$

$$\frac{d^2 u_e}{dx^2} + \frac{2m}{\hbar^2} [E - V] u_e - \frac{d^2 u_o}{dx^2} - \frac{2m}{\hbar^2} [E - V] u_o = 0$$

Add  $\rightarrow u_e$  satisfies Schrödinger's equation and subtract  $\rightarrow u_o$  satisfies Schrödinger's equation. Therefore,  $u_e, u_o$  are also solutions  $\rightarrow$  degenerate eigenvalues.

We can always choose even or odd solutions by suitable linear combinations of our solutions!

### 3 Postulates Concerning Interpretation

I. Any classical dynamic variable is represented by an operator

$$\vec{p} = i\hbar\nabla \quad , \quad E = i\hbar\frac{\partial}{\partial t}$$

For any operator  $\Omega$  we can write

$$\Omega u_\omega = \omega u_\omega$$

where  $u_\omega$  is an eigenfunction(solution) and  $\omega$  = number = eigenvalue.

II. Any physical measurement of  $\Omega$  will give one or another eigenvalue  $\omega$ .

[  $\psi$  = wave function  $\rightarrow$  may coincide with a single eigenfunction, but, in general, it will be a combination of eigenfunctions!

How can we decompose  $\psi$  into eigenfunctions of certain operators?, i.e.,

$$\psi = \sum_{\omega} A_{\omega} u_{\omega} \quad (\text{proof} \rightarrow \text{orthonormal } u_{\omega})$$

$A_{\omega}$  = expansion coefficient.

III. Probability of finding result  $\omega$  in measurement of  $\Omega$  is  $|A_{\omega}|^2$  - due to Born.

Consider

$$\Omega_E = -\frac{\hbar^2}{2m}\nabla^2 + V$$

Therefore we have

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)u_E(\vec{r}) = Eu_E(\vec{r})$$

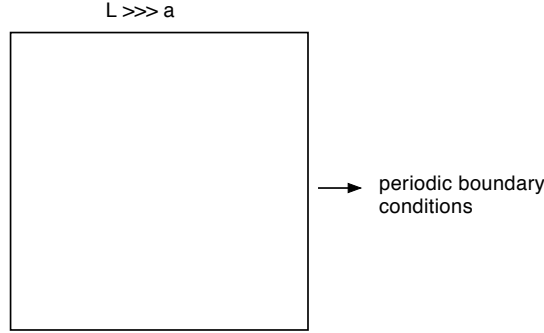
(1)  $E \rightarrow$  discrete values

$$u_E \rightarrow 0 \quad \text{as } r \rightarrow \infty$$

(2)  $E \rightarrow$  continuous values

$$u_E \rightarrow \text{finite} \quad \text{as } r \rightarrow \infty$$

Integration by parts - solution finite on surface  $\rightarrow \int dA \neq 0$  as in (1) solutions.



We have  $u(x + L) = u(x)$ . This enables us to work out (2) solutions  $\rightarrow$  extension of domain of discrete eigenvalues into region II but these are so close together that physically the  $E$  spectrum is continuous; but not mathematically!

### Energy Eigenfunctions

$$\left( \underbrace{-\frac{\hbar^2}{2m} \nabla^2 + V}_{\text{energy operator}} \right) u_E = E u_E \quad (12)$$

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) u_{E'}^* = E'^* u_{E'}^* \quad (13)$$

Multiply (13) by  $u_E$  and (12) by  $u_{E'}^*$  and subtract  $\rightarrow$  potential term cancels (aim of this procedure is the elimination of dependence on a particular potential). We then have.

$$-\frac{\hbar^2}{2m} [u_{E'}^* \nabla^2 u_E - u_E \nabla^2 u_{E'}^*] = (E - E'^*) u_{E'}^* u_E$$

Now integrate over all space

$$-\frac{\hbar^2}{2m} \int [u_{E'}^* \nabla^2 u_E - u_E \nabla^2 u_{E'}^*] d\tau = \int (E - E'^*) u_{E'}^* u_E d\tau$$

Using Gauss's law or Green's theorem  $\rightarrow$

$$-\frac{\hbar^2}{2m} \int \left( u_{E'}^* \frac{\partial u_E}{\partial n} - u_E \frac{\partial u_{E'}^*}{\partial n} \right) d\sigma = \int (E - E'^*) u_{E'}^* u_E d\tau$$

If  $E$  and  $E'$  are discrete  $\rightarrow u_E$  decreases exponentially as  $r \rightarrow \infty$ , which gives

$$\int \left( u_{E'}^* \frac{\partial u_E}{\partial n} - u_E \frac{\partial u_{E'}^*}{\partial n} \right) d\sigma \rightarrow 0 \quad , \quad \left( u_E, \frac{\partial u_E}{\partial n} \right) \rightarrow 0$$

for a large enough volume!

**Digression:** Define  $(\psi^*, A\psi) \equiv \int \psi^* A\psi d\tau$ . Then

$$\begin{aligned} (\psi_n^*, H\psi_m) &= E_m(\psi_n^*, \psi_m) = (H\psi_n^*, \psi_m) = E_n^*(\psi_n^*, \psi_m) \\ &\rightarrow (E_m - E_n^*)(\psi_n^*, \psi_m) = 0 \\ m = n &\rightarrow (\psi_n^*, \psi_n) \neq 0 \rightarrow E_m = E_m^* \rightarrow E_m = \text{real} \end{aligned}$$

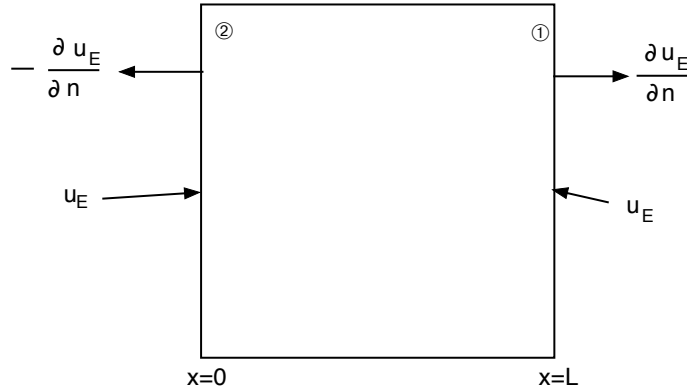
Nothing surprising here since the eigenvalues of a Hermitian operator are real. In addition,

$$m \neq n \rightarrow (E_m - E_n)(\psi_n^*, \psi_m) = 0 \rightarrow (\psi_n^*, \psi_m) = 0 \rightarrow \text{orthogonal}.$$

Again not surprising for Hermitian operators. more on these points later.

**Box Normalization:**  $E$  and  $E'$  are in the continuum, i.e.,  $u_E$ , etc do not go to zero for large  $r$ ,  $\rightarrow$  periodic boundary conditions, i.e.,

$$u(x + L, y, z) = u(x, y, z)$$



Normal derivatives opposite but equal in magnitude  $\rightarrow$  cancellation of all terms  $\rightarrow \int (\dots) d\sigma = 0$ , i.e.,

$$\left. \begin{aligned} (u_{E'}^*)_1 &= (u_{E'}^*)_2 \\ \left(\frac{\partial u_E}{\partial n}\right)_1 &= -\left(\frac{\partial u_E}{\partial n}\right)_2 \end{aligned} \right\} \text{true for all corresponding points}$$

and similarly for  $u_E$  and  $\frac{\partial u_{E'}}{\partial n}$  terms  $\rightarrow$  exact cancellation! Therefore in general we have

$$(E - E'^*) \int u_{E'}^* u_E d\tau = 0$$

which is the orthonormality integral!

Case 1:  $u_{E'} = u_E \rightarrow E'^* = E$  since  $\int u_E^* u_E d\tau \neq 0$ , i.e.,  $u_E^* u_E = |u_E|^2 = \text{positive definite} \rightarrow E - E'^* = 0 \rightarrow E = E'^*$ , but  $E = E'$  in this case and therefore  $E = E^* \rightarrow \text{real } E$ .

Thus, same eigenfunctions  $\rightarrow$  same eigenvalues, but same eigenvalues  $\nrightarrow$  same eigenfunctions!

Case 2:  $E' \neq E$  then  $\int u_{E'}^* u_E d\tau = 0 \rightarrow$  orthogonal wave functions  $\rightarrow$  any two eigenfunctions belonging to different eigenvalues are orthogonal!

Case 3:  $E' = E$ ,  $u_{E'} \neq u_E$  (degenerate eigenvalues which are extremely common in 2 and 3 dimensions)  $\rightarrow u_{ES}$  where  $E$  gives the energy eigenvalue and  $S$  specifies which eigenfunction.

If  $E$  (eigenvalues) are the same for several configurations, then we can form any linear combination of theses  $\rightarrow$  solution is  $\sum \alpha_S u_{ES}$ ! This implies that we can construct orthogonal eigenfunctions, i.e., construction of an orthogonal set of degenerate eigenfunctions.

**Example:**  $u_1$  and  $u_2$  are orthogonal, then

$$\left. \begin{array}{l} \frac{1}{\sqrt{2}}(u_1 + u_2) \\ \frac{1}{\sqrt{2}}(u_1 - u_2) \end{array} \right\} \text{ are also orthogonal, etc}$$

We normalize eigenfunctions by requiring that

$$\int |u_E|^2 d\tau = 1$$

When all eigenfunctions are normalized and orthogonal  $\rightarrow$  *orthonormal set*.

Now consider a general operator  $\Omega$  (go through same steps as with  $E$ )  $\rightarrow$

$$\int [u_{\omega'}^* (\Omega u_{\omega}) - (\Omega u_{\omega'}^* u_{\omega})] d\tau = \text{surface integral} = 0$$

If this is so  $\rightarrow \Omega = \text{hermitian operator}$  and as in the energy case,  $\omega = \text{real}$  and  $u_{\omega}$ 's are orthogonal!

On physical grounds, if  $\Omega$  represents a dynamical variable, i.e., it has meaning in classical mechanics  $\rightarrow$  operating with  $\Omega$  should  $\rightarrow$  real measurement value which will be  $\omega$ . This implies that all dynamical variables must be represented by Hermitian operators  $\rightarrow$  we will always get real eigenvalues (this is the converse of the prior argument, i.e., now assume  $\omega = \text{real} = \omega^* \rightarrow$  Hermitian  $\Omega$  and from 3rd postulate  $\rightarrow$  orthogonality. Q.E.D).

In problem set:

$$\frac{d}{dt} \langle x^2 \rangle = \frac{1}{m} \langle xp + px \rangle = \frac{1}{m} \langle \text{hermitian operator} \rangle$$



$xp \neq px$ , i.e.,

$$(px - xp)u = -i\hbar \frac{\partial}{\partial x}(xu) + i\hbar x \frac{\partial u}{\partial x} = i\hbar u$$

or operator  $px - xp = i\hbar$  This implies that all eigenvalues are not real;  $= -i\hbar \rightarrow$  not hermitian  $\rightarrow px - xp \neq$  dynamical variable. Note that

$$\begin{aligned} I &= xp + px \\ II &= px - xp \end{aligned}$$

$$\left. \begin{aligned} I + II &= 2px \\ I - II &= 2xp \end{aligned} \right\} \text{ not hermitian}$$

Only the symmetric expression  $xp + px$  gives a hermitian operator! This implies that order in operators is all important!! (unlike in classical mechanics where  $2xp = 2px$ ).

Therefore, when we transfer from C.M. to Q.M. we can pick correct operators by requiring the hermitian property!

$$\int u_{E'}^* u_E d\tau = 0 \quad \text{if } E' \neq E \quad \text{by proof}$$

$$\int u_{ES'}^* u_{ES} d\tau = 0 \quad \text{if } S' \neq S \quad \text{by construction}$$

$$\int u_{ES}^* u_{ES} d\tau = 1 \quad (\text{normalization}) \quad \text{by construction}$$

$E$  real  $\rightarrow$  hermitian operator. Every physical operator must be hermitian!

### Definition of a Hermitian Operator

$$\int \phi^* \Omega \psi d\tau = \int (\Omega^* \phi^*) \psi d\tau$$

In general, wave function  $\psi(\vec{r}, t)$  and eigenfunction  $u_E(\vec{r})$ . We drop time dependence for now.

Assume,

$$\psi(\vec{r}) = \sum_E A_E u_E(\vec{r}) \quad (14)$$

if the set of  $u_E$  is complete! This means that, in general

$$\int (\psi(\vec{r}) - \sum_E A_E u_E(\vec{r}))^2 d\tau = 0$$

Now

$$\begin{aligned} \int u_{E'}^*(\vec{r}) \psi(\vec{r}) d\tau &= \int d\tau u_{E'}^* \sum_E A_E u_E(\vec{r}) \\ &= \sum_E A_E \int d\tau u_{E'}^* u_E \\ &= A_{E'} \end{aligned} \quad (15)$$

This is not true only for energy operators! In general we have

$$\text{coefficient of eigenfunction} = \int (\text{complex conjugate of the eigenfunction})(\text{wave function})d\tau$$

Putting (15) into (14)

$$\begin{aligned}\psi(r) &= \sum_E u_E(r) \int u_E^*(\vec{r}') \psi(\vec{r}') d\tau' \\ &= \int \psi(\vec{r}') d\tau' \sum_E u_E(r) u_E^*(\vec{r}')\end{aligned}$$

This equation is true for all  $\psi(\vec{r})$  satisfying equation (14)  $\rightarrow$  any function that can be Fourier analyzed (almost all)! Therefore, assume  $\psi(\vec{r})$  is not “too singular”  $\rightarrow \psi(\vec{r})$  can be chosen arbitrarily  $\rightarrow \psi(\vec{r})$  must not be dependent on any other point  $\rightarrow$

$$\sum_E u_E(r) u_E^*(\vec{r}') = 0 \quad \text{for } \vec{r}' \neq \vec{r}$$

i.e.,

$$\psi(\vec{r}) = \psi(\vec{r}) \underbrace{\int_{\text{over region with } \vec{r}=\vec{r}'} d\tau' \sum_E u_E(\vec{r}) u_E^*(\vec{r})}_{=1}$$

This implies the *closure property* - holds for eigenfunctions of any hermitian operator.

If closure holds  $\rightarrow$  complete set!

### Probability Function

$$\begin{aligned}\sum_E |A_E|^2 &= \sum_E \int u_E(\vec{r}') \psi^*(\vec{r}') d\tau' \int u_E^*(\vec{r}) \psi(\vec{r}) d\tau \\ &= \int \psi^*(\vec{r}') \psi(\vec{r}) d\tau \underbrace{\int \sum_E \int u_E(\vec{r}') u_E^*(\vec{r}) d\tau'}_{=1 \rightarrow \vec{r}=\vec{r}'} \\ &= \int \psi^*(\vec{r}) \psi(\vec{r}) d\tau = 1\end{aligned}$$

Similarly,

$$\langle f(\Omega) \rangle = \sum_{\omega} f(\omega) |A_{\omega}|^2$$

$$\begin{aligned}\langle E_{operator} \rangle &= \langle H \rangle = \sum_E E |A_E|^2 \\ &= \sum_E E \int u_E(\vec{r}') \psi^*(\vec{r}') d\tau' \int u_E^*(\vec{r}) \psi(\vec{r}) d\tau\end{aligned}$$

Now

$$Eu_E^* = Hu_E^* = \left( \underbrace{-\frac{\hbar^2}{2m}\nabla^2 + V}_H \right) u_E^*$$

Thus, the last integral (using partial integration - surface term  $\rightarrow 0$ ) gives

$$\int u_E^*(\vec{r}) \left( -\frac{\hbar^2}{2m}\nabla^2 + V \right) \psi(\vec{r}) d\tau$$

Therefore

$$\langle H \rangle = \int \underbrace{(\sum_E A_E^* u_E^*)}_{\psi^*(\vec{r})} H \psi(\vec{r}) d\tau = \int \psi^* H \psi d\tau$$

**Return now to the Time Dependence:**  $\psi(\vec{r}, t)$

At given time  $t$  we can expand

$$\psi(\vec{r}, t) = \sum_E A_E(t) u_E(\vec{r})$$

This is true for any arbitrary function. We then have

$$A_E(t) = \int u_E^*(\vec{r}) \psi(\vec{r}, t) d\tau$$

Now assume

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi$$

then we have

$$i\hbar \sum_E \frac{dA_E(t)}{dt} u_E(\vec{r}) = \sum_E A_E(t) H u_E(\vec{r})$$

But we know that

$$H u_E(\vec{r}) = E u_E(\vec{r}) = \sum_E A_E(t) E u_E(\vec{r})$$

We see that the  $u_E$  form a complete set  $\rightarrow$  coefficients of  $u_E$  in two  $\sum$ 's are equal or

$$i\hbar \frac{dA_E(t)}{dt} = E A_E(t) \rightarrow A_E(t) = A_E(0) e^{-i \frac{Et}{\hbar}}$$

and therefore

$$\psi(\vec{r}, t) = \sum_E A_E(0) e^{-i \frac{Et}{\hbar}} u_E(\vec{r})$$

This is true only for functions solving Schrödinger's equation with potential  $V$ !

If  $\psi(\vec{r}, 0)$  is known  $\rightarrow A_E(0) \rightarrow$  knowledge of  $\psi(\vec{r}, t)$  for all  $t$ !

## Summary

### Orthonormality Condition

$$\int u_{E'S'}^* u_{ES} d\tau = \delta_{EE'} \delta_{SS'}$$

### Expansion Coefficient

$$A_E = \int u_E^* \psi d\tau$$

### Closure Property

$$\sum_E u_E^*(\vec{r}') u_E(\vec{r}) = \delta(\vec{r} - \vec{r}') = \begin{cases} 0 & \vec{r} \neq \vec{r}' \\ \int \delta(\vec{r} - \vec{r}') d\tau' = 1 & \end{cases}$$

$$\sum_E |A_E|^2 = 1$$

$$A_E(t) = A_E(0) e^{-i \frac{E t}{\hbar}}$$

$$\begin{aligned} \psi(\vec{r}, t) &= \sum_E \int d\tau' u_E^*(\vec{r}') \psi(\vec{r}', 0) e^{-i \frac{E t}{\hbar}} u_E(\vec{r}) \\ &= \int d\tau \psi(\vec{r}', 0) K(\vec{r}, \vec{r}', t) \end{aligned}$$

where

$$K = \text{Kernal} = \sum_E u_E^*(\vec{r}') u_E(\vec{r}) e^{-i \frac{E t}{\hbar}}$$

Knowledge of the kernel  $\rightarrow$  knowledge of the wave function  $\psi$  development for all time. We note that

$$K(\vec{r}, \vec{r}', 0) = \delta(\vec{r} - \vec{r}')$$

independent of  $V$ .

This representation of  $\psi(\vec{r}, t)$  is for a general  $\psi$ ; (a stationary state is only one term of the expansion) whereas an arbitrary  $\psi$  is an expansion in the stationary state solutions, i.e.,

$$u_E(\vec{r}) e^{-i \frac{E t}{\hbar}}$$

These  $\rightarrow$  probability constant in time, i.e.,

$$P = |\psi|^2 = |u_E(\vec{r})|^2$$

whereas for a general  $\psi$

$$P = \left| \sum_E A_E(0) e^{-i \frac{E t}{\hbar}} u_E(\vec{r}) \right|^2 \neq \text{independent of time!}$$

This is due to the cross-product terms or “interference terms”.

In *classical mechanics* for an oscillator

$$x = A \sin(\omega t + \gamma)$$

and initial conditions  $\rightarrow A, \gamma$ .  $A, \gamma \rightarrow$  knowledge about the actual state of the oscillator!

In *quantum mechanics* the general form of a solution is similar, i.e.,

$$\psi(\vec{r}, t) = \sum_E A_E(0) e^{-i \frac{E t}{\hbar}} u_E(\vec{r})$$

which implies an infinite number of constants of the motion.

The  $A_E(0) \rightarrow$  knowledge of the system  $\rightarrow$  observation of the system must  $\rightarrow A_E(0)$ ; but what measurements?

Alternatively, in *quantum mechanics*

$$x = x_0 \pm \Delta x$$

$$p = p_0 \pm \Delta p$$

$\rightarrow$  we can represent this knowledge in the form of a wave packet and if  $\delta x \Delta p = \hbar$  (minimum uncertainty)  $\rightarrow$  Gaussian wave function  $\rightarrow$  exact knowledge of the form of the wave packet!

Otherwise (i.e., for  $\delta x \Delta p > \hbar$ )  $\rightarrow$  some arbitrariness in  $A_E(0)$ !!

### Momentum Eigenfunctions

$$-i\hbar \nabla u_p = \vec{p} u_p(\vec{r})$$

$$\rightarrow u_p = C e^{i \frac{\vec{p} \cdot \vec{r}}{\hbar}}$$

We want to make the  $u_p$  “countable”  $\rightarrow$  use of *Box Normalization* with periodic boundary condition  $u(x+L) = u(x) \rightarrow$

$$u_k = C e^{i \vec{k} \cdot \vec{r}}$$

For boundary conditions to be satisfied

$$k_x = \frac{2\pi n_x}{L}, k_y = \frac{2\pi n_y}{L}, k_z = \frac{2\pi n_z}{L}$$

$\rightarrow u \neq 0$  at boundaries. For a rigid box  $x \sin \frac{\pi x}{L} \rightarrow 0$  at boundaries.

$C =$  normalization constant  $= L^{-3/2}$ , i.e.,

$$\begin{aligned} \int u_{k'}^* u_k d\tau &= L^{-3} \int_0^L dx e^{i(k_x - k'_x)x} \int_0^L dy e^{i(k_y - k'_y)y} \int_0^L dz e^{i(k_z - k'_z)z} \\ &= L^{-3} L^3 \left[ \frac{e^{i(k_x - k'_x)L}}{i(k_x - k'_x)} \frac{e^{i(k_y - k'_y)L}}{i(k_y - k'_y)} \frac{e^{i(k_z - k'_z)L}}{i(k_z - k'_z)} \right] \\ &= \delta_{k_x k'_x} \delta_{k_y k'_y} \delta_{k_z k'_z} \end{aligned}$$

**Closure**

$$\sum_k u_k^*(\vec{r}') u_k(\vec{r})$$

Consider only the  $x$ -coordinate:

$$\begin{aligned} & L^{-1} \sum_{k_x} e^{ik_x(x-x')} \quad (\text{an } \infty \text{ sum}) \\ &= L^{-1} \sum_{n_x=-N}^N e^{i \frac{2\pi n_x}{L}(x-x')} \\ &= L^{-1} e^{-i \frac{2\pi}{L}(x-x')N} \frac{e^{\frac{2\pi i}{L}(x-x')(2N+1)} - 1}{e^{\frac{2\pi i}{L}(x-x')} - 1} \end{aligned}$$

As  $N \rightarrow \infty$  with  $x - x' \ll L$ , keeping only 1st and 2nd terms in expansion of exponentials, we have,

$$\begin{aligned} & L^{-1} \frac{e^{\frac{2\pi i}{L}N(x-x')} - e^{-\frac{2\pi i}{L}N(x-x')}}{\frac{2\pi i}{L}(x-x')} \\ &= \frac{1}{\pi} \frac{\sin \frac{2\pi}{L}N(x-x')}{x-x'} \end{aligned}$$

Now  $x - x' \approx 0 \rightarrow$  the last expression is  $= \frac{2N}{L}$  and  $x - x'$  large ( $(x - x') \gg \frac{L}{2N} \rightarrow$  the expression is

$$\sim \frac{1}{\pi(x-x')}$$

For closure we wanted

$$\begin{aligned} f_n &= 0 & x \neq x' \\ f_n &\text{large} & x = x' \end{aligned}$$

We have a function which is large  $\frac{2N}{L}$  at  $x - x' \approx 0$  and  $= \frac{1}{\pi(x-x')}$   $\approx$  small for  $x - x'$  large. But in the limit  $N \rightarrow \infty$  we have

$$\sum_k = \begin{cases} 0 & \text{everywhere except} \\ & \text{for } x = x' \end{cases}$$

We can get a better function by using a Gaussian:

$$\sum_{n_x} e^{-n_x^2 \alpha} e^{ik_x(x-x')} \quad \alpha \text{ small}$$

We then have

$$\sum \rightarrow \int e^{-n_x^2 \alpha} \dots dn_x$$

$\rightarrow$  better function and as  $\alpha \rightarrow 0$

$$\sum = 0 \text{ for } x \neq x'$$

which is what we want;(uniform convergence here rather than oscillating as before). But 1st discussion is simplest!

The potential consider here can be infinite at a point and still have a finite wave function, but if  $V$  is infinite in a *region*  $\rightarrow \psi = 0$  in this region.

### The Delta Function

$$\text{Definition} \equiv \begin{cases} \delta(x) = 0 & x \neq 0 \\ \int_{-x_2}^{x_1} \delta(x) dx = 1 \end{cases}$$

One representation is

$$\lim_{g \rightarrow \infty} \frac{\sin gx}{gx} = 0 \quad x \neq 0$$

$$\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\sin gx}{gx} d(gx) = 1$$

Another representation is

$$\lim_{\alpha \rightarrow \infty} \pi^{1/2} \alpha e^{-\alpha^2 x^2} = 0 \quad (x \neq 0)$$

### Some Theorems

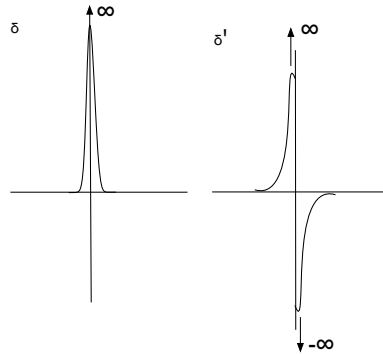
$$\int f(x) x \delta'(x) dx = - \int f(x) \delta(x) dx$$

$$\delta(ax) = \frac{1}{a} \delta(x) \quad \text{etc, ....}$$

From closure discussion

$$\sum_E U_E^*(\vec{r}') u_E(\vec{r}) = \delta(x - x') \delta(y - y') \delta(z - z') = \delta(\vec{r} - \vec{r}')$$

For the  $\delta$ -function in the form  $\lim_{\alpha \rightarrow \infty} \pi^{1/2} \alpha e^{-\alpha^2 x^2}$  we have



$$\int \delta(x-a)\delta(x-b)dx = \delta(a-b)$$

$$\int \delta(a-b)f(b)db = f(a)$$

Using  $\delta$ -functions:

$$\begin{aligned} \int_{-\infty}^{\infty} e^{i(k_x-l_x)x}dx &= \lim_{g \rightarrow \infty} \int_{-g}^g e^{i(k_x-l_x)x}dx \\ &= \frac{e^{i(k_x-l_x)g} - e^{-i(k_x-l_x)g}}{i(k_x-l_x)} \\ &= \frac{2 \sin(k_x-l_x)g}{(k_x-l_x)} \quad (\text{limit as } g \rightarrow \infty) \end{aligned}$$

This is all done by considering an infinite space as the limit of a finite space. The result of the limit is

$$2\pi\delta(k_x-l_x)$$

where  $\frac{1}{\sqrt{2\pi}}$  is the normalization factor for the wave function, i.e., in infinite space (no box normalization)  $C = (2\pi)^{-3/2}$ . Therefore,

$$\int u_l^* u_k d\tau = \delta(k_x-l_x)\delta(k_y-l_y)\delta(k_z-l_z) = \delta(\vec{k}-\vec{l})$$

Box normalization in large limit is the same as infinite space or  $\delta$ -function normalization, i.e., discreteness in continuum is so fine that it physically does not change the continuum!

Since  $\psi$  is symmetrical in  $k$  and  $r$ , i.e.,

$$\psi = C e^{i\vec{k}\cdot\vec{r}} = C e^{i\vec{r}\cdot\vec{k}}$$

$\rightarrow$   $\delta$ -function normalization, closure becomes in  $k$ -space

$$(2\pi)^{-3} \int dk_x dk_y dk_z e^{-i\vec{k}\cdot\vec{r}'} e^{i\vec{k}\cdot\vec{r}} = \delta(\vec{r}-\vec{r}')$$

$\rightarrow$  same as before with difference of  $ks$  replaced by difference of coordinates. The result  $\rightarrow$  closure and orthonormality are the same!!

This all  $\rightarrow$  expansion in momentum eigenfunctions

$$\begin{aligned} \psi(\vec{r}) &= \int \psi(\vec{r}') \delta(\vec{r}-\vec{r}') d\tau' \\ &= \int \psi(\vec{r}') \sum_k u_k^*(\vec{r}') u_k(\vec{r}) d\tau' \\ &= \sum_k A_k u_k(\vec{r}) \end{aligned} \tag{16}$$

where

$$A_k = \int u_k^*(\vec{r}') \psi(\vec{r}') d\tau'$$



In the energy case “completeness” was assumed.  $A_k$  was determined  $\rightarrow$  if implication true, then  $\Sigma = \delta$ .

But here we do the opposite:

(1) prove closure theorem by explicit evaluation of  $\int$  or  $\Sigma$

(2)  $\rightarrow \Sigma = \delta$

(3)  $\rightarrow$  proof of  $A_k$  expression

whereas in the energy treatment it was assumed!

Using this relation for  $A_k$  it makes sense to define  $|A(\vec{k})|^2$ .

$$\begin{aligned} A_k &= (2\pi)^{-3/2} \int e^{-i\vec{k}\cdot\vec{r}'} \psi(\vec{r}') d\tau' \\ &= \text{Fourier transform of } \psi(r') \text{ into } k\text{-space} = A(\vec{k}) \quad (\text{momentum wave function}) \end{aligned} \quad (17)$$

$\rightarrow$  a particle has a momentum wave function  $A(\vec{k})$  where

$$\sum_k |A(\vec{k})|^2 = 1 \quad \text{for box normalization}$$

$$\int |A(\vec{k})|^2 dk_x dk_y dk_z = 1 \quad \text{for } \delta\text{-function normalization}$$

There can never be a physical difference between either of these two types of solutions!! Now

$$\langle \vec{p} \rangle = \hbar \sum \vec{k} |A_k|^2 = -i\hbar \int \psi^* \nabla \psi d\tau$$

**Assumption:**  $\vec{p}$  is a hermitian operator.

**Proof:**

$$\begin{aligned} -i\hbar \int u^* \nabla \psi d\tau &= \int (u^* p) \psi d\tau \\ &\text{integrating by parts } \rightarrow \\ &= +i\hbar \int \nabla u^* \psi d\tau \quad (\text{surface integral } \rightarrow 0), i\hbar \nabla = p^* \\ &= \int (p^* u^*) \psi d\tau \end{aligned}$$

Any operator is hermitian if this is true!

**Momentum Eigenfunctions**

$$u_k = C e^{i\vec{k}\cdot\vec{r}} \quad \vec{k} = \frac{\vec{p}}{\hbar}$$

(1) Artificially discrete; box periodic

$$\rightarrow C = L^{-3/2}$$

$$\rightarrow C^2 \int d\tau = \frac{1}{L^3} d\tau = 1 \quad \text{over entire box}$$

$\rightarrow$  normalization. There is one state for each  $(n_x, n_y, n_z)$ . Therefore,

$$\sum_{n_x, n_y, n_z} \rightarrow \left(\frac{L}{2\pi}\right)^3 \int dk_x dk_y dk_z$$

$\rightarrow$  number  $\sim L^3$  which exactly balances the  $1/L^3$  dependence of the wave function. Now

$$\begin{aligned} \left(\frac{L}{2\pi}\right)^3 dp_x dp_y dp_z &= \frac{\text{volume of box} \cdot \text{volume in momentum space}}{(2\pi\hbar)^3} \\ &= \frac{\text{volume in phase space}}{h^3} \end{aligned}$$

(2) Keep continuous spectrum (limit of infinite box).  $C = (2\pi)^{-3/2} \rightarrow$  wave functions independent of size of box with amplitude  $C$  everywhere.

Number of quantum states  $= \int dk_x dk_y dk_z \rightarrow$  infinite  $\int |\psi|^2 d\tau$ . Thus, we need new conditions:

$$\text{continuous normalization} \quad \int u_l^* u_k d\tau = \delta(\vec{k} - \vec{l})$$

$$\text{closure} \quad \int u_k^*(\vec{r}') u_k(\vec{r}) d^3k = \delta(\vec{r} - \vec{r}')$$

These are exactly alike since the wave function is symmetric in  $k$  and  $r$ .

Expansion:

$$A_k = \int u_k^* \psi(\vec{r}) d\tau \quad \left\{ \begin{array}{l} \text{from assumption of completeness} \rightarrow \\ \text{expansion exists} \rightarrow A_k \end{array} \right.$$

For *free particles* ( $V = 0$ ):  $u_k$  also energy eigenfunctions, but  $u_E$  not necessarily a momentum eigenfunction (not true with a potential). Therefore

$$A_k = A_k(0) e^{-i \frac{E_k t}{\hbar}} \quad , \quad E_k = \frac{\hbar^2 k^2}{2m}$$

## Schiff - Section 12

$$\begin{aligned} (\Delta x)^2 &= \langle (x - \langle x \rangle)^2 \rangle \quad (= 0 \text{ only if } x = \langle x \rangle \text{ always}) \\ &= \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle = \langle x^2 \rangle - 2\langle x \rangle^2 + \langle x \rangle^2 \\ &= \langle x^2 \rangle - \langle x \rangle^2 \end{aligned}$$

Let

$$\alpha = x - \langle x \rangle \quad , \quad \beta = -i\hbar \frac{d}{dx} - \langle p \rangle$$

Then we have

$$\begin{aligned} (\Delta x)^2 (\Delta p_x)^2 &= \int \psi^* \alpha^2 \psi d\tau \int \psi^* \beta^2 \psi d\tau \\ &= \int (\alpha^* \psi^*) (\alpha \psi) d\tau \int (\beta^* \psi^*) (\beta \psi) d\tau \quad (\text{integration by parts}) \\ &\geq \left| \int (\beta^* \psi^*) (\alpha \psi) d\tau \right|^2 \quad (\text{by Schwartz's inequality}) \\ &\quad (= \text{sign if and only if } \beta \psi = \gamma \alpha \psi \text{ for all values}) \\ &\geq \left| \int \psi^* \beta \alpha \psi d\tau \right|^2 \\ &= \left| \psi^* \left[ \frac{1}{2}(\beta \alpha - \alpha \beta) + \frac{1}{2}(\beta \alpha + \alpha \beta) \right] \psi \right|^2 \\ &= \left| \int \psi^* \frac{1}{2}(\beta \alpha - \alpha \beta) \psi d\tau \right|^2 + \left| \int \psi^* \frac{1}{2}(\beta \alpha + \alpha \beta) \psi d\tau \right|^2 \end{aligned}$$

This  $\rightarrow$  the cross-term = 0  $\rightarrow$

$$\text{Re} \left( \int \psi^* (\beta \alpha - \alpha \beta) \psi d\tau \right)^* \left( \int \psi^* (\beta \alpha + \alpha \beta) \psi d\tau \right) = 0$$

But

$$\begin{aligned} \left( \int \underbrace{\psi^* \beta \alpha \psi}_{A^*} d\tau \right)^* &= \int \underbrace{\psi^* \beta \alpha \psi}_A d\tau \\ \rightarrow \text{Re}[(A - A^*)^* (A + A^*)] &= \text{Re}[A^{*2} - A^2] = 0 \end{aligned}$$

Therefore

$$(\Delta x)^2 (\Delta p_x)^2 \geq \left| \int \psi^* \frac{1}{2}(\beta \alpha - \alpha \beta) \psi d\tau \right|^2$$

with equality only if 2nd  $|\dots|^2 = 0$ .

In classical mechanics,  $\alpha$  and  $\beta$  are numbers  $\rightarrow$

$$(\Delta x)^2 (\Delta p_x)^2 = 0$$

but in quantum mechanics they are operators and therefore the order of operation is important! Therefore

$$\beta \alpha - \alpha \beta = \left( -i\hbar \frac{d}{dx} - \langle p \rangle \right) (x - \langle x \rangle)$$

Operating on  $\psi \rightarrow$  this expression is  $= -i\hbar$ . Therefore

$$(\Delta x)^2 (\Delta p_x)^2 \geq \frac{1}{4} \hbar^2 \left| \int \psi^* \psi d\tau \right|^2$$

Therefore

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

For equality or minimum uncertainty we must have  $\alpha\psi = \gamma\beta\psi$  and we want

$$\int \psi^* (\beta\alpha + \alpha\beta\psi) d\tau = 0 \quad (18)$$

Thus,

$$\frac{\hbar}{i} \frac{d\psi}{dx} = \left( \langle p \rangle + \frac{1}{\gamma} (x - \langle x \rangle) \right) \psi$$

which implies

$$\psi = \exp \frac{i}{\hbar} \left[ \frac{1}{2\gamma} x^2 + \left( \langle p \rangle - \frac{1}{\gamma} \langle x \rangle \right) x \right] + \text{arbitrary constant}$$

Using the results

$$\psi^* \alpha \beta \psi = \psi^* \frac{\alpha^2}{\gamma} \psi$$

$$\begin{aligned} \psi^* \beta \alpha \psi &= (\beta^* \psi^*) \alpha \psi \\ &= \frac{1}{\gamma^*} (\alpha^* \psi^*) \alpha \psi \\ &= \frac{1}{\gamma^*} \psi^* \alpha^2 \psi \rightarrow Q.E.D. \end{aligned}$$

equation (18) becomes

$$\left( \frac{1}{\gamma} + \frac{1}{\gamma^*} \right) \int \underbrace{\psi^* \alpha^2 \psi}_{\text{positive definite}} d\tau = 0$$

which  $\rightarrow \gamma = \text{pure imaginary!}$  From Schiff:

$$\psi = (2\pi(\Delta x)^2)^{-1/4} \exp \left( -\frac{(x - \langle x \rangle)^2}{4(\Delta x)^2} + i \frac{\langle p \rangle x}{\hbar} \right)$$

Why is  $\gamma$  so simply given?:

$$\frac{i}{\gamma \hbar} = \lambda \rightarrow \psi = C e^{-\frac{1}{2}\lambda(x-\langle x \rangle)^2 + \dots}$$

$$\begin{aligned} \int |\psi|^2 dx &= C^2 \sqrt{\frac{\pi}{\lambda}} \\ \int |\psi|^2 (x - \langle x \rangle)^2 dx &= \frac{1}{2\lambda} = (\Delta x)^2 \\ \rightarrow \gamma &= \frac{i}{\lambda \hbar} = \frac{2i}{\hbar^2} (\Delta x)^2 \end{aligned}$$

$$A_k(0) = \int u_k^* \psi dx \rightarrow \psi(x, 0)$$

$$A_k(t) = A_k(0) e^{-\frac{E_k t}{\hbar}}$$

It is no restriction if we let  $\langle x \rangle = \langle p \rangle = 0$ . Now using box normalization to find  $A_k(0)$ :

$$L^{-1/2} \int e^{ikx} \psi dx = L^{-1/2} \int (\dots) dx e^{-\frac{x^2}{4(\Delta x)^2} - ikx} = \dots e^{-k^2 (\Delta x)^2}$$

→ gaussian in  $\Delta x$  and  $k$ . Therefore the probability of finding  $x$  falls off as  $\frac{1}{\Delta x}$  and similarly for  $k$ .

If  $\langle p \rangle \neq 0 \rightarrow$

$$e^{-(k - \langle k \rangle)^2 (\Delta x)^2}$$

→ packet centered about  $\langle k \rangle$ . Now

$$\begin{aligned} \psi(x, t) &= \sum_k A_k(0) e^{-\frac{i}{\hbar} \frac{\hbar^2 k^2 t}{2m}} u_k \\ &\text{using } \sum_k \rightarrow \frac{L}{2\pi} \int dk \\ &= (2\pi)^{-1/4} \left( \Delta x + \frac{i\hbar t}{2m\Delta x} \right)^{-1/2} \exp \left( -\frac{x^2}{4(\Delta x)^2 + \frac{2i\hbar t}{m}} \right) \end{aligned}$$

→ after time  $t$  we still have a gaussian but the packet has spread (also some oscillations)

$$|\psi|^2 \sim \exp \left( -\frac{x^2 \cdot 2(\Delta x)^2}{4(\Delta x)^4 + \left( \frac{\hbar t}{m} \right)^2} \right) = \exp \left( -\frac{x^2}{2(\Delta x)^2 + \frac{1}{2} \left( \frac{\hbar t}{m\Delta x} \right)^2} \right)$$

At time  $t$

$$\langle x^2(t) \rangle = (\Delta x)^2 + \left( \frac{\hbar t}{m\Delta x} \right)^2 = (\Delta x)^2 + \left( \frac{\Delta p t}{m} \right)^2$$

→ spreading packet for + or - time (symmetric in time).

*Classical limit* of electron in orbit; makes sense only for electron localization in orbit after several orbits! Compatible with uncertainty principle only if angular momentum in orbit  $\gg \hbar$ .

## Solvable problems

### Harmonic Oscillator:

$$F = kx \rightarrow V = \frac{1}{2} kx^2$$

In classical mechanics

$$\omega = \sqrt{\frac{k}{m}} \rightarrow V = \frac{1}{2} m \omega^2 x^2$$

In one dimension:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dx^2} + \frac{1}{2} m \omega^2 x^2 u = E u$$

Let  $x = a\xi \rightarrow$

$$-\frac{\hbar^2}{2ma^2} u'' + \frac{1}{2} m \omega^2 a^2 \xi^2 u = E u$$

$$u'' + \lambda u - \xi^2 u = 0 \rightarrow u'' + (\lambda - \xi^2) u = 0$$

where

$$\lambda = \frac{2ma^2}{\hbar^2} E, \quad a^4 = \frac{\hbar^2}{m^2 \omega^2} \rightarrow \lambda = \frac{2E}{\hbar \omega} \rightarrow \text{dimensionless}$$

For  $\xi \rightarrow \infty$

$$u'' \approx \xi^2 u \rightarrow u \sim e^{\pm \frac{1}{2} \xi^2} \quad (\text{we use minus sign for boundedness})$$

Therefore let us assume a solution of the form

$$u = e^{-\frac{1}{2} \xi^2} H(\xi)$$

Substitution gives (removes  $\xi^2$  term)

$$H'' - 2\xi H' + (\lambda - 1)H = 0$$

Let

$$H = \sum_{\nu} a_{\nu} \xi^{\nu}$$

Then

$$H'' = \sum_{\nu} a_{\nu} \xi^{\nu-2} \nu(\nu-1)$$

Let  $\nu = \nu + 2$

$$H'' = \sum_{\nu} (\nu+2)(\nu+1) a_{\nu+2} \xi^{\nu}$$

$$2\xi H' = \sum_{\nu} 2a_{\nu} \nu \xi^{\nu}$$

$$(\lambda - 1)H = \sum_n u(\lambda - 1) a_{\nu} \xi^{\nu}$$

$$\rightarrow \sum_{\nu} \xi^{\nu} (a_{\nu+2}(\nu+2)(\nu+1) - a_{\nu} 2\nu + (\lambda - 1)a_{\nu}) = 0$$

$$\rightarrow a_{\nu+2}(\nu+2)(\nu+1) - a_{\nu} 2\nu + (\lambda - 1)a_{\nu} = 0$$

$$\rightarrow \frac{a_{\nu+2}}{a_{\nu}} = \frac{2\nu - \lambda + 1}{(\nu+2)(\nu+1)}$$

Lowest term  $s$  and  $a_{s-2} = 0$  or else series starts with negative power of  $\xi \rightarrow$  pole at 0.

$$\nu + 2 = s \rightarrow 0 = \frac{a_{s-2}}{a_s} = 0 = \frac{s(s-1)}{2s - \lambda - 3} \rightarrow s(s-1) = 0$$

$\rightarrow s = 0, 1$  for 1st term

To make  $\nu = n$  the last term

$$\rightarrow \frac{a_{n+2}}{a_n} = 0$$

or

$$2\nu - \lambda + 1 = 2n - \lambda + 1 = 0 \rightarrow \lambda = 2n + 1$$

$\rightarrow$  polynomial of degree  $n$ ; if not, then for large  $\nu$  we have

$$\frac{a_{\nu+2}}{a_\nu} \approx \frac{2}{\nu}$$

Now assuming

$$a_\nu = \frac{C}{\left(\frac{\nu}{2}\right)!}$$

then

$$\begin{aligned} a_{\nu+2} &= \frac{C}{\left(\frac{\nu+2}{2}\right)!} = \frac{C}{\left(\frac{\nu}{2} + 1\right)!} \\ &= \frac{C}{\left(\frac{\nu}{2}\right)! \left(\frac{\nu}{2} + 1\right)} = \frac{a_\nu}{\left(\frac{\nu}{2} + 1\right)} \approx a_\nu \frac{2}{\nu} \end{aligned}$$

which satisfies the recursion relation. Therefore

$$H = C \sum_\nu \frac{\xi^\nu}{\left(\frac{\nu}{2}\right)!} = C \sum_p \frac{(\xi^2)^p}{p!} \quad \left(\text{using } \frac{\nu}{2} = p\right)$$

or

$$H = Ce^{\xi^2} \quad \text{for large } \xi$$

Therefore

$$u \sim Ce^{+\frac{\xi^2}{2}}$$

which blows up for any arbitrarily large  $\nu$ . Therefore, we must cut off the power series at  $n$

$$\rightarrow E_n = \hbar\omega \left(n + \frac{1}{2}\right) = \text{eigenvalues}$$

This also implies a “zero-point energy”

$$E_0 = \frac{\hbar\omega}{2}$$

We know that

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

$p^2$  and  $x^2$  are positive definites related by the uncertainty principle  $\rightarrow$  both  $p^2$  and  $x^2$  cannot be zero simultaneously  $\rightarrow E_0$ , i.e.,

$$\langle p^2 \rangle = \frac{\hbar^2}{4\langle x^2 \rangle}$$

Therefore  $E = \min$ ; by substituting and making two terms equal or

$$= \frac{\hbar^2}{4\langle x^2 \rangle m} = m\omega^2 \langle x^2 \rangle$$

or

$$\langle x^2 \rangle = \frac{\hbar}{2m\omega}$$

and

$$E_{min} = \frac{1}{2}m\omega^2 \frac{\hbar}{2m\omega} + O\left(\frac{1}{2}m\omega^2 \frac{\hbar}{2m\omega}\right) = m\omega^2 \frac{\hbar}{2m\omega} = \frac{\hbar\omega}{2}$$

The lowest state wave function is

$$u_0 = e^{-\frac{1}{2}\xi^2}$$

which corresponds to a gaussian, i.e., the zero point wave function corresponds to the minimum packet.

$$|u_0|^2 = e^{-\xi^2} \rightarrow \langle \xi^2 \rangle = \int \xi^2 |u_0|^2 d\xi = \frac{\sqrt{\pi}}{2}$$

Therefore

$$\langle x^2 \rangle = \frac{1}{2}a^2 = \frac{\hbar}{2m\omega}$$

For the eigenfunctions we have  $H =$  Hermite polynomials, which are even or odd depending on  $n$  even or odd!

### Generating Functions

$$S(\xi, s) = e^{-\xi^2 - (s-\xi)^2} = e^{-s^2 + 2\xi s} = \sum_n \frac{s^n}{n!} H_n(\xi)$$

$$\begin{aligned} \frac{\partial S}{\partial \xi} &= 2sS = \sum_n \frac{s^n}{n!} H'_n \\ &= 2 \sum_n \frac{s^{n+1}}{n!} H_n \\ &= 2 \sum_n \frac{s^n}{(n-1)!} H_{n-1} \end{aligned} \tag{19}$$

Therefore

$$\begin{aligned} H'_n &= 2nH_{n-1} \\ \frac{\partial S}{\partial s} &= (-2s_2\xi)S = \sum_n \frac{s^{n-1}}{(n-1)!} H_n = \sum_n \frac{s^n}{n!} H_{n+1} \end{aligned}$$

Therefore

$$\begin{aligned} H_{n+1} &= 2\xi H_n - 2nH_{n-1} \\ H'_{n+1} &= 2\xi H'_n + 2H_n - 2nH'_{n-1} \end{aligned}$$



But also

$$H'_{n+1} = 2(n+1)H_n$$

Therefore

$$2\xi H'_n + 2H_n - H'' = 2(n+1)H_n \rightarrow H''_n - 2\xi H'_n + 2nH_n = 0$$

This is precisely our original equation! From generating function:

$$H_n = \frac{d^n}{ds^n}(S) \Big|_{s=0}$$

$$S = e^{\xi^2} f(\xi - s)$$

$$\frac{\partial S}{\partial s} = -\frac{\partial S}{\partial \xi}$$

Therefore

$$\frac{\partial^n S}{\partial s^n} = e^{\xi^2} (-1)^n \frac{\partial^n}{\partial \xi^n} e^{-(\xi-s)^2} \Big|_{s=0}$$

Therefore letting  $s = 0$  we get

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

$\rightarrow$  highest power of  $\xi \rightarrow (2\xi)^n \rightarrow H_n = (2\xi)^n + \text{lower powers}$ . Therefore we have for the harmonic oscillator

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right)$$

$$u_n = N_n e^{-\frac{1}{2}\xi^2} H_n(\xi)$$

$$H_n = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2}) = (2\xi)^n + \text{lower powers} \quad (20)$$

Now

$$\int u_n u_m dx = N_n N_m a \int_{-\infty}^{\infty} e^{-\xi^2} H_n H_m d\xi$$

Assume  $n \geq m$ , insert (20) for  $H_n$  and a polynomial for  $H_m$ . Therefore we have

$$\int u_n u_m dx = N_n N_m a \int_{-\infty}^{\infty} d\xi e^{-\xi^2} (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2}) H_m (\text{as a polynomial})$$

After  $n$  integrations by parts (where all integrated out terms  $\rightarrow 0$ ) we get

$$\int u_n u_m dx = N_n N_m a \int_{-\infty}^{\infty} d\xi e^{-\xi^2} \frac{d^n}{d\xi^n} (H_m)$$

This says that if  $m < n$  the result is zero  $\rightarrow$  orthonormality. This implies  $m = n$  and we then have

$$\int u_n u_n dx = N_n^2 a \int_{-\infty}^{\infty} d\xi e^{-\xi^2} 2^n n! = 1 = N_n^2 a 2^n n! \sqrt{\pi}$$

or

$$N_n = \pi^{-1/4} (2^n n! a)^{-1/2}$$

Now consider

$$x_{nm} = \int x u_n u_m dx \rightarrow \text{generalization of expectation value expression}$$

i.e., for

$$\psi = \sum A_n u_n$$

then  $\int x \psi^* \psi dx \rightarrow$  need knowledge of products  $u_n u_m$ .

$x_{nm} \rightarrow$  matrix element  $\rightarrow$  from prior work

$$x_{nm} = N_n N_m a \int_{-\infty}^{\infty} d\xi e^{-\xi^2} \frac{d^n}{d\xi^n} (\xi H_m)$$

This expression is  $\neq 0$  only if  $\xi H_m$  contains  $\xi^n$  or higher

$$\rightarrow m+1 \geq n \text{ or } m = n-1, n$$

If  $m = n$ , we have

$$\int_{-\infty}^{\infty} x u_n^2 dx = \int_{-\infty}^{\infty} (\text{odd function } dx = 0$$

For  $m = n+1$

$$x_{nm} = x_{n,n-1} = N_n N_{n-1} a^2 \sqrt{\pi} 2^{n-1} n!$$

Therefore

$$x_{n,n-1} = a \frac{2^{n-1}}{2^{n/2} 2^{(n-1)/2} \frac{n!}{\sqrt{n!} \sqrt{(n-1)!}}} = a \sqrt{\frac{n}{2}} \quad (m = n-1)$$

For  $m > n \rightarrow m = n+1$

$$x_{n,n+1} = a \sqrt{\frac{n+1}{2}} \quad (m = n+1)$$

These are the matrix coordinates for the oscillator. Now  $a = \sqrt{\frac{\hbar}{m\omega}} \rightarrow$  size of region in  $x$  over which the wave extends.

**Comparison of CM and QM** (considering figure 11 in Schiff).

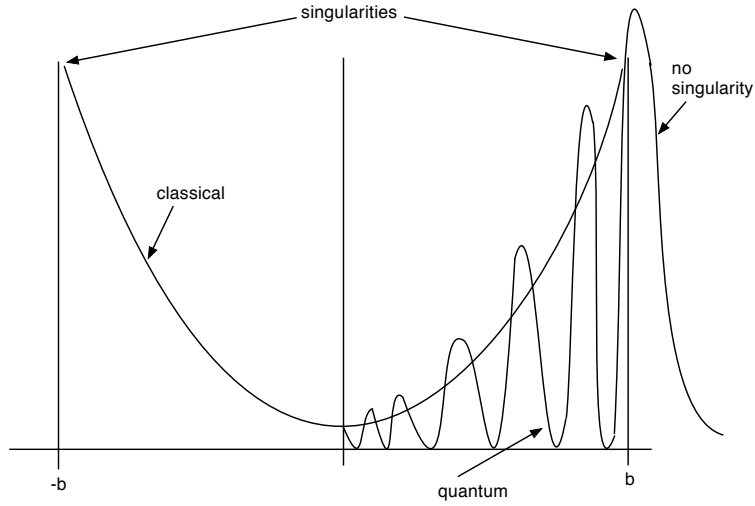
The wave function ( $n$ ) has  $n$  nodes (zeros). For Schiff ( $n = 10$ ) and for figure below ( $n = 12$ ). The wave function is compared with the classical density function  $x = b \sin \omega t$ , i.e.,

$$P(x \pm dx) \sim \tau_{x \pm dx} \sim \frac{dx}{V_{x \pm dx}}$$

Now

$$V \sim b\omega \cos \omega t \sim \sqrt{b^2 - x^2}$$

$P \sim \frac{1}{V} \rightarrow$  oscillator most likely to be at  $a \pm b$



We get the highest peak at the classical singularity of the classical density function. For  $|x| > b$  wave function goes to zero slowly (not instantly).

Quantum mechanical zeros  $\rightarrow$  no probability of particle being there, but exact knowledge of position  $\rightarrow \infty$  velocity uncertainty  $\rightarrow$  particle can pass through these regions!

### Choosing $b$

$$\frac{1}{2}m\omega^2 b^2 = E = \hbar\omega \left(n + \frac{1}{2}\right) \quad \text{classical turning point}$$

$x > b \rightarrow$  exponentially decreasing wave function. This follows from the differential equation

$$u'' + \left[E - \frac{1}{2}m\omega^2 x^2\right]u = 0$$

$E - \frac{1}{2}m\omega^2 x^2 > 0$  for  $|x| < b \rightarrow$  oscillations

$E - \frac{1}{2}m\omega^2 x^2 < 0$  for  $|x| > b \rightarrow$  exponentials

Further comparisons are:

$$\langle V \rangle = \frac{1}{2}m\omega^2 \langle x^2 \rangle = \frac{1}{2}\omega^2 a^2 \left(n + \frac{1}{2}\right) = \frac{1}{2}\hbar\omega \left(n + \frac{1}{2}\right) = \frac{1}{2}E$$

Similarly,

$$\langle KE \rangle = \frac{1}{2}E$$

This result is due to symmetry, i.e.,  $V \sim x^2$  and  $Ke \sim p^2$ . It is just the “virial theorem”.

We note that the result  $\langle x \rangle = x_1$  does not  $\rightarrow$  high probability of finding particle

at  $x_1 \rightarrow$  only that there is an equal probability of particle being at  $x > x_1$  or  $x < x_1$ .

### Oscillating Wave Packet

$$\begin{aligned}\psi &= \sum A_n u_n e^{-\frac{i}{\hbar} E_n t} = \sum A_n u_n \underbrace{e^{-i\omega\left(n+\frac{1}{2}\right)t}}_{\text{no } t \text{ dependence re } \hbar} \\ &= \underbrace{e^{-\frac{1}{2}i\omega t}}_{\text{phase factor only}} \sum A_n u_n e^{-i\omega n t}\end{aligned}$$

Thus, we have a periodic function of  $t$  with period  $\frac{2\pi}{\omega}$ .

$\rightarrow$  for any arbitrary wave function of an oscillator, a repeating density distribution with period  $\frac{2\pi}{\omega}$ .

$\rightarrow$  equally spaced energy levels!

$\rightarrow$  packet moves left or right for  $T = \frac{2\pi}{\omega}$ ; it can spread, etc, but at  $(t_0 + T)$  it returns to  $x_0$  with exactly the same shape.

### For a Minimum Packet:

$$e^{-\frac{1}{2}\alpha^2(x-c)^2} \quad \text{at } t=0 \quad (\alpha = \frac{1}{a} \text{ in Schiff})$$

Over the course of time  $\rightarrow$  spreading but after  $t=T$  it returns to original shape!

In Schiff - expand  $A_n \rightarrow$

$$\begin{aligned}A_n &= \frac{\xi_0^n e^{-\xi_0^2}}{\sqrt{2^n n!}} \quad \xi_0 = \frac{c}{a} \quad c \text{ is initial position} \\ |\psi(x, t)|^2 &= \frac{1}{\sqrt{\pi a}} e^{-(x-c \cos \omega t)^2 \alpha^2}\end{aligned}$$

$\rightarrow \psi$  concentrated about  $c \cos \omega t$ . This  $\rightarrow$  remains as a minimum packet, but with center moving as a classical oscillator

$$x_{nm} = a\sqrt{\frac{n}{2}} \quad n = m + 1$$

For harmonic oscillator

$$|\psi(t + 2\pi n/\omega)|^2 = |\psi(t)|^2$$

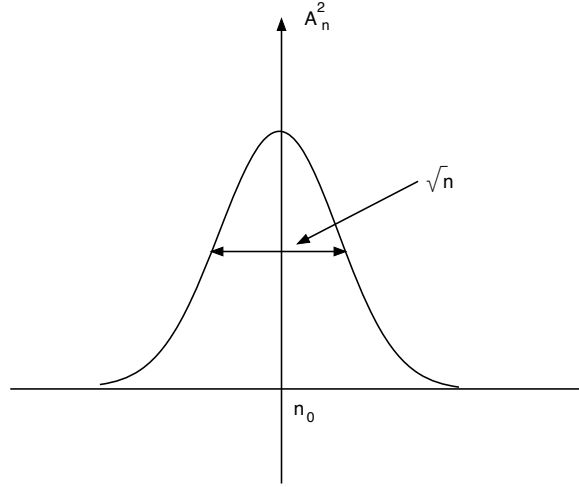
Maximum  $A_n$  for  $n =$  classical energy of oscillator with amplitude  $c$ .

(1) we construct a wave packet at  $t=0$ ; localized at  $c \pm a = x(0)$

(2) momentum at  $t=0$ ,  $\langle p \rangle = 0$   $p(0) = \pm \hbar/a$

(3) energy is  $\frac{1}{2}m\omega^2 c^2 \pm \hbar\omega\sqrt{n}$

$\rightarrow$  classical due to spread of  $x$  and  $p$



**Spherically Symmetric -  $V(r)$**

**Separation of the wave equation**

$$\nabla^2 u + \frac{2m}{\hbar^2} (E - V(r))u = 0 \quad (r, \theta, \varphi)$$

Now  $\nabla^2 u \rightarrow$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \varphi^2}$$

$$u = R(r)Y(\theta, \varphi)$$

Substitution implies that

$$\begin{aligned} & - \left( \underbrace{\frac{1}{Y} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{Y} \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2}}_{f(\theta, \varphi) \text{ only}} \right) \\ & = \underbrace{\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2m}{\hbar^2} (E - V(r))r^2}_{f(r) \text{ only}} \\ & = \lambda = \text{constant} \end{aligned}$$

The  $\theta, \varphi$  equation is independent of  $V$ , i.e.,  $Y(\theta, \varphi)$  is independent of  $V, E$ . It depends only on the separation parameter  $\lambda \rightarrow$  spherical harmonics which are applicable to any spherically symmetric potential!

$$Y = e^{im\varphi} f(\theta) = P_{\lambda m}(\omega) e^{im\varphi}$$

where  $\omega = \cos \theta$  and  $2n + 1 = \lambda$ . This implies that

$$\frac{d}{d\omega} \left( (1 - \omega^2) \frac{dP}{d\omega} \right) + \left( \lambda - \frac{m^2}{1 - \omega^2} \right) P = 0$$

This is symmetric in  $\omega \rightarrow P$  solutions are either even or odd in  $\omega$ . There are two singular points, namely,  $\omega = \pm 1$ .

Near  $\omega = +1$

$$P = (1 - \omega)^\alpha (1 + a_1(1 - \omega) + \dots)$$

$\alpha$  comes from substitution

$$\rightarrow \alpha = \pm \frac{m}{2} \quad (\text{no minus} \rightarrow \text{singularities})$$

The power series must terminate

$$\text{solution} \rightarrow \lambda = \ell(\ell + 1)$$

$\ell$  is an integer,  $\ell \geq |m|$  or no solution exists

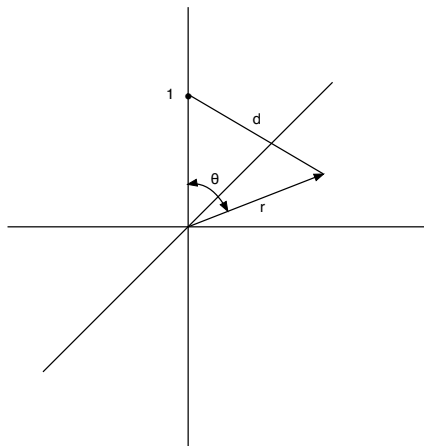
$m = 0 \rightarrow$  Legendre polynomials

$m \neq 0 \rightarrow$  Associated Legendre polynomials

Another way: consider  $\nabla^2 u = 0$  when  $E - V = 0$ . Solutions  $x, x^2 - y^2$ , etc  $\rightarrow$  possible solutions are polynomials in  $x, y, z$ , i.e.,  $u = r^n f(\theta, \varphi)$ . The  $r$ -equation  $\rightarrow$

$$\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) = (n + 1)n = \lambda$$

$\rightarrow$  a simple solution  $= \frac{1}{d}$  where  $d$  as shown below



thus the simple solution is

$$\frac{1}{d} = \frac{1}{\sqrt{1 - 2r \cos \theta + r^2}} = \sum r^\ell P_\ell(\cos \theta)$$

→ by expansion → expansion coefficients are solutions! This implies that the function  $\frac{1}{d}$  is the generating function.

In general,

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

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

Parity:  $P_\ell$  highest power is given by

$$\frac{d^\ell}{d\omega^\ell} (\omega^{2\ell} \dots) = \omega^\ell$$

→ even or odd as  $\ell$  even or odd.

$Y_{\ell m}$  functions: Using parity - let  $\vec{r} \rightarrow -\vec{r}$ , then

$$\begin{aligned} |r| &\rightarrow |r| \\ \theta &\rightarrow \pi - \theta \quad \omega \rightarrow -\omega \\ \varphi &\rightarrow \pi + \varphi \quad e^{im\varphi} \rightarrow (-1)^m e^{im\varphi} \end{aligned}$$

The above properties are just geometry!. We then have

$$P_\ell^m \rightarrow (-1)^{\ell-m} (1 - \omega^2)^{m/2} \frac{d^m}{d\omega^m} P_\ell$$

and therefore

$$Y_{\ell m}(\vec{r} \rightarrow -\vec{r}) = (-1)^\ell Y_{\ell m}(\vec{r})$$

Thus,

$$P_\ell^m(x) \sim (1 - x^2)^{m/2} \frac{d^m}{dx^m} P_\ell^0(x)$$

with  $x = \cos \theta$  and  $-\ell \leq m \leq \ell$  and  $\ell > m$ . We then get

$$P_0^m = 1 \quad , \quad P_1^0 = x = \cos \theta$$

$$P_1^1 = \sqrt{1 - x^2} = \sin \theta \quad , \quad P_2^0 = \frac{1}{2}(3 \cos^2 \theta - 1)$$

$$P_2^1 = 3 \cos \theta \sin \theta \quad , \quad P_2^2 = 3 \sin^2 \theta$$

Normalization:  $-1 \leq x \leq 1$

$$P_\ell(x); \quad Y_\ell^m(\theta, \varphi) = P_\ell^m(x) e^{im\varphi}$$

$$\int_{-1}^1 P_\ell(x) P_m(x) dx = 0 \quad \ell \neq m$$

Substitute

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

and integrate by parts ( $\ell$  times)  $\rightarrow$

$$= (-1)^\ell \frac{1}{2^\ell \ell!} \int_{-1}^1 (x^2 - 1)^\ell \underbrace{P_m^{(\ell)}(x)}_{(x^m)^{(\ell)}} dx$$

$\ell > m \rightarrow 0$ . If  $\ell < m$  relabel at beginning  $m \rightarrow \ell$  and  $\ell \rightarrow m \rightarrow m < \ell \rightarrow 0$ .  
Therefore  $\ell = m$ .

$$P_\ell^{(\ell)}(x) = \frac{(2\ell)!}{2^\ell \ell!}$$

$$\begin{aligned} \int_{-1}^1 &= \frac{(-1)^\ell (2\ell)!}{(2^\ell \ell!)^2} \int_{-1}^1 (x^2 - 1)^\ell dx \\ &= 2 \frac{(2\ell)!}{(2^\ell \ell!)^2} \underbrace{\int_0^1 (1 - x^2)^\ell dx}_{\text{Beta function } (1/2, \ell+1)} \\ &= \frac{\Gamma(1/2) \Gamma(\ell+1)}{\Gamma(\ell+3/2)} \frac{(2\ell)!}{(2^\ell \ell!)^2} = \frac{2}{2\ell+1} \end{aligned}$$

Therefore

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

and

$$\int_{-1}^1 P_\ell^m P_{\ell'}^{m'} dx = \frac{2}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \delta_{\ell\ell'} \delta_{mm'}$$

For normalizing of the  $Y$ 's:

$$\begin{aligned} \int_0^{2\pi} \int_{-1}^1 Y_\ell^m Y_{\ell'}^{m'} d(\cos \theta) d\varphi \\ = \frac{4\pi}{2\ell+1} \frac{(\ell+m)!}{(\ell-m)!} \delta_{\ell\ell'} \delta_{mm'} \end{aligned}$$

Therefore,

$$Y_\ell^m = \sqrt{\frac{2\ell+1}{4\pi}} \frac{(\ell-m)!}{(\ell+m)!} P_\ell^m e^{im\varphi} \quad (\text{Bethe})$$

Other alternatives exist also. Thus,

$$u = R(r)Y(\theta, \varphi)$$

$$\frac{\chi}{r} = R \rightarrow$$



$$\frac{d^2\chi}{dr^2} + \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{\ell(\ell+1)}{r^2} \right] \chi = 0$$

Now consider orbital motion:

$$L = \text{angular momentum} = mvr = m\omega r^2$$

Force =  $m\omega^2 r = \frac{L^2}{mr^3} \rightarrow$  comes from fictitious potential  $V = -\frac{L^2}{2mr^2}$ . In our case we have

$$\frac{\ell(\ell+1)\hbar^2}{2mr^2}$$

$$\vec{L} = \vec{r} \times \vec{p} \rightarrow L_x = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

Now

$$\frac{\partial}{\partial z} = \frac{\partial\varphi}{\partial z} \frac{\partial}{\partial\varphi} + \frac{\partial\theta}{\partial z} \frac{\partial}{\partial\theta}$$

and similarly for  $\frac{\partial}{\partial y} \rightarrow$

$$L_x = -i\hbar \left( \left( y \frac{\partial\varphi}{\partial z} - z \frac{\partial\varphi}{\partial y} \right) \frac{\partial}{\partial\varphi} + \left( y \frac{\partial\theta}{\partial z} - z \frac{\partial\theta}{\partial y} \right) \frac{\partial}{\partial\theta} \right)$$

or

$$\begin{aligned} L_x &= i\hbar \left( \sin\varphi \frac{\partial}{\partial\theta} + \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right) \\ L_y &= i\hbar \left( -\cos\varphi \frac{\partial}{\partial\theta} + \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right) \\ L_z &= -i\hbar \frac{\partial}{\partial\varphi} \end{aligned}$$

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

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{r^2\hbar^2}$$

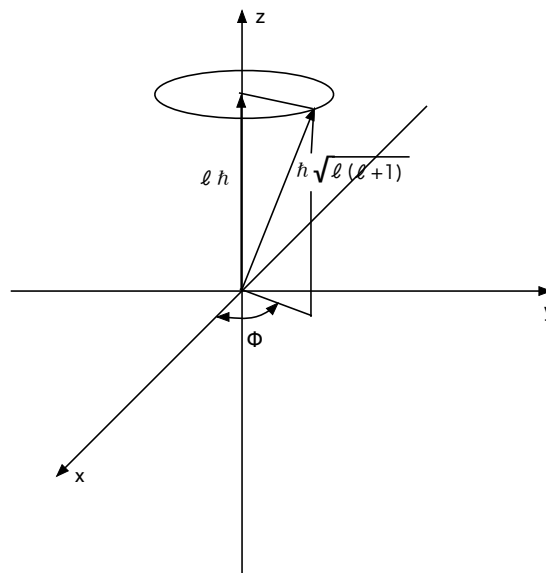
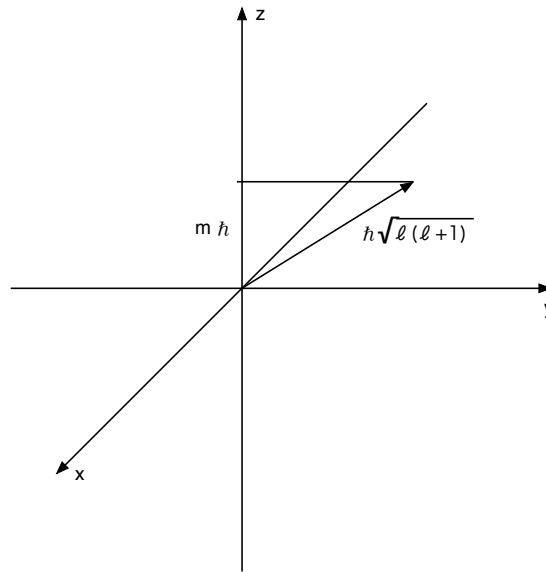
This gives Schrödinger's equation(separated) if  $V = V(r)$

$$-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) \right) + V(r)R - \frac{\ell(\ell+1)\hbar^2}{2mr^2} R = ER$$

$$L^2 Y_{\ell m}(\theta, \varphi) = \ell(\ell+1)\hbar^2 Y_{\ell m}(\theta, \varphi)$$

$$L_z Y_{\ell m}(\theta, \varphi) = m\hbar Y_{\ell m}(\theta, \varphi)$$

$\rightarrow Y_{\ell m}$  are eigenfunctions of  $L^2$  and  $L_z$ . Therefore  $\ell \equiv$  "orbital angular momentum quantum number (actual magnitude is  $\hbar\sqrt{\ell(\ell+1)}$ ) and  $m \equiv$  "magnetic" quantum number with  $-\ell \leq |L_z| \leq \ell$ . Two pictures illustrate a way of visualizing this situation:



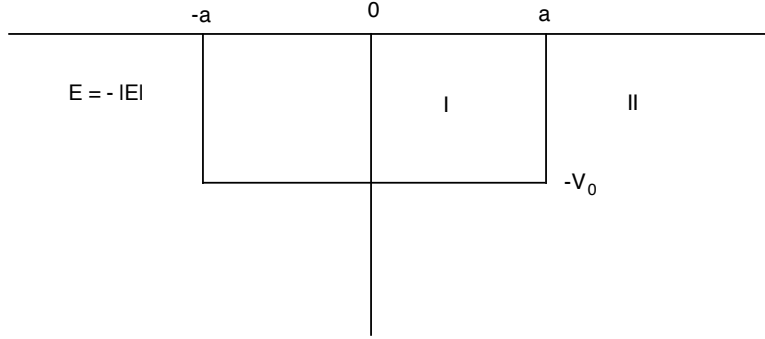
$\Delta L_z \delta \varphi \geq \hbar$  ( conjugate variables )

**Some Systems:** Remember the relations

$$\frac{\chi}{r} = R$$

$$\frac{d^2 \chi}{dr^2} + \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{\ell(\ell+1)}{r^2} \right] \chi = 0$$

Consider a square well, radius  $a$ , depth  $-V_0$  as shown



In region I:

$$\frac{d^2 \chi_\ell}{dr^2} + \frac{2m}{\hbar^2} \left[ \underbrace{V_0 - |E|}_{\text{constant}} - \frac{\ell(\ell+1)}{r^2} \right] \chi_\ell = 0$$

In region II:

$$\frac{d^2 \chi_\ell}{dr^2} + \frac{2m}{\hbar^2} \left[ \underbrace{-|E|}_{\text{constant}} - \frac{\ell(\ell+1)}{r^2} \right] \chi_\ell = 0$$

In region I:

$$\alpha^2 = \frac{2m}{\hbar^2} (V_0 - |E|) \rightarrow \left( \frac{d^2}{dr^2} + \alpha^2 - \frac{\ell(\ell+1)}{r^2} \right) \chi_\ell = 0$$

In region II:

$$\beta^2 = \frac{2m}{\hbar^2} |E| \rightarrow \left( \frac{d^2}{dr^2} - \beta^2 - \frac{\ell(\ell+1)}{r^2} \right) \chi_\ell = 0$$

Let  $\rho = \alpha r$  to get

$$\left( \frac{d^2}{d\rho^2} + 1 - \frac{\ell(\ell+1)}{\rho^2} \right) Z_\ell = 0$$

Now the cylindrical Bessel equation is

$$J_k'' + \frac{1}{x} J_k' + \left( 1 - \frac{n^2}{x^2} \right) J_k = 0$$

which implies that

$$Z_\ell(\rho) = \sqrt{x} J_{\ell+1/2}(x)$$

and

$$R_\ell(\rho) = \sqrt{\frac{\pi}{2x}} J_{\ell+1/2}(x) \equiv j_\ell(x) \rightarrow \text{spherical Bessel functions}$$

$$n_\ell(x) \equiv (-1)^{\ell+1} \sqrt{\frac{\pi}{2x}} J_{-\ell-1/2}(x) \rightarrow \text{spherical Neumann functions}$$

Solutions are given by combinations of

$$xj_\ell(x) \text{ and } xn_\ell(x)$$

### Properties

Near origin:

$$j_\ell(x) \rightarrow \frac{x^\ell}{(2\ell+1)!!}$$

$$n_\ell(x) \rightarrow \frac{(2\ell+1)!!}{x^{\ell+1}}$$

As  $x \rightarrow \infty$ :

$$j_\ell(x) \rightarrow \frac{\sin\left(x - \frac{\ell\pi}{2}\right)}{x}$$

$$n_\ell(x) \rightarrow -\frac{\cos\left(x - \frac{\ell\pi}{2}\right)}{x}$$

$$j_0(x) = \frac{\sin x}{x} \quad , \quad n_0(x) = -\frac{\cos x}{x}$$

$$j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \quad , \quad n_2(x) = \frac{\cos x}{x^2} - \frac{\sin x}{x}$$

Going back to the bound state problem

$$Z_\ell \sim xj_\ell(x)$$

Asymptotically

$$j_\ell(x) \rightarrow \text{sine}$$

$$n_\ell(x) \rightarrow \text{cosine}$$

Hence,

$$x(j_\ell + n_\ell) \sim e^{ix}$$

### Hydrogen Atom

We neglect the motion of the proton  $\rightarrow \mu_{reduced} \rightarrow m_e$ . For a two-particle system

$$V = V(x_1, x_2, y_1, y_2, z_1, z_2) \quad \text{and} \quad \psi = \psi(x_1, x_2, y_1, y_2, z_1, z_2)$$

$$\begin{aligned} |\psi|^2 d\tau_1 d\tau_2 &= |\psi(x_1, x_2, y_1, y_2, z_1, z_2)|^2 d\tau_1 d\tau_2 \\ &= \text{probability of finding particle 1 at } \vec{r}_1 \text{ and particle 2 at } \vec{r}_2 \end{aligned}$$

$$\int d\tau_2 |\psi(\vec{r}_1, \vec{r}_2)|^2 = \text{probability density of particular 1 being near } \vec{r}_1$$

and similarly for particle 2.

KE Operators:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right) - \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x_2^2} + \dots \right)$$

This follows from

$$E_T = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(\vec{r}_1, \vec{r}_2) = i\hbar \frac{\partial}{\partial t}$$

all operating on  $\psi(x_1, \dots, z_2)$ .

Now introduce

$$x = x_1 - x_2 \quad , \quad MX = m_1 x_1 + m_2 x_2 \quad X = \text{CM coordinate}$$

We get

$$-\frac{\hbar^2}{2m_1} \left( \frac{\partial^2}{\partial x_1^2} + \dots \right) \psi - \frac{\hbar^2}{2m_2} \left( \frac{\partial^2}{\partial x_2^2} + \dots \right) \psi + V(\vec{r}_1, \vec{r}_2) \psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$\frac{\partial}{\partial x_1} = \frac{\partial}{\partial x} - \frac{m_1}{M} \frac{\partial}{\partial X}$$

Therefore

$$\frac{1}{m_1} \frac{\partial^2}{\partial x_1^2} = \frac{1}{m_1} \left( \frac{\partial^2}{\partial x^2} + \frac{2m_1}{M} \frac{\partial^2}{\partial x \partial X} + \left( \frac{m_1}{M} \right)^2 \frac{\partial^2}{\partial X^2} \right)$$

and similarly for  $x_2$ . Addition  $\rightarrow$  mixed terms cancel. Therefore continuing for all and substituting we get the coefficient of

$$\frac{\partial^2}{\partial X^2} \rightarrow \frac{m_1 + m_2}{M^2} = \frac{1}{M}$$

$$\frac{\partial^2}{\partial x^2} \rightarrow \frac{1}{m_1} + \frac{1}{m_2} = \frac{1}{\mu}$$

Thus,

$$\psi = e^{-i\mathcal{E}t/\hbar} u(x, y, z) U(X, Y, Z)$$

where  $\mathcal{E}$  = total energy.

$$-\frac{\hbar^2}{2M} \nabla^2 U = E' U$$

which is a free particle equation  $\rightarrow$  plane wave solution.

$$-\frac{\hbar^2}{2\mu} \nabla^2 u + V u = E u$$

this is precisely the equation we would get if we considered the proton fixed at the origin and we replaced  $m_e$  by  $\mu$ . We also have

$$\mathcal{E} = E + E'$$

Now the nucleus has charge  $Ze$  so that

$$V = -\frac{Ze^2}{r}$$

where  $r$  is now a relative coordinate; proton at the origin. Thus we consider the situation where the proton and the electron are point charges which can be well-localized and their interaction is given by the classical law of force.

### Relative Motion

$$-\frac{\hbar^2}{2\mu}\nabla^2 u - \frac{Ze^2}{r}u = Eu$$

$$u = R(r)Y_{\ell m}(\theta, \varphi)$$

We get the radial equation

$$\frac{\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\ell(\ell+1)}{r^2}R\right) + \left(E + \frac{Ze^2}{r}\right)R = 0$$

Now let  $\rho = \alpha r$ . We get

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) - \frac{\ell(\ell+1)}{\rho^2}R + \frac{2\mu}{\hbar^2\alpha^2}(-|E|)R + \frac{2\mu}{\hbar^2\alpha}\frac{Ze^2}{\rho}R = 0$$

Now let

$$\frac{2\mu}{\hbar^2\alpha^2}(-|E|) = -\frac{1}{4} \rightarrow |E| = \frac{\hbar^2\alpha^2}{8\mu}$$

We consider only negative  $E$  for these  $\rightarrow$  bound states (discrete spectrum). There is a continuous spectrum for positive  $E$ . If we choose

$$\frac{2\mu Ze^2}{\hbar^2\alpha} = \lambda$$

we have the equation

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) - \frac{\ell(\ell+1)}{\rho^2}R - \frac{1}{4}R + \frac{\lambda}{\rho}R = 0$$

Large  $\rho \rightarrow$  :

$$\frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0$$

$$\rightarrow R = e^{-\frac{1}{2}\rho} \quad \text{asymptotically}$$

We assume

$$R = e^{-\frac{1}{2}\rho}F(\rho)$$

where  $F(\rho) \rightarrow 0$  for large  $\rho$ . Substitution gives

$$F'' + \left(\frac{2}{\rho} - 1\right)F' + \left(\frac{\lambda - 1}{\rho} - \frac{\ell(\ell+1)}{\rho^2}\right)F = 0$$

Let

$$F = \sum_{\nu} a_{\nu} \rho^{s+\nu}$$

Substituting and considering the term  $\rho^{s+\nu+2}$  we get

$$a_\nu[(s+\nu)(s+\nu-1+2) - \ell(\ell+1)] + a_{\nu-1}[\lambda-1 - (s+\nu-1)] = 0$$

$\nu = 0 \rightarrow$  1st term;  $a_{-1} = 0$

$$\rightarrow s(s+1) - \ell(\ell+1) = 0$$

$s = \ell \rightarrow$  OK

$s = \ell - 1 \rightarrow$  discontinuity at origin  $\rightarrow$  reject

Rewriting we get

$$a_\nu \underbrace{[\ell(\ell+1) + \nu(2\ell+1) + \nu^2 - \ell(\ell+1)]}_{\nu(2\ell+1+\nu)} - a_{\nu-1}(\ell + \nu - \lambda) = 0$$

or

$$\frac{a_\nu}{a_{\nu-1}} = \frac{\ell + \nu - \lambda}{\nu(2\ell+1+\nu)}$$

$a_0 = 1 \rightarrow$  all others known.

Two choices:

I series terminates at  $\nu = n \rightarrow \lambda = \ell + n' + 1 = \text{integer} = n$

or

II series does not terminate  $\rightarrow \lambda \neq \text{integer}$ . Therefore for large  $\nu$

$$\frac{a_\nu}{a_{\nu-1}} \approx \frac{1}{\nu}$$

This says that

$$a_\nu \approx \frac{c}{\nu!}$$

$\rightarrow$  for large  $\rho \sum a_\nu \rho^\nu \rightarrow c e^\rho \rightarrow$  no good !! This means that termination is necessary.

In general we do not obtain eigenfunctions by forcing the power series to terminate; this is only true when one has a 2-term recursion formula, i.e., for a 3-term recursion relation a wave function can be well-defined at  $\infty$  without termination of the power series.

For  $n \geq \ell + 1$

$$\alpha = \frac{2\mu Z e^2}{\hbar^2 n} \quad n = \text{principal quantum number}$$

$$\begin{aligned}\frac{\hbar^2}{\mu e^2} &= a_0 = \text{1st Bohr radius} \approx 0.529 \times 10^{-8} \text{ cm} \\ &= \text{atomic unit of length (Hartree)}\end{aligned}$$

Therefore,

$$\begin{aligned}\alpha &= \frac{2Z}{na_0} \quad \left( \frac{1}{\alpha} = \text{length scale} \right) \\ E &= -\frac{\hbar^2 \alpha^2}{8\mu} = -\frac{Z^2 e^2}{2a_0} \frac{1}{n^2} \\ \frac{e^2}{a_0} &= \text{atomic unit of energy} \\ \frac{1}{2} \frac{e^2}{a_0} &= Ry = \textbf{Rydberg}\end{aligned}$$

Therefore

$$\begin{aligned}E &= -\frac{Z^2}{n^2} Ry \\ Ry &= \frac{\mu e^4}{2\hbar^2} \rightarrow Ry_\infty = \frac{m_e e^4}{2\hbar^2} \quad (\infty \text{ nuclear mass} \rightarrow \mu \rightarrow m_e) \\ Ry &= 109,737.31 \pm 0.15 \text{ cm}^{-1}\end{aligned}$$

$E_n$  does not depend on  $\ell$  and  $m \rightarrow$  degeneracy whenever we have  $V(r)$  (symmetric)  $\rightarrow$  there is always degeneracy in  $m \rightarrow 2\ell + 1$  (possible values of  $m$ ) degenerate eigenfunctions.

Only for  $V = \text{constant}/r \rightarrow$  additional degeneracy in  $\ell$ !

Another example: 3-Dimensional Oscillator -  $V = \frac{1}{2}m\omega^2 r^2 \rightarrow$  spherically symmetric.

Separation is possible in other coordinates, i.e.,

A) 3-dim oscillator

1) cartesian

B) Parabolic separation of Coulomb potential

1) scattering of a particle by Coulomb field ( $E > 0$ )

2) Stark effect - H atom with superimposed field  $\rightarrow$

$$V = \underbrace{eFz}_{\mathcal{E}} - \frac{e^2}{r}$$

Not separable in spherical coordinates!



Now consider the eigenfunctions  $R_{n,\ell}$ ; there is a different Schrödinger's equation for each  $\ell$ ! The  $R_{n,\ell}$  are orthogonal (since  $R_{n,\ell}$  and  $R_{n,\ell'}$  satisfy different Schrödinger's equations). Remember

$$\chi = rR$$

$$\frac{d^2\chi}{dr^2} + \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{\ell(\ell+1)}{r^2} \right] \chi = 0$$

For given  $\ell$

$$\int \chi_{n\ell} \chi_{n'\ell} dr = \delta_{nn'}$$

The radial quantum number:  $n_r = n - \ell - 1 \geq 0$  = number of radial nodes of the eigenfunction!

Unit of length =  $\frac{a_0}{Z}$

$$R_{10} = 2e^{-r}$$

$$R_{20} = \frac{1}{\sqrt{2}} e^{-\frac{1}{2}r} \left( 1 - \frac{1}{2}r \right)$$

$$R_{21} = \frac{1}{2\sqrt{6}} e^{-\frac{1}{2}r} r$$

$$R_{30} = \frac{2}{3\sqrt{3}} e^{-\frac{1}{3}r} \left( 1 - \frac{2}{3}r + \frac{2}{27}r^2 \right)$$

$$R_{43} = \frac{1}{768\sqrt{35}} e^{-\frac{1}{4}r} r^3$$

$R_{n\ell}^2 r^2 dr$  = probability of finding electron between  $r$  and  $r + dr$ !

$$P_\ell^m \cos m\phi \rightarrow \ell \text{ nodes}$$

We have  $m$  planes  $\phi = \text{constant}$  and  $\ell - m$  cones  $\theta = \text{constant}$ .  $n_r = n - \ell - 1$  spheres  $r = \text{constant}$ . The wave function vanishes on all these surfaces. Total number of surfaces =  $n - 1$  nodal surfaces (neglecting point  $r = 0$  and line  $\theta = 0$ , i.e., we consider only surfaces). These facts of nodal surfaces wrt  $n$  are true for any differential equation (general concept) whereas  $E$  wrt  $n$  is only true for the Coulomb potential.

### Radial Wave Functions wrt Laguerre Polynomials

We have the generating function

$$\frac{e^{-\frac{\rho s}{1-s}}}{1-s}$$

$$F = \rho^\ell \left[ 1 + \frac{\ell+1-n}{1!(2\ell+2)} \rho + \frac{(\ell+1-n)(\ell+2-n)}{2!(2\ell+2)(2\ell+3)} \rho^2 + \dots + \dots \rho^{n-\ell-1} \right]$$

$\rightarrow \rho^\ell F(-n_r, 2\ell+2, \rho) = \text{confluent hypergeometric function}$

$$F(\alpha, \beta, \rho) = 1 + \frac{\alpha}{\beta 1!} \rho + \frac{\alpha(\alpha+1)}{\beta(\beta+1)2!} \rho^2 + \dots$$

This works for  $n_r \neq \text{integer} \rightarrow n$  imaginary. i.e.,

$$n = \sqrt{\frac{Ry}{-E}} \rightarrow E = -\frac{Ry}{n^2} \quad \text{for } n = ki \quad (E, k > 0)$$

Imaginary  $n \rightarrow$  same hypergeometric function. For  $E > 0$ ,  $e^{irk}$  and  $e^{-ikr}$  are good  $\rightarrow$  no termination of series.

$$L_{n+\ell}^{2\ell+1} = L = \text{Laguerre polynomial} = \frac{-(n+\ell)!}{(2\ell+1)!(n-\ell-1)!} F(-n_r, 2\ell+1, \rho)$$

$$R_{n\ell} = \frac{\sqrt{(n+\ell)!}}{\sqrt{(2\ell+1)!}\sqrt{(n-\ell-1)!}} \frac{1}{\sqrt{2n}} \left( \frac{2Z}{na_0} \right)^{3/2} e^{-\frac{1}{2}\rho} \rho^\ell F(\alpha, \beta, \rho)$$

For small  $\rho$ :

$$\begin{aligned} R &\sim \rho^\ell & (\ell \rightarrow \text{orbital angular momentum}) \\ &\rightarrow \text{low } \ell \rightarrow \text{close to nucleus} \\ &\rightarrow \text{high } \ell \rightarrow \text{far from nucleus} \end{aligned}$$

This implies that nuclear effects occur mainly in states of low  $\ell$ ; these are effects having to do with the structure of the nucleus, i.e., size  $\rightarrow$  shift in energy levels and isotope effect; hyperfine structure due to magnetic moment of the nucleus.

For large  $\rho$ , the behavior is determined by  $n$  or the energy  $\rightarrow$  motion at large distances is governed by the energy of the state.

Let us calculate  $\langle r^\nu \rangle$  in units of  $\frac{a_0}{Z}$ .

$$\langle r \rangle = \frac{1}{2}(3n^2 - \ell(\ell+1))$$

$$\langle r^2 \rangle = \frac{n^2}{2}(5n^2 + 1 - 3\ell(\ell+1))$$

$$\begin{aligned} \langle (r - \langle r \rangle)^2 \rangle &= \langle r^2 \rangle - \langle r \rangle^2 \\ &= \frac{1}{4}(n^4 - \ell^2(\ell+1)^2 + 2n^2) \end{aligned}$$

$\ell$  small  $\sim n^4 \rightarrow$  large possible  $r$  deviations  $\rightarrow$  very eccentric orbit

$\ell$  large  $\sim n^3 \rightarrow$  small possible  $r$  deviations  $\rightarrow$  circular orbit

$$\langle r^{-1} \rangle = \frac{1}{n^2}$$

$$\langle r^{-2} \rangle = \frac{1}{n^2(\ell+1/2)}$$

$$\langle r^{-3} \rangle = \frac{1}{n^3\ell(\ell+1/2)(\ell+1)}$$

We then have

$$\langle V \rangle = \langle -Ze^2 r^{-1} \rangle = -\frac{ze^2}{a_0} \frac{1}{n^2}$$

But we also have

$$E = -\frac{ze^2}{2a_0} \frac{1}{n^2}$$

Thus,

$$\langle V \rangle = 2E \rightarrow \text{virial theorem} \rightarrow E_k = -E > 0$$

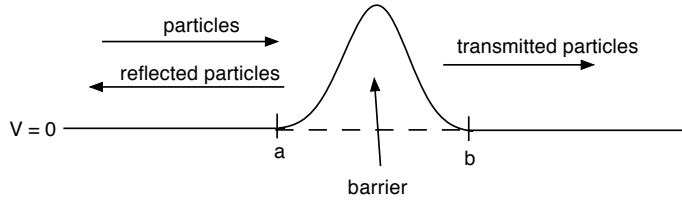
$$\ell = 0 \quad \langle r^{-3} \rangle = \infty \rightarrow \int_0^\infty r^{-3} R^2 r^2 dr \rightarrow \infty$$

$\ell = 0 \rightarrow$  s-states; small  $r$  or  $\rho \rightarrow$

$$R \sim n^{-3/2}(1 + O(\rho)) \rightarrow R^2(0) \sim n^{-3} \rightarrow \text{nuclear effects} \sim n^{-3}.$$

### Collision Theory

Continuous energy spectrum  $E > 0$ . Consider 1-dimensional motion (shown below):



Outside the barrier the solutions are linear combinations of  $e^{\pm ikx}$  depending on experimental conditions, i.e., if particle incident only from the left we have

$$\begin{aligned} x < a & \quad Ae^{ikx} + Be^{-ikx} \\ x > b & \quad Ce^{ikx} \end{aligned}$$

From conservation law

$$\nabla \cdot \vec{S} + \frac{\partial \rho}{\partial t} = 0$$

Consider this as a stationary problem independent of time! Then

$$\nabla \cdot \vec{S} = -\frac{\partial \rho}{\partial t} = 0 \rightarrow \frac{dS}{dx} = 0$$

This says that the net current of particles is constant. Now

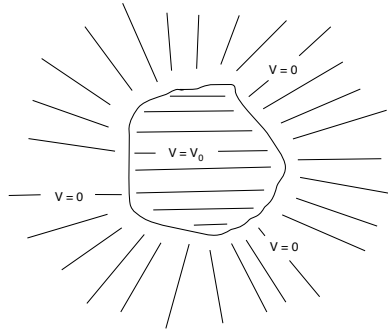
$$\begin{aligned} S &= \frac{\hbar}{2im} \left( \psi^* \frac{d\psi}{dx} - \psi \frac{d\psi^*}{dx} \right) \\ &= \underbrace{v(|A|^2 - |B|^2)}_{\text{net incident current}} \quad x < a \\ &= \underbrace{v|C|^2}_{\text{transmitted current}} \quad x > b \end{aligned}$$

Therefore

$$\begin{aligned}\text{transmission coefficient} &= T = \frac{|C|^2}{|A|^2} \\ \text{reflection coefficient} &= R = \frac{|B|^2}{|A|^2}\end{aligned}$$

with  $R + T = 1$ .

In 3 dimensions, the asymptotic form of the wave function for a scattering region as shown



is:

$$u = e^{ikz} + \frac{e^{ikr}}{r} f(\theta, \varphi)$$

where the first term represents the incident particles in the  $z$ -direction (plane wave) and the second term represents a spherical wave going in all spherically symmetric direction radially outward from the scatterer.

Why  $\frac{1}{r}$ ? Consider large  $r$ :

$$\begin{aligned}\nabla^2 u + k^2 u &= 0 \\ \frac{1}{r} \frac{\partial^2}{\partial r^2} (ru) + \underbrace{\frac{1}{r^2} \nabla_{\theta, \varphi}^2}_{O\left(\frac{1}{k^2 r^2}\right) \text{ wrt last term}} u + k^2 u &= 0\end{aligned}$$

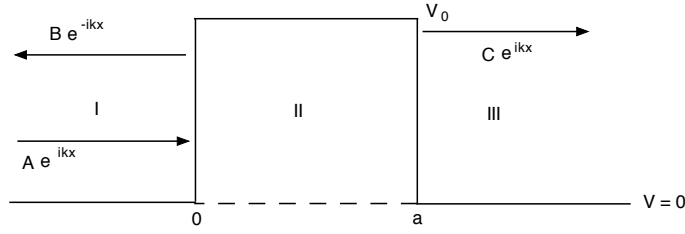
Therefore we get

$$ru = e^{\pm ikr} \rightarrow u = \frac{e^{\pm ikr}}{r}$$

A 2nd justification: the out going current

$$\frac{f^2}{r^2} \Delta \Omega = \frac{f^2}{r^2} r^2 d\omega \neq g(r) \rightarrow \text{OK}$$

Back to 1-dimensional problem. Consider



$$\frac{d^2 u}{dx^2} + k^2 u = 0 \quad \text{in I and III}$$

This implies

$$u = e^{\pm ikx} \quad k^2 = \frac{2mE}{\hbar^2}$$

In region II:

$$\frac{d^2 u}{dx^2} + \underbrace{\frac{2m}{\hbar^2}(E - V_0)}_{\alpha^2} u = 0$$

Let  $E > V_0$ , then

$$u = F e^{i\alpha x} + G e^{-i\alpha x}$$

**Matching Conditions**

At  $x = 0$ :

$$\begin{aligned} A + B &= F + G \\ k(A - B) &= \alpha(F - G) \end{aligned}$$

At  $x = a$ :

$$\begin{aligned} C e^{ika} &= F e^{i\alpha a} + G e^{-i\alpha a} \\ k C e^{ika} &= \alpha(F e^{i\alpha a} - G e^{-i\alpha a}) \end{aligned}$$

These imply that

$$\begin{aligned} \frac{C}{A} &= \frac{4\alpha k e^{i(\alpha-k)a}}{(\alpha+k)^2 - (\alpha-k)^2 e^{2ika}} \\ \frac{B}{A} &= \frac{(k^2 - \alpha^2)(1 - e^{2ika})}{(\alpha+k)^2 - (\alpha-k)^2 e^{2ika}} \end{aligned}$$

**Probabilities**

$$\begin{aligned} \left| \frac{C}{A} \right|^2 &= \left\{ 1 + \frac{V_0^2 \sin^2 \alpha a}{4E(E - V_0)} \right\}^{-1} \\ \left| \frac{B}{A} \right|^2 &= \left\{ 1 + \frac{4E(E - V_0)}{V_0^2 \sin^2 \alpha a} \right\}^{-1} \end{aligned}$$

We have

$$\left| \frac{B}{A} \right|^2 + \left| \frac{C}{A} \right|^2 = 1 \rightarrow \text{conservation of probability, as expected}$$

As  $E \rightarrow V_0$ ,  $\alpha \rightarrow 0$  we have

$$\sin^2 \alpha a \sim (\alpha a)^2 \sim \alpha^2 a^2 = \frac{2m}{\hbar^2}(E - V_0)a^2$$

This implies that

$$\left| \frac{C}{A} \right|^2 \rightarrow \left\{ 1 + \frac{mV_0 a^2}{2\hbar^2} \right\}^{-1}$$

For  $E \gg V_0$  we have  $\sin^2 \alpha a \approx 1$  and therefore

$$\left| \frac{C}{A} \right|^2 \approx \left( 1 + \frac{V_0^2}{E^2} \right)^{-1} \rightarrow 1$$

But  $\sin \alpha a = 0$  for  $\alpha a = n\pi \rightarrow$  for certain energies

$$\left| \frac{C}{A} \right|^2 = 1$$

which is the wave property of barrier transmission.

Now consider  $E < V_0$ ; let  $\alpha^2 \rightarrow -\beta^2 \rightarrow$  substitution  $\alpha = i\beta$ . We have

$$\sin ikx = i \sinh kx$$

which gives

$$\left| \frac{C}{A} \right|^2 = \left\{ 1 + \frac{V_0^2 \sinh^2 \beta a}{4E(V_0 - E)} \right\}^{-1}$$

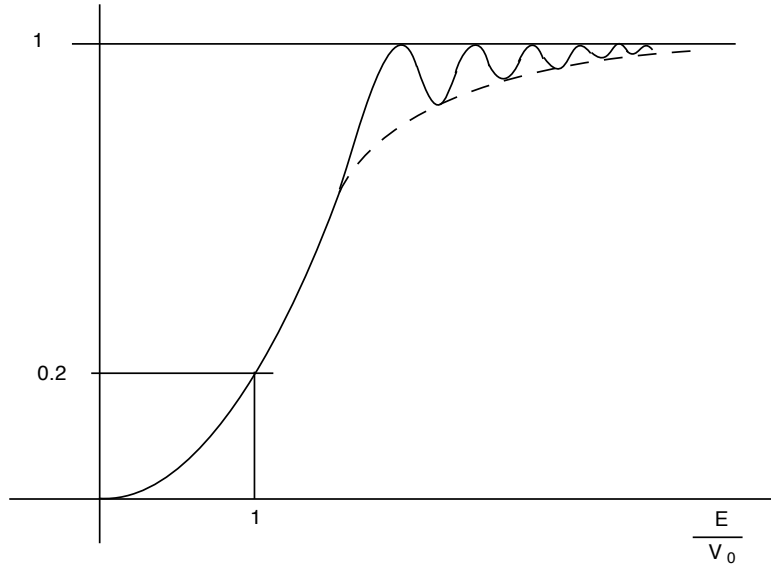
For  $E \rightarrow 0$ , assuming that

$$\beta a \sim \sqrt{\frac{2mV_0 a^2}{\hbar^2}} \gg 1$$

we have  $\sinh^2 \beta a \gg 1$  and therefore

$$\left| \frac{C}{A} \right|^2 \sim \frac{16E(V_0 - E)}{V_0^2} e^{-2\beta a}$$

which goes linearly to zero. A picture of what happens is shown below.



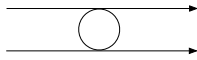
Now back to 3 dimensions. We have

$$u(r, \theta, \varphi) = A \left\{ e^{ikz} + \frac{e^{ikr}}{r} f(\theta, \varphi) \right\}$$

Substitution for probability flux at large distance

$$v|A|^2 + v|A|^2 \frac{|f(\theta, \varphi)|^2}{r^2}$$

Why no cross term? In practical experiments we have configuration below:



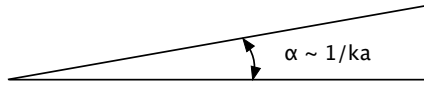
where  $a = \Delta x = \Delta y$  = beam width. This implies that

$$\Delta k_x = \Delta k_y \sim \frac{1}{a}$$

Theoretically we have infinite plane waves

$$e^{ikz - (x^2 + y^2)/2a^2}$$

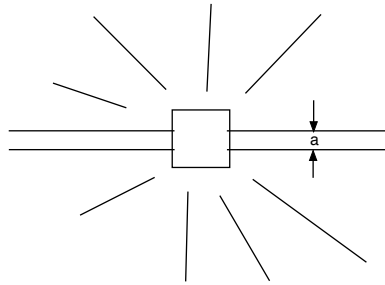
Uncertainties  $\rightarrow$  beam diverges as shown



such that  $f(\theta, \varphi)$  for divergent beam  $\sim f(\theta, \varphi)$  for  $z$  beam which  $\rightarrow$  scattered wave

$$\frac{e^{ikr}}{r} f(\theta, \varphi)$$

If  $x$  and  $y > a$ , then we have the situation shown below



where there are no counters in the beam region. This  $\rightarrow$  cross term of negligible magnitude due to gaussian!

### 3-Dimensional Scattering

We have wave function

$$u(r, \theta, \varphi) = A \left\{ e^{ikz} + \frac{e^{ikr}}{r} f(\theta, \varphi) \right\}$$

with arrangement as shown:



The incoming flux is given by

$$\text{incoming flux} = \frac{\# \text{ particles}}{\text{unit area} \cdot \text{sec}}$$

We count

$$\frac{\# \text{ particles scattered in a solid angle } \Delta\omega_0}{\text{sec}}$$

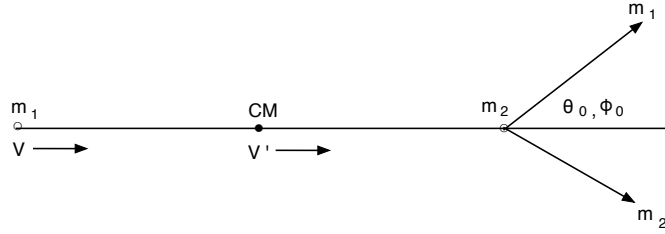
$$\text{cross section} = \frac{\# \text{ particles scattered in a solid angle } \Delta\omega_0 / \text{sec}}{\text{incoming flux} \cdot \text{number of scattering centers}} = \sigma_0(\theta_0, \varphi_0) \text{ in lab}$$



In CM with  $\theta, \varphi$

$$\sigma(\theta, \varphi) = |f(\theta, \varphi)|^2$$

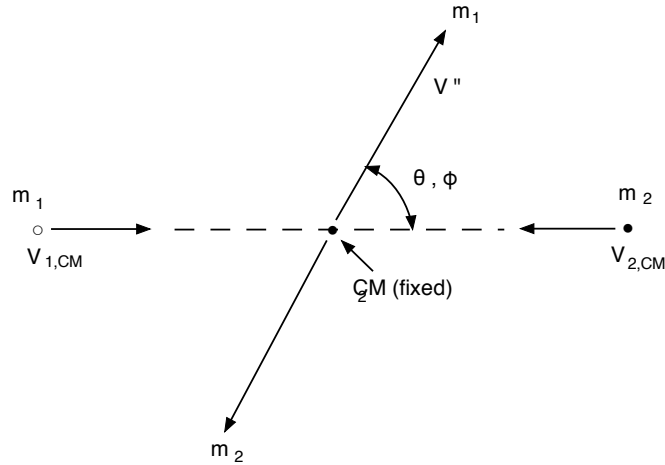
In lab we have the picture



where

$$V' = V_{CM} = \frac{m_1 V}{m_1 + m_2}$$

and in the CM we have the picture



where

$$V_{1,CM} = \frac{m_2 V}{m_1 + m_2} \quad , \quad V_{2,CM} = \frac{m_1 V}{m_1 + m_2}$$

We have

$$\vec{V}_{particle,CM} + \vec{V}' = \vec{V}_{particle,lab}$$

which gives the two relations

$$\begin{aligned} V'' \cos \theta + V' &= V \cos \theta_0 \\ V'' \sin \theta &= V \sin \theta_0 \end{aligned} \tag{21}$$

We define  $\varphi = \varphi_0$  and then have

$$\tan \theta_0 = \frac{\sin \theta}{\gamma + \cos \theta} \quad \gamma = \frac{V'}{V''} = \frac{m_1}{m_2}$$

In lab

$$E_0 = \frac{1}{2} m_1 V^2$$

In CM, add

$$V' = \frac{m_1 V}{m_1 + m_2}$$

to CM system  $\rightarrow$  lab system. This gives as we saw above

$$\tan \theta_0 = \frac{\sin \theta}{\gamma + \cos \theta}$$

Now

$$\sigma_0(\theta_0, \varphi_0) d\omega_0 = \sigma(\theta, \varphi) d\omega$$

where  $d\omega = \sin \theta d\theta d\varphi$ . Then

$$\sigma_0(\theta_0, \varphi_0) d\omega_0 = \sigma(\theta, \varphi) \frac{d \cos \theta}{d \cos \theta_0}$$

or

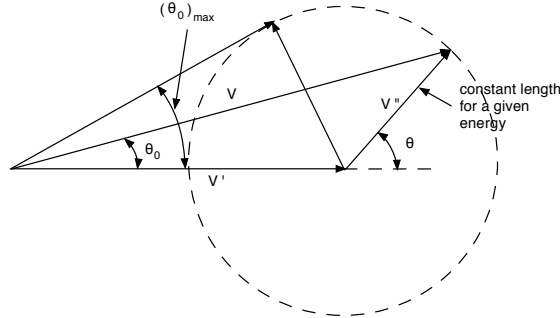
$$\sigma_0 = \sigma \frac{(1 + \gamma^2 + 2\gamma \cos \theta)^{3/2}}{|1 + \gamma \cos \theta|}$$

$$\text{total cross section} = \sigma_T = \int_{4\pi} \sigma(\theta, \varphi) d\omega$$

which is independent of the system. Now if  $m_1 \gg m_2 \rightarrow \gamma \gg 1$ , then

$$\gamma = \frac{m_1}{m_2} = \frac{V'}{V''} \gg 1 \rightarrow \exists (\theta_0)_{max}$$

$$\sin (\theta_0)_{max} = \frac{m_2}{m_1} = \frac{1}{\gamma}$$



→ cone of  $\frac{1}{2}$ -angle  $\theta_0$  in lane system. For a given  $\theta_0$  there are two  $V$ s.

$$\gamma = 1 \rightarrow (\theta_0)_{max} = \frac{\pi}{2} \rightarrow \theta_0 = \frac{1}{2}\theta$$

If  $\gamma < 1 \rightarrow$  all  $\theta_0$  are possible.

Eigenvalue equation:

$$\begin{aligned} H\psi &= E_0\psi \\ E_0 &= E + E' \end{aligned}$$

where

$$E' = \frac{1}{2}(m_1 + m_2) \left( \frac{m_1}{m_1 + m_2} V^2 \right)^2 = \frac{m_1}{m_1 + m_2} E_0 \rightarrow \text{CM motion}$$

$$E = \frac{m_2}{m_1 + m_2} E_0 \rightarrow \text{relative motion}$$

and for relative motion

$$-\frac{\hbar^2}{2\mu} \nabla^2 u(\vec{r}) + V(\vec{r})u(\vec{r}) = Eu(\vec{r})$$

For  $V(\vec{r})$  spherically symmetric, the asymptotic wave function is

$$u(r) \rightarrow e^{ikz} + \frac{e^{ikr}}{r} f(\theta)$$

The independence of  $\varphi \rightarrow$  no preference.

$$u(\vec{r}) = \sum_{\ell} R_{\ell}(r) P_{\ell}(\cos \theta) = \sum_{\ell} \frac{\chi_{\ell}(r)}{r} P_{\ell}(\cos \theta)$$

where  $\chi_{\ell}$  satisfies

$$\frac{d^2 \chi_{\ell}}{dr^2} + \left[ \frac{2\mu}{\hbar^2} [E - V(r)] - \frac{\ell(\ell+1)}{r^2} \right] \chi_{\ell} = 0$$

where we define

$$k^2 = \frac{2\mu E}{\hbar^2} \quad , \quad U(r) = \frac{2\mu}{\hbar^2} [E - V(r)]$$

Suppose that  $U(r) \rightarrow 0$  faster than  $\frac{1}{r^2}$  as  $r \rightarrow \infty$ . Then, large  $r \rightarrow$  Bessel's equation.

$$\begin{aligned} R_{\ell}(r) &\rightarrow B_{\ell} j_{\ell}(kr) - C_{\ell} n_{\ell}(kr) \\ &\equiv A_{\ell} (\cos \delta_{\ell} j_{\ell}(kr) - \sin \delta_{\ell} n_{\ell}(kr)) \\ &\rightarrow A_{\ell} \left\{ \cos \delta_{\ell} \frac{\sin(kr - \ell\pi/2)}{kr} - \sin \delta_{\ell} \frac{\cos(kr - \ell\pi/2)}{kr} \right\} \\ &= \frac{A_{\ell}}{kr} \sin(kr - \ell\pi/2 + \delta_{\ell}) \end{aligned}$$

where  $\delta_\ell$  = phase shift. If  $U = 0 \rightarrow \delta_\ell = 0$  or solution =  $j_\ell(r)$ . But  $U \rightarrow \delta_\ell$ .

Now

$$e^{ikz} = \sum_{\ell} a_{\ell} P_{\ell}(\cos \theta)$$

or

$$e^{ikr \cos \theta} = \sum_{\ell} c_{\ell} j_{\ell}(kr) P_{\ell}(\cos \theta)$$

i.e.,  $e^{ikz}$  solves  $(\nabla^2 + k^2)\phi = 0$  This  $\rightarrow c_{\ell} j_{\ell}(kr) P_{\ell}(\cos \theta)$  is also a solution. From the orthogonality properties of the  $P_{\ell}$  we have

$$e^{ikr \cos \theta} = \sum_{\ell} (2\ell + 1) i^{\ell} j_{\ell}(kr) P_{\ell}(\cos \theta)$$

i.e.,

$$\begin{aligned} \int_{-1}^1 e^{ix\omega} P_m d\omega &= \int_{-1}^1 \sum_{\ell} c_{\ell} j_{\ell}(kr) P_{\ell}(\cos \theta) P_m d\omega \\ &\rightarrow \ell = m \\ &= \frac{1}{ix} e^{ix\omega} P_m \Big|_{-1}^1 - \frac{1}{ix} \int_{-1}^1 e^{ix\omega} P'_m d\omega \\ &\rightarrow c_{\ell} \text{ eventually} \end{aligned}$$

Therefore

$$\begin{aligned} u(r, \theta) &= \sum_{\ell=0}^{\infty} \frac{A_{\ell}}{kr} \sin(kr - \ell\pi/2 + \delta_{\ell}) P_{\ell}(\cos \theta) \\ &= \sum_{\ell} (2\ell + 1) i^{\ell} j_{\ell}(kr) P_{\ell}(\cos \theta) + f(\theta) \frac{e^{ikr}}{r} \end{aligned}$$

i.e., we replace  $j_{\ell}$  by  $\frac{\sin(kr - \ell\pi/2)}{kr}$  for large  $r$ . Therefore

$$\begin{aligned} \sum_{\ell} \frac{A_{\ell}}{kr} P_{\ell}(\cos \theta) \frac{e^{i(kr + \dots)} - e^{-i(kr + \dots)}}{2i} \\ = \sum_{\ell} \frac{(2\ell + 1) i^{\ell}}{kr} \frac{e^{i(kr + \dots)} - e^{-i(kr + \dots)}}{2i} P_{\ell}(\cos \theta) + f(\theta) \frac{e^{ikr}}{r} \end{aligned}$$

This implies that

$$\left. \begin{aligned} e^{ikr} \sum_{\ell} A_{\ell} e^{-i\ell\pi/2 + i\delta_{\ell}} P_{\ell} \\ = \sum_{\ell} (2\ell + 1) i^{\ell} e^{-i\ell\pi/2} P_{\ell} + 2ikf(\theta) \\ e^{-ikr} \sum_{\ell} A_{\ell} e^{-i\ell\pi/2 - i\delta_{\ell}} P_{\ell} \\ = \sum_{\ell} (2\ell + 1) e^{i\ell\pi/2} P_{\ell} \end{aligned} \right\} \text{equating coefficients}$$

Therefore

$$A_\ell = (2\ell + 1)i^\ell e^{i\delta_\ell}$$

This gives

$$\begin{aligned} & \sum_\ell (2\ell + 1)i^\ell e^{i\delta_\ell} i^{-\ell} e^{i\delta_\ell} P_\ell \\ &= \sum_\ell (2\ell + 1)P_\ell + 2ik f(\theta) \\ &\rightarrow f(\theta) = \frac{1}{2ik} \sum_\ell (2\ell + 1)(e^{2i\delta_\ell} - 1)P_\ell(\cos \theta) \end{aligned}$$

Then we have

$$\begin{aligned} \sigma(\theta) &= |f|^2 = \frac{1}{k^2} \left| \sum_\ell (2\ell + 1)(e^{i\delta_\ell} \sin \delta_\ell) P_\ell(\cos \theta) \right|^2 \\ \sigma_T &= 2\pi \int_{-1}^1 \sigma(\theta) d(\cos \theta) \quad \left\{ \int_{-1}^1 P_\ell P_m d\omega = \frac{2}{2\ell + 1} \delta_{\ell m} \right. \\ &= \frac{4\pi}{k^2} \sum_\ell \sin^2 \delta_\ell (2\ell + 1) \end{aligned}$$

This gives

$$\begin{aligned} f(0) &= \frac{1}{2ik} \sum_\ell (2\ell + 1) \underbrace{[(\cos 2\delta_\ell - 1) + i \sin 2\delta_\ell]}_{-2 \sin^2 \delta_\ell} \\ Im f(0) &= \frac{1}{k} \sum_\ell (2\ell + 1) \sin^2 \delta_\ell \end{aligned}$$

so that

$$\sigma_T = 4\pi Im f(0)$$

Thus, summarizing we have

$$\begin{aligned} u &= e^{ikz} + \frac{e^{ikr}}{r} f(\theta) \\ f(\theta) &= \frac{1}{2ik} \sum_\ell (2\ell + 1)(e^{2i\delta_\ell} - 1)P_\ell(\cos \theta) \\ \sigma(\theta) &= |f(\theta)|^2 \\ \sigma_T &= \frac{4\pi}{k^2} \sum_\ell (2\ell + 1) \sin^2 \delta_\ell = 4\pi Im f(0) \end{aligned}$$

### General Optical Theorem

The wave function must include scattered waves from unchanged scatterers and changed scatterers. We have

$$\text{Radial outward current} = Re \left( \left( \frac{\hbar}{2im} \right) \left( \psi^* \frac{\partial \psi}{\partial r} - \psi \frac{\partial \psi^*}{\partial r} \right) \right)$$

$$\psi = \psi_1 + \psi_2$$

$$(\text{only } \psi_1 \text{ terms}) \quad \psi_1 = e^{ikz}$$

→ as much incoming current as outgoing current (no net current).

$$(\text{only } \psi_2 \text{ terms}) \quad \psi_2 = \frac{e^{ikr}}{r} f(\theta)$$

where the  $\frac{1}{r}$  factor is due to radial outward current =  $v\sigma_T$ .

For total radial outward current through large sphere = 0, we need to calculate the interference terms! Consider

$$\begin{aligned} & \int \left( \frac{\hbar}{2im} \right) \left( \psi^* \frac{\partial \psi}{\partial r} - \psi \frac{\partial \psi^*}{\partial r} \right) r^2 d\omega \\ &= \frac{\hbar}{2im} r^2 \int d\omega \left( \psi_1^* \frac{\partial \psi_2}{\partial r} - \psi_2 \frac{\partial \psi_1^*}{\partial r} \right) - \frac{\hbar}{2im} r^2 \int d\omega \left( \psi_1 \frac{\partial \psi_2^*}{\partial r} - \psi_2^* \frac{\partial \psi_1}{\partial r} \right) \\ &= \text{Re} \frac{\hbar}{2im} r^2 \int d\omega \left( \psi_1^* \frac{\partial \psi_2}{\partial r} - \psi_2 \frac{\partial \psi_1^*}{\partial r} \right) \\ &= \text{Re} \frac{\hbar}{2im} r^2 \int d\omega \left( \overbrace{e^{-ikz} ik \frac{e^{ikr}}{r} f(\theta)}^K + O\left(\frac{K}{kr^2}\right) - \underbrace{(-ik \cos \theta)}_{dz/dr} e^{-ikz} ik \frac{e^{ikr}}{r} f(\theta) \right) \\ &= \text{Re} \frac{\hbar}{im} r^2 \int d\omega \left( \frac{ik}{r} f(\theta) e^{ikr(1-\cos \theta)} (1 + \cos \theta) \right) \\ &= \text{Re} \underbrace{\frac{\hbar k}{m}}_v r 2\pi \int_0^\pi \sin \theta d\theta f(\theta) e^{ikr(1-\cos \theta)} (1 + \cos \theta) \end{aligned}$$

integrate by parts →

$$\begin{aligned} &= 2\pi r v \text{Re} \left[ \frac{1}{ikr} e^{ikr(1-\cos \theta)} f(\theta) (1 + \cos \theta) \right]_0^\pi \\ &\quad - \frac{1}{ikr} \int e^{ikr(1-\cos \theta)} \frac{d}{d \cos \theta} [f(\theta) (1 + \cos \theta)] d \cos \theta \end{aligned}$$

now  $\frac{1}{irk} \rightarrow$  small for large  $kr \gg 1 \rightarrow$  neglect

$$= \frac{4\pi v}{k} \text{Re} \left( -\frac{f(0)}{i} \right) = -\frac{4\pi v}{k} \text{Im} f(0)$$

now total outward current = 0 →

$$= v\sigma_T - \frac{4\pi v}{k} \text{Im} f(0)$$

$$\rightarrow \sigma_T = \frac{4\pi}{k} \text{Im} f(0)$$

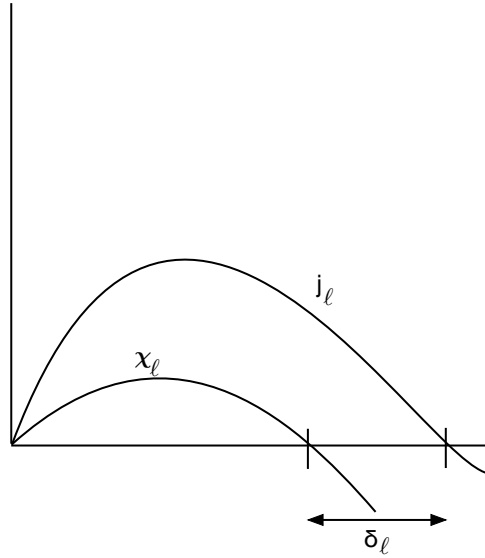
**Phase shift -  $\delta_\ell$**

$$\chi_\ell'' + \left( \overbrace{k^2 - \frac{\ell(\ell+1)}{r^2}}^M - U \right) \chi_\ell = 0$$

For free particle:

$$J_\ell(\rho) = \rho j_\ell(\rho) \rightarrow \bar{j}_\ell'' + \left( \underbrace{k^2 - \frac{\ell(\ell+1)}{r^2}}_N \right) \bar{j}_\ell = 0$$

For  $U < 0$ ,  $M > N \rightarrow$  curvature is always less positive for  $\chi_\ell$  as shown



$\rightarrow \chi_\ell$  crosses axis before  $\bar{j}_\ell$ . Therefore

$\delta_\ell > 0$  if  $U < 0 \rightarrow$  attractive potential

$\delta_\ell < 0$  if  $U > 0 \rightarrow$  repulsive potential

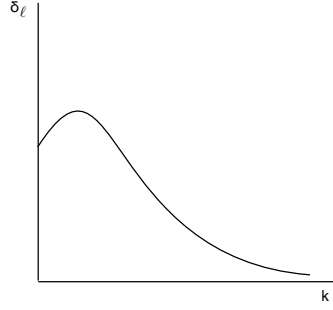
In  $f(\theta)$  formulas, we can replace  $\delta_\ell$  by  $\delta_\ell + n\pi$  without changing  $f(\theta)$ .

If  $\delta_\ell = n\pi \rightarrow e^{2i\delta_\ell} - 1 = 0$ , or the potential wave  $\ell$  does not contribute to the scattering!

Experiment tells us  $\delta_\ell$  only to an excess over a multiple of  $\pi \rightarrow$

$$\delta_{\ell, meas} = p\pi \quad p < 1$$

$\rightarrow \delta_{\ell, theory} = p\pi + n\pi$  - all are possible. Now at high energy  $\delta_\ell \rightarrow 0$ , i.e.,



### Calculation of $\delta_\ell$

$U$  is appreciable only for  $r < a$ . Outside we have

$$\bar{j}_\ell \cos \delta_\ell - \bar{n}_\ell \sin \delta_\ell$$

while inside we know that

$$\frac{\chi'_\ell}{\chi_\ell}(a) = \gamma_\ell \quad (\text{not the same as in Schiff})$$

It is obtained by integration of the differential equation up to  $r = 1$ . This implies that

$$\tan \delta_\ell = \frac{k\bar{j}'_\ell - \gamma_\ell \bar{j}_\ell}{k\bar{n}'_\ell - \gamma_\ell \bar{n}_\ell}$$

For an atom ( $n\ell$ ) with  $n_r = n - \ell - 1$

$$\delta_\ell(k=0) > n_r\pi \quad n_r = \text{number of nodes of wave function in atom } (E < 0)$$

$$E > 0 \rightarrow \text{nodes} > n_r$$

$\rightarrow$  for Ra,  $n = 7$ ,  $\ell = 0 \rightarrow \delta_\ell > 6\pi$ ; actually  $\approx 9\pi$ .

For small  $ka$  ( $ka \ll 1$ ) we have

$$\bar{j}_\ell \sim \frac{\rho^\ell}{(2\ell+1)!!} \quad , \quad \bar{n}_\ell \sim -\frac{(2\ell+1)!!}{\rho^{\ell+1}}$$

$$\frac{\bar{j}'_\ell}{\bar{j}_\ell} \sim \frac{\ell+1}{\rho} \quad , \quad \frac{\bar{n}'_\ell}{\bar{n}_\ell} \sim -\frac{\ell}{\rho}$$

so that

$$\begin{aligned} \tan \delta_\ell &= \frac{\left(\frac{\ell+1}{ka}k - \gamma_\ell\right) \bar{j}_\ell}{\left(\frac{\ell}{ka}k + \gamma_\ell\right) (-\bar{n}_\ell)} = \left(\frac{\ell+1 - \gamma_\ell a}{\ell + \gamma_\ell a}\right) \frac{\bar{j}_\ell}{-\bar{n}_\ell} \\ &= \frac{(\ell+1 - \gamma_\ell a)}{(\ell + \gamma_\ell a)} \left(\frac{(ka)^{2\ell+2}}{(2\ell-1)!!(2\ell+1)!!}\right) \end{aligned}$$



$\rightarrow \tan \delta_\ell \rightarrow 0$  as  $ka \rightarrow 0$ . Now consider

$$\begin{aligned} \frac{e^{2i\delta_\ell} - 1}{2i} &= e^{i\delta_\ell} \sin \delta_\ell \\ &= \sin \delta_\ell \cos \delta_\ell + i \sin^2 \delta_\ell \\ &= \frac{\tan \delta_\ell}{1 + \tan^2 \delta_\ell} (1 + i \tan \delta_\ell) \\ &= \frac{1}{\cot \delta_\ell - i} \end{aligned}$$

For  $\tan \delta_\ell$  small ( $ka \ll 1$ ) we have

*Im part*  $\ll$  *Re part*

$$\frac{e^{2i\delta_\ell} - 1}{2i} \approx \tan \delta_\ell \rightarrow \text{“f” is real}$$

$A_\ell$  = scattered amplitude of  $\ell$ th partial wave

$$\begin{aligned} &= \frac{2\ell + 1}{k} \tan \delta_\ell \\ &= \frac{\ell + 1 - \gamma_\ell a}{\ell + \gamma_\ell a} a \frac{(ka)^{2\ell+1}}{(2\ell - 1)!!} \end{aligned}$$

For  $\ell = 0$ ,  $A_0 \sim a$  (size of scatterer). Thus  $a_0 \neq 0$  as  $ka \rightarrow 0$ . All other  $A_\ell$  ( $\ell \neq 0$ )  $\rightarrow$  as  $ka \rightarrow 0$ .

For very small  $ka$  this implies that

$$f(\theta) = A_0 \rightarrow \text{independent of } \theta$$

Example: slow neutron scattering by nuclei ( $ka \ll 1$ ) is isotropic! or slow neutron scattering is all s-wave. This is valid up to  $Z = 10$ ; after this resonances change the picture!!

Page 114 Schiff: Angular distribution when  $\ell = 0$  and  $\ell = 1$  contribute.

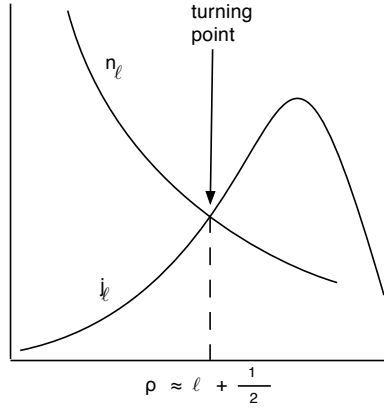
$$\begin{aligned} A_0 &= \frac{1 - \gamma a}{\gamma a} a = \frac{1}{\gamma} - a \\ \sigma_T &= 4\pi A_0^2 = 4\pi a^2 \end{aligned}$$

For larger  $ka$ :

$$\bar{j}_\ell'' + \left(1 - \frac{\ell(\ell+1)}{\rho^2}\right) \bar{j}_\ell = 0$$

We have

$$1 - \frac{\ell(\ell+1)}{\rho^2} = \begin{cases} 0 < & \rho \text{ large} \\ 0 > & \rho \text{ small} \end{cases}$$



$$\bar{j}_\ell'' = 0 \rightarrow \text{turning point} \rightarrow \rho \approx \ell + 1/2$$

$$\bar{j}_\ell(kr) \text{ small if } kr < \ell + 1/2$$

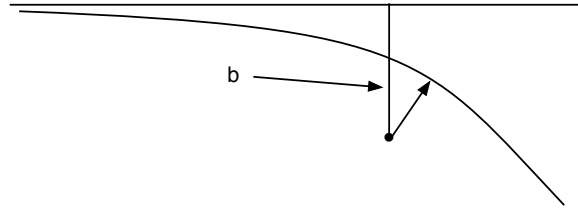
$$\frac{\ell + 1}{\rho} \frac{\bar{j}_\ell'}{\bar{j}_\ell} > 0 \text{ if } kr < \ell + 1/2$$

$$\bar{n}_\ell \text{ large for } kr < \ell + 1/2$$

$$\frac{\bar{n}_\ell'}{\bar{n}_\ell} \text{ is reasonable for } kr < \ell + 1/2$$

$\rightarrow \tan \delta_\ell \sim \bar{j}/\bar{n} \ll 1$  ( $ka < \ell + 1/2$ ) unless denominator or numerator vanish. Therefore  $A_\ell$  is small for  $\ell + 1/2 > ka \rightarrow \sum$  for  $f(\theta)$  converges. This implies that for  $\ell$  large enough  $\sum$  will always converge  $\rightarrow A_\ell$  small *to* for angular momentum  $\ell \rightarrow$  very little contribution to the scattering.

Now, angular momentum =  $pb = \hbar(\ell + 1/2)$ , where  $b$  = impact parameter as shown.



For a scatterer of size  $a \rightarrow$  no scattering for  $b > a$  which implies

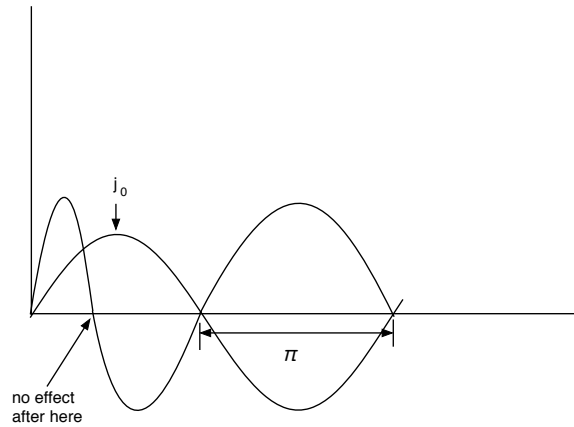
$$b = \frac{\ell + 1/2}{k}$$

If  $b > a$  there is no scattering classically. For  $b \gtrsim a$  no scattering in QM. This is due to fact that one cannot define orbit of particle exactly  $\rightarrow$  uncertainty of a few units in  $\ell$ ! The actual condition is  $\ell + 1/2 > ka + c(ka)^{1/2} \rightarrow$  that QM  $\rightarrow$  CM in the limit of high quantum numbers (i.e., high  $\ell$ ).

Low energy limit of scattering formula - mostly s-wave ( $\ell = 0$ )  $\rightarrow$  isotropic scattering in C.M. system or

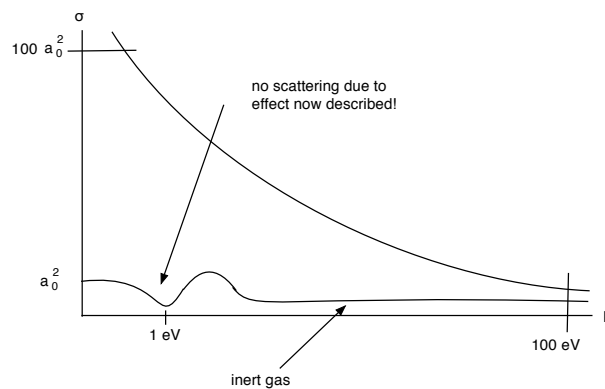
$$\sigma(\theta, \varphi) = \frac{1}{k^2} \sin^2 \delta_0$$

It is possible that  $\frac{\sin \delta_0}{k}$  is small for small  $k$ .



$\rightarrow \delta_0 = \pi \rightarrow$  no s-scattering also (or  $\delta_0 = n\pi$ ) and since there is no  $\ell > 0$  scattering  
 $\rightarrow$  i.e. this happens  $\sigma$  at low  $k$  is very small  $\rightarrow$  Ramsauer Townsend effect!

Scattering of Hg:



Faxen and Holtmark developed the theory!

Why?

For noble gases:

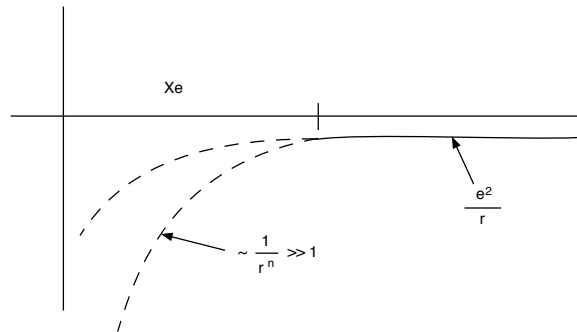
Small size  $\rightarrow (\ell > 0) \delta_e l l$  stays small

$$\frac{\tan \delta_\ell}{k} \sim (ka)^{2\ell} \rightarrow \text{small} \rightarrow \delta_e l l \text{ small}$$

But why is  $\delta_0$  a multiple of  $\pi$ ?

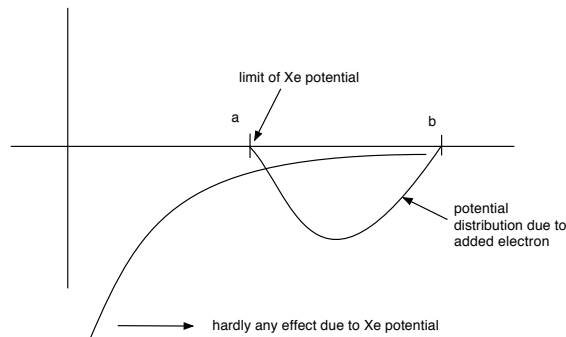
Consider the alkali atoms:

Binding energy  $= E \sim -\frac{Ry}{2^2} \rightarrow$  behavior as a H-atom of quantum number 2 (but for cesium  $n = 6$ ). For cesium



we get a Coulomb potential outside Xe structure, but since  $n = 2$  whereas it should be  $n = 6 \rightarrow 4$  more oscillations in wave function  $\rightarrow$  different potential of cesium wrt Xe in radius of structure.

Scattering outside Xe structure  $= 0$ , but inner potential  $\rightarrow 4$  more oscillations of wave function  $\rightarrow \delta_0 \approx 4\pi$  for Xe at low energy; it is  $\approx 3\pi$  for Kr;  $\approx 2\pi$  for Ar;  $\approx \pi$  for N; and no effect for Helium.



But above is Cs structure with potential now extending to  $b \rightarrow$  large effect to the Cs potential  $\rightarrow$  large scattering for  $\ell > 0$  for small  $k$ !

### Scattering from a Rigid Sphere

Here we have  $U = 0$  at  $r = a$ , which implies that

$$\tan \delta_\ell = \frac{\bar{j}_\ell}{\bar{n}_\ell}$$

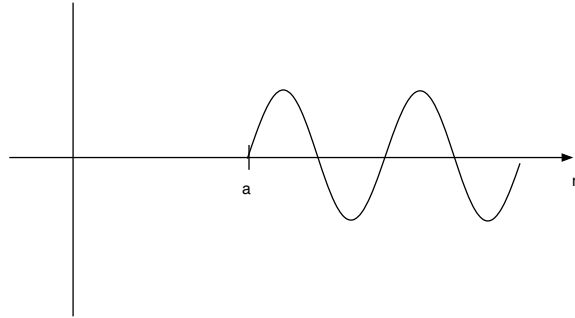
For  $\ell = 0$

$$\begin{aligned} \tan \delta_0 &= \frac{\sin ka}{-\cos ka} = -\tan ka \\ \rightarrow \delta_0 &= -ka \quad \text{no added } \pi \end{aligned}$$

Therefore

$$\chi_0 = \sin k(r - a)$$

This  $\rightarrow$  rigid sphere merely shifts wave function by  $a$  to the right  $\rightarrow$  a negative phase shift!



For  $ka \ll 1$

$$\tan \delta_\ell = -\frac{(ka)^{2\ell+1}}{(2\ell-1)!!(2\ell+1)!!}$$

The  $\ell = 0$  shift is the largest  $\rightarrow$

$$\frac{\sin \delta_0}{k} = -a = f(\theta) \quad ka \ll 1$$

Therefore

$$\sigma = 4\pi a^2 \rightarrow \text{scattering cross section of sphere} = 4 \times \text{target area } (\pi a^2)$$

### High Energy Behavior:

$$\sin^2 \delta_\ell = \frac{\bar{j}_\ell^2}{\bar{n}_\ell^2 + \bar{j}_\ell^2} \quad ka \text{ large}$$

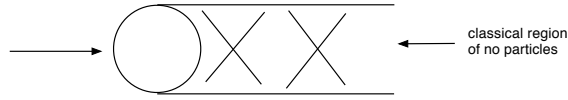
On the average  $j_\ell \sim n_\ell \rightarrow \approx 1/2$  (only if  $\ell < ka$  i.e.,  $j_\ell < n_\ell$  if  $\ell > ka$ ).

$$\sigma_T = \frac{4\pi}{k^2} \sum_{\ell} (2\ell + 1) \sin^2 \delta_{\ell} = \frac{2\pi}{k^2} (ka)^2 = 2\pi a^2$$

$\rightarrow$  all partial waves hitting the sphere give a contribution of  $1/2$  but those having parameter  $> a \rightarrow$  no contribution. But this result is different from the classical result ( $\pi a^2$ ).

### Why Difference?

Diffraction scattering:



scattered amplitude:

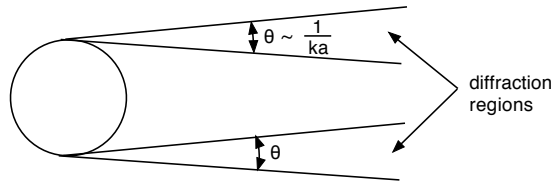
$$f(\theta) = \frac{1}{2ik} \sum_{\ell} (2\ell + 1) (e^{2i\delta_{\ell}} - 1) P_{\ell}(\cos \theta)$$

If we sum only the terms corresponding to the  $(-1)$  term we get the correct result ( $\rightarrow$  shadow); we also get a shadow if we use the exact forms of  $j_{\ell}(kr)$ , i.e.,

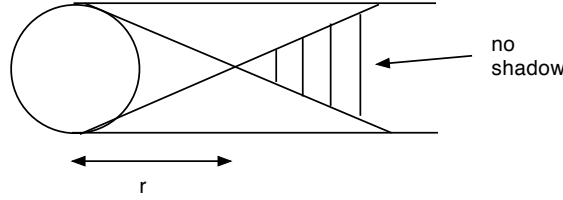
$$|e^{2i\delta_{\ell}}|^2 = |1|^2 \rightarrow \text{cancellation} \rightarrow \text{shadow}$$

The mixed terms  $\rightarrow 0$ .

The shadow is made up of partial waves; at large distance there is no longer a shadow, but we get diffraction



this is due to the uncertainty principle, i.e., we can not describe anything which is geometrically precise!



where

$$r = \frac{a}{\theta} \approx ka^2$$

Up to this distance we get a shadow but now beyond  $\rightarrow$  additional scattering all in angle of order  $1/ka \rightarrow$  correspondence to cross-section  $\sim \pi a^2 \rightarrow \sigma_T = \pi a^2 + \pi a^2$ , where first part is direct normal scattering (as classically) and second part is diffraction scattering.

### Scattering by a Square Well

For  $ka \ll 1$

$$\tan \delta_\ell = \frac{\ell + 1 - \gamma_\ell a}{\ell + \gamma_\ell a} \frac{(ka)^{2\ell+1}}{[(2\ell - 1)!!]^2 (2\ell + 1)}$$

with

$$\gamma = \frac{\bar{j}'_\ell}{\bar{j}_\ell}$$

How?

$\gamma_\ell =$  value of logarithmic derivative inside at  $a$

$$= \frac{1}{\chi_\ell(a)} \left( \frac{d\chi_\ell}{dr} \right)_a$$

For square well on the inside we have

$$\chi_\ell = \bar{j}_\ell(\alpha r) \quad \alpha^2 = \frac{2\mu}{\hbar^2} (E + V_0)$$

where we have assumed that  $V = -V_0$  for  $r < a$ .

For  $ka$  small, all phase shifts are small except if the denominator is near zero.

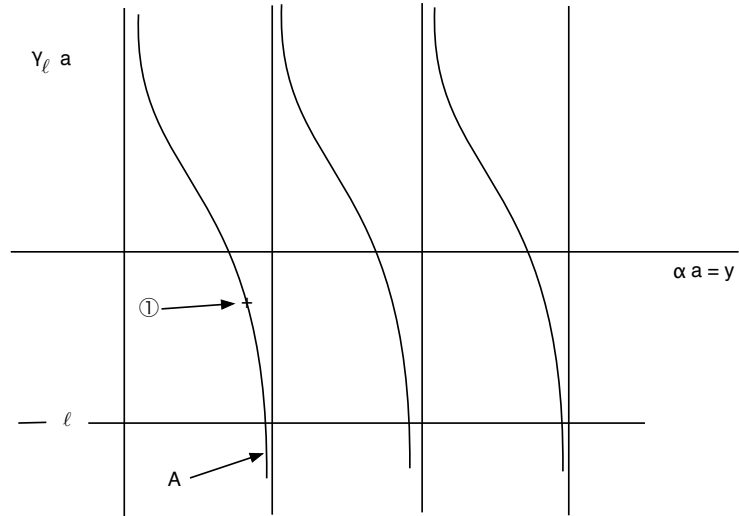
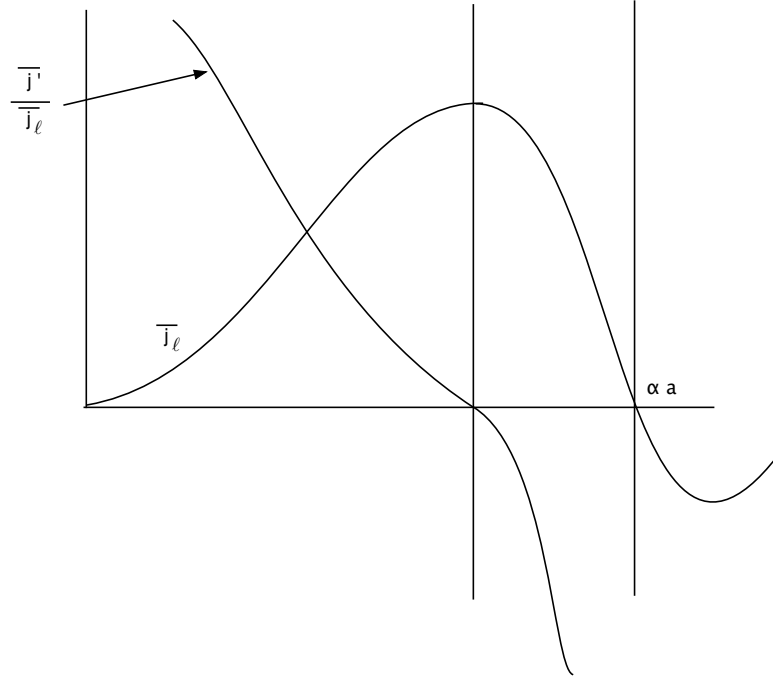
Assume that  $k = 0$ . Then

$$\ell + \gamma_\ell^0 a = \zeta_\ell \ll 1$$

$$\gamma_\ell a \sim f(\alpha a)$$

$$\alpha^2 = \alpha_0^2 + k^2$$

$$\ell + \gamma_\ell a = \zeta_\ell - b_\ell k^2 a^2$$



where curve A is given by

$$\frac{y}{\bar{j}_\ell} \frac{d\bar{j}_\ell}{dy} = \frac{\gamma_\ell}{\alpha} \alpha a = \gamma_\ell a$$

Therefore for certain values of  $\alpha a$ ,  $\gamma_\ell a = -\ell$ , which implies a zero denominator.



Given a  $V_0$  consider point ①. Therefore

$$\begin{aligned}\gamma_\ell^0 a + \ell > 0 &\rightarrow \zeta_\ell \\ \rightarrow \ell + \gamma_\ell a &= \zeta_\ell - b_\ell k^2 a^2\end{aligned}$$

For a square well  $b = 1/2$ . At some  $k = k_1$ , the denominator = 0

$$\rightarrow \tan \delta_\ell \rightarrow \infty \rightarrow \delta_\ell = (n + 1/2)\pi$$

This is a resonance.

$$\sigma_\ell \rightarrow 4\pi \frac{\sin^2 \delta_\ell}{k^2} (2\ell + 1) \rightarrow \max \text{ for a given } \ell = \frac{4\pi}{k^2} (2\ell + 1)$$

In the neighborhood of the resonance

$$\frac{\sin^2 \delta_\ell}{k^2} = \frac{1}{k^2} \frac{\tan^2 \delta_\ell}{1 + \tan^2 \delta_\ell}$$

Letting  $x = ka$

$$\tan \delta_\ell \approx \frac{2\ell + 1}{\zeta_\ell - b_\ell x^2} \frac{x^{2\ell+1}}{[(2\ell - 1)!!]^2 (2\ell + 1)}$$

Therefore

$$\frac{\sin^2 \delta_\ell}{k^2} = \frac{a^2 x^{4\ell}}{x^{4\ell+2} + [(2\ell - 1)!!]^4 (\zeta_\ell - b_\ell x^2)^2}$$

For  $\ell = 0$

$$\frac{\sin^2 \delta_\ell}{k^2} = \frac{a^2}{x^2 + (\zeta_0 - b_0 x^2)^2}$$

Now  $\zeta_0$  is small,  $b = 1/2$  which gives

$$(\zeta_0 - b_0 x^2)^2 = \zeta_0^2 - 2b_0 \zeta_0 x^2 + b_0^2 x^4 \approx \zeta_0^2$$

where we have neglected small terms, i.e., for  $x, \zeta_0$  small  $\rightarrow$  resonance  $\rightarrow$  can neglect! Therefore

$$\begin{aligned}\sigma_0 &= \frac{4\pi a^2}{x^2 + \zeta_0^2} \\ \zeta_0 &= \gamma_{\ell=0}^{E=0} a = \gamma_0^0 a\end{aligned}$$

Therefore

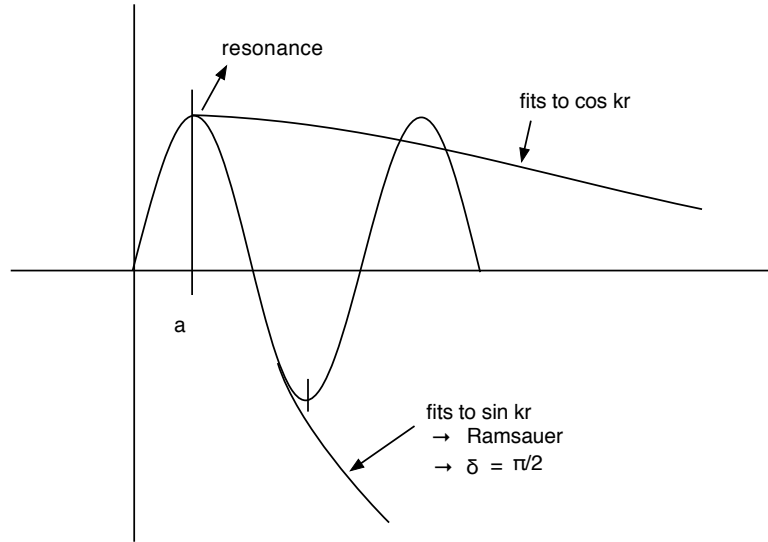
$$\sigma = \frac{4\pi}{k^2 + (\gamma_0^0)^2}$$

This implies that  $\gamma$  either + or - before 1/4-wave  $\rightarrow V$  strong enough to give 1 bound state; after 1/4-wave not strong enough!

### N-P Scattering at Low Energy

$$\gamma_0 = \frac{\bar{j}_0'}{j_0} = \frac{\alpha \cos \alpha a}{\sin \alpha a} = \alpha \cot \alpha a$$

The  $\sigma$  formula is value for small  $\gamma_0^0$  or  $\alpha a \approx (n + 1/2)\pi \rightarrow$  high resonance for potential in which we can put  $n(1/4)$ -wave cycles of wave function as opposed to the Ramsauer effect which requires 1/2 wave length  $\rightarrow$  a pronounced non-resonance.



For the neutron-proton system:

$$\left. \begin{array}{l} {}^1S \text{ state } \gamma_0 > 0 \\ {}^3S \text{ state } \gamma_0 < 0 \end{array} \right\} \text{ bound states}$$

$$\rightarrow \sigma = \frac{A}{E + \text{constant}}$$

**Resonances**

$$\tan \delta_\ell = \frac{\ell + 1 - \gamma_\ell a}{\ell + \gamma_\ell a} \frac{(ka)^{2\ell+1}}{[(2\ell - 1)!!]^2 (2\ell + 1)}$$

$$\gamma a = -\ell + \zeta_\ell - b_\ell (ka)^2$$

For  $x = ka$

$$\tan \delta_\ell = \frac{x^{2\ell+1}}{[(2\ell - 1)!!]^2} \frac{1}{\zeta_\ell - b_\ell x^2}$$

For  $\ell = 0$

$$\sigma = \frac{4\pi}{k^2 + \gamma_0^2} \quad \gamma_0 = \frac{\bar{j}'_0}{\bar{j}_0}$$

Small  $\gamma_0$  at small  $k \rightarrow$  large  $\sigma$ .

$$\gamma_0 \sim \alpha_0 \cot \alpha_0 a \quad \alpha_0 \sim \frac{2mV_0}{\hbar^2}$$

Resonance  $\rightarrow$  bound state for  $E \approx 0$ . For  $\ell \neq 0$   $x = ka$

$$\cot \delta_\ell = \frac{\frac{\zeta_\ell}{b_\ell} - x^2}{\gamma_\ell}$$

where

$$\gamma_\ell = \frac{x^{2\ell+1}}{[(2\ell-1)!!]^2 b_\ell}$$

Therefore

$$\cot \delta_\ell = \frac{x_0^2 - x^2}{\gamma_\ell}$$

$$\sin^2 \delta_\ell = \frac{1}{1 + \cot^2 \delta_\ell}$$

Therefore

$$\frac{\sin^2 \delta_\ell}{k^2} = \frac{1}{k^2} \frac{\gamma_\ell^2}{(x_0^2 - x^2) + \gamma_0^2}$$

$$4\pi(2\ell+1) \frac{\sin^2 \delta_\ell}{k^2} = \sigma_\ell = \text{scattering cross section for the } \ell\text{th partial wave}$$

$$(\sigma_\ell)_{max} = \frac{4\pi(2\ell+1)}{k^2} \quad x^2 = x_0^2$$

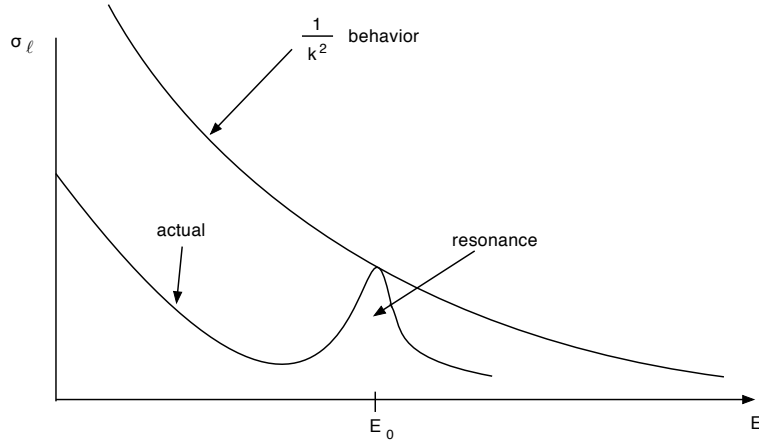
For amplitude  $A_\ell$

$$kA_\ell = \frac{1}{\cot \delta_\ell - i} = \frac{\gamma_\ell}{x^2 - x_0^2 - i\gamma_\ell}$$

For  $x^2 = (ka)^2 \sim E$

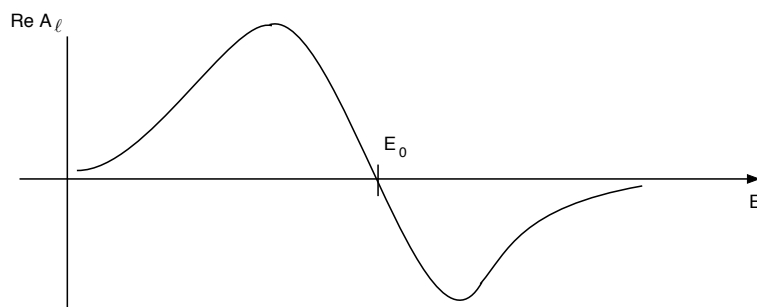
$$kA_\ell = \frac{-\frac{1}{2}\Gamma_\ell}{E - E_0 + \frac{i}{2}\Gamma_\ell}$$

$$\sigma_\ell \sim |A_\ell|^2 \approx \frac{1}{k^2} \frac{\frac{1}{4}\Gamma_\ell^2}{(E - E_0)^2 + \frac{1}{4}\Gamma_\ell^2}$$

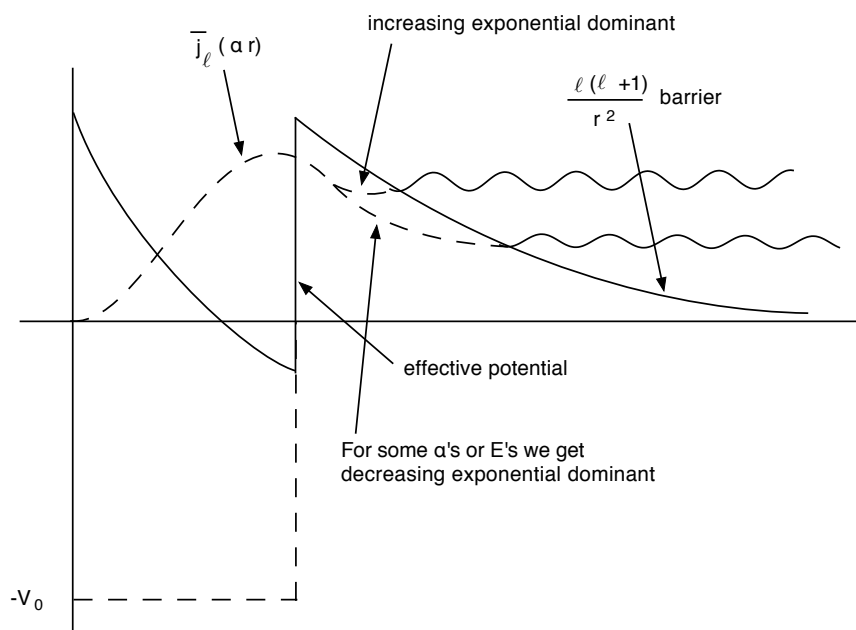


where we have for the resonance

$$|E - E_0| \lesssim \frac{\Gamma_\ell}{2} \rightarrow \text{measure of width} \quad \Gamma_\ell = \frac{1}{2} \text{ width}$$



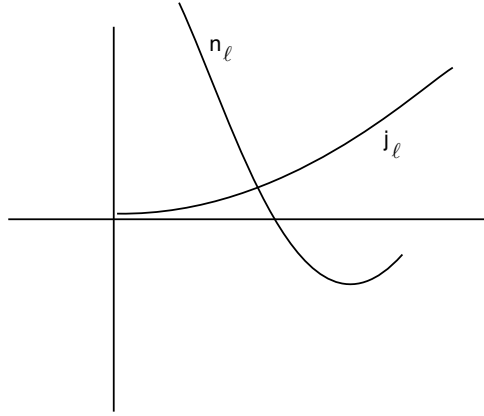
At resonance  $\text{Re } A_\ell$  changes sign. At resonance  $\text{Im } A_\ell = 1$



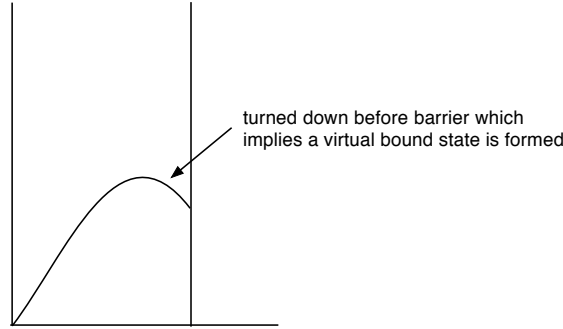
Inside barrier  $\rightarrow$  solution

$$j_\ell(ka) - \tan \delta_\ell n_\ell(ka)$$

For small  $ka$



At special energies  $\rightarrow$  tie onto  $n_\ell \rightarrow$  decreasing exponential coefficient  $n_\ell \gg$  coefficient  $j_\ell$  or  $\tan \delta_\ell \sim \infty$ . For this case particle comes into the well and at these particular energies we have the situation similar to  $\ell = 0$  behavior, i.e.,



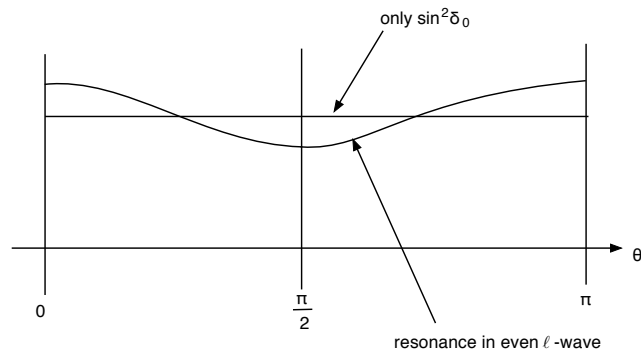
S-wave scattering always exists! If resonance for some  $\ell$  we should expect to see resonance superimposed on the general s-wave cross-section.

At low energy  $E <$  for no p-wave contributions

$$kf(\theta) = e^{i\delta_0} \sin \delta_0 + (2\ell + 1)e^{i\delta_\ell} \sin \delta_\ell P_\ell(\cos \theta)$$

$$\sigma(\theta) = \frac{1}{k^2} \left( \sin^2 \delta_0 + 2(2\ell + 1) \sin \delta_0 \sin \delta_\ell \cos(\delta_\ell - \delta_0) P_\ell + (2\ell + 1)^2 \sin^2 \delta_\ell P_\ell^2 \right)$$

For just s-wave



$\sigma \rightarrow \ell$  odd or even  $\rightarrow$  form of  $P_\ell$ s.

1st term  $\rightarrow \sin^2 \delta_0$ ; we can determine the sign of  $\delta_0$  by considering behavior on both side of the resonance!

### Scattering in a Coulomb Field

$$V(r) < \frac{C}{r^{2+\varepsilon}} \quad \text{as } r \rightarrow \infty$$

$$V(r) = \frac{ZZ'e^2}{r}$$

A measure of the Coulomb force is given by

$$n = \frac{\mu ZZ'e^2}{\hbar^2 k^2} = \frac{ZZ'e^2}{\hbar v} \sim \frac{\text{Coulomb force}}{E}$$

$$\left. \begin{array}{l} \text{large } n \rightarrow \text{large } F \\ \text{small } n \rightarrow \text{small } F \end{array} \right\} \text{ given } E$$

It turns out that

$$u \approx e^{\pm i(kr - n \log r)}$$

at large  $r$  due to the fact that the force is a long range force  $\rightarrow$  phase changes (small) even at large  $r$ !

**Parabolic Coordinates** We choose parabolic coordinates

$$\xi = r - z, \quad \eta = r + z, \quad \varphi = \text{varphi}$$

$\rightarrow$  Coulomb problem is separable, i.e.,

$$\psi = f(\xi)g(\eta)\Phi(\varphi)$$

$$z = \frac{1}{2}(\eta - \xi)$$

$$u_c = e^{ikz} f \rightarrow \text{at large } \sim \frac{e^{ikr}}{r}$$

to get this

$$f = \frac{eik(r-z)}{r-z} \text{ or } f = f(\xi)$$

Substituting and separating gives

$$\xi \frac{d^2 f}{d\xi^2} + (1 - ik\xi) \frac{df}{d\xi} - nkf = 0$$

Assuming  $f = \text{power series} \rightarrow$

$$f = CF(-in, 1, ik\xi) \rightarrow \text{hypergeometric function}$$

We want to write down two solutions which are given as series in  $\left(\frac{1}{\xi}\right)$

$$F = W_1 + W_2$$

$$W_1(\xi) = \frac{1}{\Gamma(1+in)} (-ik\xi)^{in} g(-in, -in, -ik\xi)$$

$$W_2(\xi) = \frac{1}{\Gamma(-in)} e^{ik\xi} (ik\xi)^{-1-in} g(1+in, 1+in, ik\xi)$$

$$g(a, b, x) = 1 + \frac{ab}{1!} \frac{1}{x} + \frac{q(q+1) \cdot b(b+1)}{2!} \frac{1}{x^2} + \dots$$

$$(-i)^{in} = e^{n\pi/2}$$

$$W_1(\xi) = \frac{1}{\Gamma(1+in)} e^{n\pi/2} e^{in \log(k\xi)} (1 + \dots)$$

$$W_2(\xi) = \frac{1}{\Gamma(-in)} \frac{1}{ik\xi} e^{n\pi/2} e^{-in \log(k\xi)} (1 + \dots)$$

$$u = e^{ikz} f = e^{ikz} CF = C e^{ikz} (W_1 + W_2)$$

$$\xi = r - z$$

$$\log k(r-z) = \log \left( \underbrace{\frac{k(r-z)}{2kr}}_{\sin^2 \frac{\theta}{2}} \right) + \log 2kr$$

$$u = \frac{C e^{n\pi/2}}{\Gamma(1+in)} \left[ e^{i(kz+n \log k(r-z))} \left( 1 + O\left(\frac{1}{r}\right) \right) \right. \\ \left. + \frac{\Gamma(1+in)}{\Gamma(-in)} \frac{1}{ik} \overbrace{\frac{r-z}{r}}^{f_c(\theta)} e^{-in \log \sin^2 \frac{\theta}{2}} e^{i(kr-n \log 2kr)} \left( 1 + O\left(\frac{1}{r}\right) \right) \right]$$

At large  $r$  incoming plane wave is distorted to

$$e^{i(kz+n \log k(r-z))}$$

and scattered wave is distorted to

$$A \frac{e^{i(kr-n \log 2kr)}}{r}$$

where  $A = f_c(\theta) \rightarrow$  Coulomb scattering amplitude.

$$\sigma_c(\theta) = |f_c(\theta)|^2$$

where

$$f_c = \frac{-in}{i} \frac{\Gamma(1+in)}{\Gamma(1-in)} \frac{e^{in \log \sin^2 \frac{\theta}{2}}}{2k \sin^2 \frac{\theta}{2}}$$

and we have used

$$\Gamma(x+1) = x\Gamma(x) \rightarrow \Gamma(1-in) = -in\Gamma(-in)$$

Now

$$\frac{\Gamma(1+in)}{\Gamma(1-in)} = \frac{f(z)}{f(z^*)} = \frac{|f(z)|e^{in_0}}{|f(z)|e^{-in_0}} = e^{2in_0}$$

Therefore

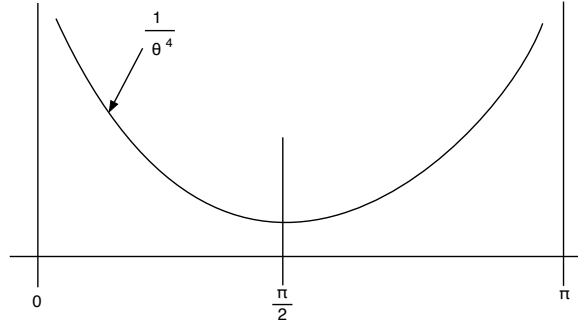
$$f_c(\theta) = ne^{2in_0} \frac{e^{-in \log \sin^2 \frac{\theta}{2} + i\pi}}{2k \sin^2 \frac{\theta}{2}}$$

$$\sigma(\theta) = \frac{n^2}{4k^2 \sin^4 \frac{\theta}{2}} \quad n = \frac{ZZ'e^2}{kv}$$

Therefore

$$\sigma(\theta) = \left( \frac{ZZ'e^2}{2\hbar kv \sin^2 \frac{\theta}{2}} \right)^2$$

If  $p$  and  $v$  are calculated relativistically  $\rightarrow \sigma$  holds.





Returning to the phase factor.

The classical limit:

$$\lambda = \frac{1}{k}$$

is the length associated with incoming particle - it is a measure of the wave nature of the particle.

$$d = \text{measure of the range of the force} = \left| \frac{ZZ'e^2}{\frac{1}{2}\mu v^2} \right|$$

→ wave properties are important when  $d < \lambda$  and we use classical treatment when  $d \gg \lambda$  or

$$\frac{ZZ'e^2}{\hbar v} \gg 1 \text{ or } n \gg 1$$

The shift  $(\lambda d)^{1/2} = \text{spread of wave packet} \ll d \rightarrow \text{same result.}$

For unit incident flux

$$C = \frac{1}{\sqrt{v}} \Gamma(1 + in) e^{-n\pi/2}$$

For small distances

$$u_c \sim CF \sim C$$

Therefore

$$\begin{aligned} |u_c(0)|^2 &= |C|^2 = \frac{1}{v} |\Gamma(1 + in)|^2 e^{-n\pi} \\ &= \text{probability of finding particle at the origin when we originally sent them in at unit flux} \end{aligned}$$

Now

$$\Gamma(x)\Gamma(1-x) = \frac{\pi}{\sin \pi x}$$

$$\begin{aligned} |u_c(0)|^2 &= \frac{1}{v} in \Gamma(in) \Gamma(1 - in) e^{-n\pi} \\ &= \frac{1}{v} \frac{in\pi e^{-n\pi}}{\frac{e^{n\pi} - e^{-n\pi}}{2i}} = \frac{1}{v} \frac{2n\pi}{e^{n\pi} - 1} \end{aligned}$$

The probability of finding particle at the origin → probability of particles interacting. For  $n < 0$ , large

$$|u_c(0)|^2 \sim \frac{2|n|\pi}{v} \quad \text{attractive}$$

For  $n > 0$ , large

$$|u_c(0)|^2 \sim \underbrace{\frac{2n\pi}{v} e^{-2n\pi}}_{\text{small!}} \quad \text{repulsive}$$

## Matrix Mechanics

$$\text{Spur } A = \text{Trace } A = \text{Tr } A = \text{Tr}(A) = \sum_k A_{kk}$$

$$\text{determinant } A = \det A = \det(A) = |A|$$

For a non-zero determinant

$$\left. \begin{array}{l} A^{-1}A = I \\ AA^{-1} = I \end{array} \right\} \det(A) \neq 0$$

We also have  $(AB)^{-1} = B^{-1}A^{-1}$ .

The Hermitian adjoint is equivalent to:

$$A^\dagger = A^* = \bar{A}^T$$

$$(AB)^* = B^*A^*$$

$$A^* = A \rightarrow A \text{ is hermitian}$$

$$A^* = A^{-1} \rightarrow A \text{ is unitary}$$

Transformation of matrices:

$$A' = SAS^{-1} \quad (S \text{ is non-singular})$$

Thus, for an equation of the form  $AB + CDE = F$  the form of the equation is not changed under a transformation of this kind!

Diagonals; eigenvalues:

We want  $A'$  = diagonal matrix. Rearrange the equation  $SA = A'S$  and look at the  $(k, l)$  element

$$\sum_m S_{km} \underbrace{A_{ml}}_{\text{given}} = \sum_m A'_{km} S_{ml} = A'_{kk} S_{kl}$$

where we have used the fact that  $A'$  is diagonal. Given  $k$ , we have  $N$  equations for  $l = 1, \dots, N$ .  $\rightarrow N$  linear equations,  $N$  unknowns  $S_{kl}$  (they are homogeneous equation).

These are soluble only if

$$|A_{ml} - \delta_{ml} A'_{kk}| = 0$$

$\rightarrow n$ th order algebraic equation for  $A'_{kk}$

$\rightarrow n$  roots  $\rightarrow n$  possible values of  $A'_{kk}$ ,  $\rightarrow$  eigenvalues and  $S_{km} \rightarrow$  eigenvectors.

Infinite rank (in Schiff)

$$H = \frac{p^2}{2m} + V \quad Hu_k = E_k u_k$$

$\sum_k$  = summation over discrete states + integration over continuous states

$v_n$  = a set of orthonormal functions (not necessarily eigenfunctions)

$$v_n(r) = \sum_k S_{kn} u_k(r) \quad (22)$$

$$S_{kn} = \int u_k^* v_n d\tau$$

$S_{kn}$  = unitary matrix

Consider harmonic oscillator - energy levels are discrete  $\rightarrow k$  discrete  $\rightarrow$  discrete labeling of rows!

$p$  continuous  $\rightarrow v_n = p$  eigenfunction  $\rightarrow n$  continuous!

$$u_k = \sum_n S_{kn}^* v_n$$

$$A_{nk} = S_{kn}^* = \text{expansion coefficient from (22)}$$

i.e.,

$$A_{nk} = \int v_n^* u_k d\tau = S_{kn}^* \text{ from definition of } S_{kn} !$$

$$\begin{aligned} (SS^*)_{kl} &= \sum_n S_{kn} \underbrace{S_{ln}^*}_{\bar{S}_{nl}} \\ &= \sum_n \int u_k^*(r) v_n(r) d\tau \int u_l(r') v_n^*(r') d\tau' \\ &= \int u_k^*(r) \delta(\vec{r} - \vec{r}') u_l(r') d\tau d\tau' \\ &= \int u_k^* u_l(r) d\tau \\ &= \underbrace{\delta_{kl}}_{\text{discrete}} \quad \text{or} \quad \underbrace{\delta(k-l)}_{\text{(continuous)}} \end{aligned}$$

Also  $(S^* S)_{mn} = \delta_{mn}$ .

### Dirac Notation

$$\begin{aligned} S_{kn} &= \langle k | n \rangle = \int u_k^* v_n d\tau \\ \underbrace{|n\rangle}_{\text{(ket)}} &= v_n \quad , \quad \underbrace{\langle k|}_{\text{(bra)}} = u_k^* \end{aligned}$$

Equation (22) becomes

$$|n\rangle = \sum_k \langle k | n \rangle |k\rangle$$

Note that  $S_{kn}$  = transformation matrix.

Representation:  $k \rightarrow$  energy representation or  $n$  representation!

### Hamiltonian Matrix

$$H_{nm} = \int v_n^* H v_m d\tau = \langle n | H | m \rangle$$

### Connection with expectation values:

$$\psi = \sum_n c_n v_n$$

$$\int \psi^* H \psi d\tau = \langle H \rangle$$

$$\begin{aligned} \langle A \rangle &= \int \psi^* A \psi d\tau \\ &= \sum_m \sum_n c_m^* c_n \int v_m^* A v_n d\tau \\ &= \sum_m \sum_n c_m^* c_n \langle m | A | n \rangle \end{aligned}$$

Therefore, Dirac's system  $\rightarrow \langle A \rangle$  from arbitrary  $\psi$  over arbitrary  $v_n$  (have to be orthonormal), i.e.,

$$\int u_k^* A v_n d\tau = \langle k | A | n \rangle$$

$$\begin{aligned} \langle k | S H S^* | l \rangle &= \sum_m \sum_n \langle k | S | n \rangle \langle n | H | m \rangle \langle m | S^* | l \rangle \\ &= \sum_{m,n} S_{kn} H_{nm} S_{ml}^* = \sum_{m,n} \langle k | n \rangle \langle n | H | m \rangle \langle m | l \rangle \\ &= \sum_{m,n} \int u_k^*(r) v_n(r) d\tau \int v_n^*(r') H' v_m(r') d\tau' \int v_m^*(r'') u_l(r'') d\tau'' \end{aligned}$$

where  $H'$  operates only on  $r'$ . Closure for the sum over  $m \rightarrow \delta(r' - r'')$ . Carrying out the integral over  $r'' \rightarrow u_l(r')$  etc, i.e.,

$$n \text{ sum } \sum_n v_n(r) v_n^*(r') = \delta(r - r') \text{ and } \int \rightarrow u_k^*(r')$$

$$m \text{ sum } \sum_m v_m(r') v_m^*(r'') = \delta(r' - r'') \text{ and } \int \rightarrow u_l(r')$$

Thus we end up with

$$\langle k | S H S^* | l \rangle = \int u_k^*(r') H' u_l(r') d\tau' = \int u_k^*(r') E_l u_l(r') d\tau' = E_l \delta_{kl}$$

(for continuous case the last term would have  $\delta(k - l)$  instead. Thus we get the diagonal elements.

$H_{mn}$  = matrix of Hamiltonian in  $n$  representation (not diagonal).  $SHS^*$  = diagonal matrix  $\rightarrow E_l$  = eigenvalues. Unitary transformation  $S$  transforms  $H_{mn}$  into a diagonal matrix; diagonal elements are the eigenvalues of the Hamiltonian. Diagonalization  $\rightarrow$  find  $E_k$  and eigenvectors  $\rightarrow$  transformation matrix  $\rightarrow$  eigenfunctions. The  $E_k$ s are real;  $H_{mn}$  is hermitian  $\rightarrow$  energy always represented by a hermitian matrix; this is true for any dynamical variable  $A$ .

### Unitary Transformation

$$S_{kn} = \int u_k^* v_n d\tau = \langle k | n \rangle$$

transforms from  $n$  representation to the energy representation.

### Hermitian Matrices

$$H_{mn} = \int v_m^* H v_n d\tau = \langle m | H | n \rangle$$

$$\sum_{m,n} \langle k | n \rangle \langle n | H | m \rangle \langle m | l \rangle = \langle k | H | l \rangle = E_k \delta_{kl}$$

or  $= E_k \delta(k-l)$  if the  $E_k$  are continuous.

$$\int v_m^*(r) v_n(r) d\tau = \delta_{mn}$$

$$\sum_n v_n^*(r) v_n(r') = \delta(r-r')$$

$v_n(\vec{r}) = \langle \vec{r} | n \rangle \rightarrow$  matrix which transforms from  $n \rightarrow r$  representation

$$v^*(\vec{r}) = \langle n | \vec{r} \rangle$$

$$H_{mn} \rightarrow H \delta(r-r')$$

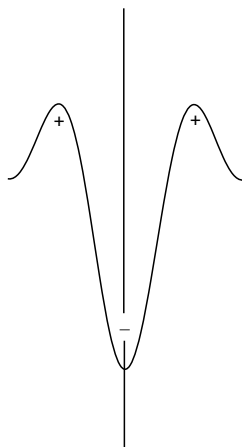
i.e.,

$$\begin{aligned} \int v_n^*(r) H v_n(r') d\tau' &= \sum_n \langle r | n \rangle H \langle n | r' \rangle \\ &= \langle r | H | r' \rangle = H_{rr'} = H \delta(r-r') \end{aligned}$$

The expressions above contain terms like

$$\frac{\partial^2}{\partial x^2} \delta(x-x')$$

Consider a delta-function as the limit of a gaussian. Then the 2nd derivative  $\rightarrow$

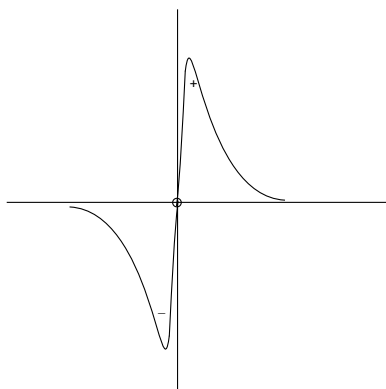


which  $\rightarrow$  a non-diagonal matrix, i.e.,

$$\begin{pmatrix} - & + & & & & \\ + & - & + & & & \\ & + & - & + & & \\ & & + & - & + & \\ & & & + & - & + \\ & & & & \ddots & \ddots & \ddots \end{pmatrix}$$

The momentum operator in the  $r$ -representation

$$p\delta(x-x') = -i\hbar \frac{d}{dx} \delta(x-x') \rightarrow$$



which  $\rightarrow$  the matrix

$$\begin{pmatrix} 0 & + & & & \\ - & 0 & + & & \\ & - & 0 & + & \\ & & - & 0 & + \\ & & & - & 0 & + \\ & & & & \ddots & \ddots & \ddots \end{pmatrix}$$

**Definition:**  $\Omega f(\vec{r}) = \int \Omega(\vec{r}, \vec{r}') f(\vec{r}') d\tau'$

**Theorem:**

$$\int \overline{g(\vec{r})} (\Omega f(\vec{r})) d\tau = \int (\Omega^* \overline{g(\vec{r})}) f(\vec{r}) d\tau$$

If  $\Omega$  is hermitian, then  $\Omega^* = \Omega$ . An example is

$$\Omega = V(\vec{r}) \delta(\vec{r} - \vec{r}')$$

Typical matrix element:

$$\int \phi^* F \psi d\tau \quad \phi, \psi \text{ any functions}$$

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad \text{is solved by both } \phi \text{ and } \psi$$

This does not  $\rightarrow$  they are eigenfunctions of  $E$  operator! Limits on  $\phi, \psi$  are that they are linear combinations of the energy eigenfunctions

$$\sum_k c_k u_k e^{-iE_k t/\hbar}$$

$$\begin{aligned} \frac{d}{dt} \int \phi^* F \psi d\tau &= \int \phi^* \frac{\partial F}{\partial t} \psi d\tau \\ &+ \frac{i}{\hbar} \int \phi^* F H \psi d\tau \\ &- \frac{i}{\hbar} \int (H^* \phi^*) F \psi d\tau \\ &\quad \underbrace{\phantom{\int \phi^* F H \psi d\tau}}_{\frac{i}{\hbar} \int \phi^* H F \psi d\tau} \\ &= \int \phi^* \left[ \frac{\partial F}{\partial t} + \frac{i}{\hbar} (F H - H F) \right] \psi d\tau \end{aligned}$$

Therefore

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \frac{i}{\hbar} \underbrace{[F, H]}_{\text{commutator}}$$

This is a matrix element equation. These equations plus commutator rules  $\rightarrow$  all of Q.M. !!

$$[x, p_x]f = x \left( -i\hbar \frac{\partial}{\partial x} \right) f - \left( -i\hbar \frac{\partial}{\partial x} \right) x f = i\hbar f$$

for any  $f$ . This implies the commutator equations

$$[x, p_x] = i\hbar \quad , \quad [x, y] = xy - yx = 0 \quad , \quad [p_x, p_y] = 0$$

$$\begin{aligned} [x^2, p_x] &= x^2 p_x - p_x x^2 \\ &= x(x p_x - p_x x) + (x p_x - p_x x) \\ &= 2i\hbar x \end{aligned}$$

$$\begin{aligned} \rightarrow [x^n, p_x] &= i\hbar n x^{n-1} \\ \rightarrow [x, p_x^n] &= i\hbar n p_x^{n-1} \end{aligned}$$

If  $f(x)$  is expandable in a power series, then

$$\rightarrow [f(x), p_x] = i\hbar \frac{df}{dx}$$

What about functions (non-power series)?

$$-i\hbar f(x) \frac{\partial}{\partial x} \psi + i\hbar \frac{\partial}{\partial x} (f\psi) = i\hbar \frac{\partial f}{\partial x} \psi$$

for any  $f$ .

$$H = \frac{p^2}{2m} + V(r)$$

$$\begin{aligned} \frac{dx}{dt} &= [x, H] \quad , \quad [x, V] = 0 \\ &= \frac{1}{2i\hbar m} [x, p^2] = \frac{1}{2i\hbar m} [x, p_x^2] \quad , \quad [x, p_y] = [x, p_z] = 0 \\ &= \frac{i\hbar}{2i\hbar m} p_x = \frac{p_x}{m} \end{aligned}$$

In matrix notation

$$\left( \frac{dx}{dt} \right)_{mn} = \frac{dx_{mn}}{dt}$$

$$\text{matrix element } (p_x)_{mn} = m \left( \frac{dx}{dt} \right)_{mn} = m \frac{dx_{mn}}{dt} \quad \text{Ehrenfest I}$$

$$\begin{aligned} \frac{dp_x}{dt} &= \frac{1}{i\hbar} [p_x, H] \quad , \quad [p_x, p^2] = 0 \\ &= \frac{-i\hbar}{i\hbar} \frac{\partial V}{\partial x} = -\frac{\partial V}{\partial x} \quad \text{Ehrenfest II} \end{aligned}$$

$$\psi = \sum_n c_n v_n \quad v_n = \text{eigenfunction of the operator } A$$

$$\phi = \sum_n b_n v_n$$



$$\langle A \rangle = \sum_n \underbrace{b_n^* A_n c_n}_{\text{unitary transformation}}$$

where the  $A_n$  are the eigenvalues.

Consider the energy representation  $\rightarrow H$  is diagonal!

$$\text{eigenfunctions of energy} = u_n e^{-iE_n t/\hbar}$$

The matrix element of the operator  $F$ :

$$\begin{aligned} F_{nm} &= \int \psi_n^* F \psi_m d\tau \quad F \neq F(t) \text{ explicitly} \\ &= \left( \int u_n^* F u_m d\tau \right) e^{-i(E_m - E_n)t/\hbar} \\ &= F_{nm}^0 e^{-i\omega_{mn}t} \end{aligned}$$

$$\frac{dF_{nm}}{dt} = -i \frac{E_m - E_n}{\hbar} F_{nm}$$

Therefore

$$\frac{(p_x)_{nm}}{m} = \left( \frac{dx}{dt} \right)_{mn} = \frac{E_m - E_n}{i\hbar} x_{nm}$$

Therefore knowledge of  $x$  matrix in  $E$  representation  $\rightarrow p$  matrix.

$$\left. \begin{array}{l} \text{The matrix of } x \text{ is calculated by } x_{nm} = \int u_n^* x u_m d\tau \\ \text{The matrix of } p \text{ is calculated by } p_{nm} = -i\hbar \int u_n^* \frac{\partial u_m}{\partial x} d\tau \end{array} \right\} \text{Both} \rightarrow \text{the same result, but one easier to calculate!}$$

$$\left( -\frac{\partial V}{\partial x} \right)_{nm} = \frac{E_m - E_n}{i\hbar} (p_x)_{nm} = - \left( \frac{E_m - E_n}{\hbar} \right)^2 x_{nm}$$

Thus,  $(p_x)_{nm} \rightarrow$  the force matrix, i.e.,

$$x_{nm} = x_{nm}^0 e^{-i\omega_{mn}t} \rightarrow \frac{dx_{nm}}{dt} = -i\omega_{mn} x_{nm}$$

so that

$$\left( -\frac{\partial V}{\partial x} \right)_{nm} = \left( \frac{dp}{dt} \right)_{nm} = \frac{d}{dt} \left( \frac{dx}{dt} \right)_{nm} = -\omega_{mn}^2 x_{nm}$$

**Sum Rules**

$$\sum_n |x_{nm}|^2 = \sum_n x_{mn} x_{nm} = (x^2)_{nn} = \text{a matrix element}$$

$$\begin{aligned}
\sum_n |x_{nm}|^2 (E_n - E_m) &= \frac{-i\hbar}{m} \sum_n x_{mn} (p_x)_{nm} \\
&= \frac{i\hbar}{m} \sum_n (p_x)_{mn} x_{nm} \quad \text{also} \\
&= \frac{i\hbar}{2m} \sum_n \underbrace{[(p_x)_{mn} x_{nm} - x_{mn} (p_x)_{nm}]}_{\text{a matrix element}} \\
&= \frac{i\hbar}{2m} (p_x x - x p_x)_{mn} = \frac{i\hbar}{2m} i\hbar = \frac{\hbar^2}{2m} \quad (\text{oscillator sum rule})
\end{aligned}$$

→ average energy due to the optical transition where  $|x_{nm}|^2$  = weighting factor!

$$\begin{aligned}
\sum_{n,m} |x_{nm}|^2 (E_n - E_m)^2 &= \frac{\hbar^2}{m^2} \sum_n (p_x)_{mn} (p_x)_{nm} \\
&= \frac{\hbar^2}{m^2} (p_x)_{mn}^2 = \text{average } (E_n - E_m)^2 \\
&= \frac{\hbar^2}{m} \sum_n x_{mn} \left( \frac{\partial V}{\partial x} \right)_{nm} = \frac{\hbar^2}{m} \left( x \frac{\partial V}{\partial x} \right)_{mn}
\end{aligned}$$

This holds for any diagonal element → for any  $V$  → virial theorem. Considering  $y$  and  $z$  also we have

$$\left( \frac{p^2}{m} \right)_{nm} = 2(E_K)_{mn} = (\vec{r} \cdot \nabla V)_{mn}$$

→ time averages in C.M. ↔ diagonal elements in energy representation.

$$V \sim r^n \rightarrow \vec{r} \cdot \nabla V = nV \rightarrow 2(E_K)_{mn} = nV_{mm}$$

$$\begin{aligned}
\frac{dF}{dt} &= \frac{\partial F}{\partial t} + \frac{1}{i\hbar} [F, H] \\
&= \frac{dF_{mn}}{dt}, \frac{\partial F_{mn}}{\partial t}
\end{aligned}$$

$$(p_x)_{mn} = -\frac{im}{\hbar} (E_n - E_m) x_{mn}$$

where  $(E_n - E_m)$  gives time dependence of the matrix elements.

$$\left( \frac{\partial V}{\partial x} \right)_{mn} = \frac{m}{\hbar^2} (E_n - E_m)^2 x_{mn}$$

→ quantum equivalent of Newton's 2nd law!

### Harmonic Oscillator

$$V = \frac{1}{2} m \omega^2 x^2$$

$$\frac{\partial V}{\partial x} = m \omega^2 x$$

$$\begin{aligned} \rightarrow m\omega^2 x_{mn} &= \frac{m}{\hbar^2} (E_n - E_m)^2 x_{mn} \\ \rightarrow \text{either } x_{mn} &= 0 \text{ or } E_n - E_m = \pm \hbar\omega \end{aligned}$$

Thus, the matrix  $(x_{mn})$  has non-vanishing elements only for those elements having  $E_n - E_m = \pm \hbar\omega$

$$x = \begin{matrix} & & n \rightarrow \\ \begin{matrix} m \\ \downarrow \end{matrix} & \begin{pmatrix} 0 & x & 0 & & \\ x & 0 & x & 0 & \\ 0 & x & 0 & x & 0 \\ & 0 & x & 0 & x & \ddots \\ & & \ddots & \ddots & \ddots & \ddots \end{pmatrix} \end{matrix}$$

i.e., diagonal elements  $\rightarrow m = n \rightarrow E_n - E_m = 0 \neq \pm \hbar\omega$ . These equations  $\rightarrow$  there must be a set of  $E_n$  such that successive energy levels differ by  $\pm \hbar\omega$

$$\rightarrow E_n = \hbar\omega(n + \alpha) \quad \alpha = \text{constant}$$

The matrix  $\rightarrow n = m - 1, m + 1$  (not the only form possible). We do not, as yet, know  $\alpha$  or whether there is only one  $\alpha$ !

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

$\rightarrow n + \alpha$  cannot be negative; call the lowest energy level  $n = 0 \rightarrow$  defines  $\alpha$ ! Assuming  $E_{m+1} - E_m = \hbar\omega$ . The  **$x$  matrix** has only elements when  $E_n - E_m = \pm \hbar\omega \rightarrow$  only  $x_{n,n-1}$  and  $x_{n,n+1}$ . Set (using fact that  $x$  is hermitian)

$$\begin{aligned} x_{n,n-1} &= Af(n) \\ x_{n-1,n} &= A^* f^*(n) \\ x_{n,n+1} &= A^* f^*(n+1) \end{aligned}$$

These are general assumptions!. Now assume that  $A$  and  $f$  are real so that

$$\begin{aligned} (x^2)_{nn} &= \sum_m x_{nm} x_{mn} = \sum_m |x_{nm}|^2 \\ &= |x_{n,n-1}|^2 + |x_{n,n+1}|^2 \\ &= |A|^2 |f(n)|^2 + |A|^2 |f(n+1)|^2 \end{aligned}$$

$\rightarrow$  calculation of  $p_x$  matrix  $\rightarrow$  virial theorem.

$\rightarrow$  diagonal elements of  $\frac{p_x^2}{2m}$  matrix = diagonal elements of the potential energy matrix.

### Virial Theorem

$$\begin{aligned} E_n &= m\omega^2 (x^2)_{nn} \rightarrow \text{diagonal elements of } x^2 \\ E_n &= m\omega^2 A^2 (f^2(n) + f^2(n+1)) = \hbar\omega(n + \alpha) \end{aligned}$$

where  $A = \sqrt{\frac{\hbar}{m\omega}}$ . Therefore we have

$$y(n) + y(n+1) = n + \alpha$$

This implies that

$$y(n) = \frac{1}{2} \left( n + \alpha - \frac{1}{2} \right) \rightarrow \text{only solution}$$

We want  $x_{0,-1} = 0$  for termination of the matrix. This implies  $\alpha = \frac{1}{2}$  (only one solution) so that we get

$$E_n = \hbar\omega \left( n + \frac{1}{2} \right)$$

The x-matrix is given by

$$x_{n,n-1} = \sqrt{\frac{\hbar}{2m\omega}} \sqrt{n}$$

with possible phase factor due to relative phase of successive wave functions.

### Classical Equations of Motion

$$\text{Lagrange: } p_i = \frac{\partial L}{\partial \dot{q}_i}$$

$$\text{Hamilton: } \dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where  $H = H(p_i, q_i)$  = energy.

$$F = F(q, p, t)$$

$$\begin{aligned} \frac{dF}{dt} &= \frac{\partial F}{\partial t} + \sum_i \left( \frac{\partial F}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial F}{\partial p_i} \frac{dp_i}{dt} \right) \\ &= \frac{\partial F}{\partial t} + \{F, H\} \end{aligned}$$

where

$$\{A, B\} = \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right) = \text{Poisson Bracket}$$

In Q.M.

$$\begin{aligned} \frac{dF}{dt} &= \frac{\partial F}{\partial t} + \frac{1}{i\hbar} [F, H] \\ \rightarrow \{F, H\} &= \frac{1}{i\hbar} [F, H] \end{aligned}$$

This is proved in Dirac.

### Canonical Transformations:

$$Q_j, P_j \rightarrow \text{classical functions of } p_i, q_i$$

Find set such that the following are satisfied

$$\{Q_j, P_k\} = \delta_{jk} \quad , \quad \{Q_j, Q_k\} = 0 = \{P_j, P_k\}$$

$n$  coordinates  $q_i \rightarrow n$  functions  $Q_j$ .

$$\frac{dQ_j}{dt} = \sum_i \left( \frac{\partial Q_j}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial Q_j}{\partial p_i} \right)$$

$H'(P_j, Q_j) \rightarrow$  old  $H$  with  $p = f_1(Q, P)$  and  $q = f_2(Q, P)$  substituted. Then

$$\frac{\partial H}{\partial p_i} = \sum_k \left( \frac{\partial H'}{\partial Q_k} \frac{\partial Q_k}{\partial p_i} + \frac{\partial H'}{\partial P_k} \frac{\partial P_k}{\partial p_i} \right)$$

This implies that

$$\begin{aligned} \frac{dQ_j}{dt} &= \sum_k \frac{\partial H'}{\partial Q_k} \sum_i \underbrace{\left( \frac{\partial Q_j}{\partial q_i} \frac{\partial Q_k}{\partial p_i} - \frac{\partial Q_k}{\partial q_i} \frac{\partial Q_j}{\partial p_i} \right)}_{\{Q_j, Q_k\}} \\ &\quad + \sum_k \frac{\partial H'}{\partial P_k} \{Q_j, P_k\} \\ &= \frac{\partial H'}{\partial P_j} \end{aligned}$$

$\rightarrow$  analogous equations in new coordinates.

Poisson relation  $\rightarrow$  in Q.M.

$$\{Q, P\} = \frac{1}{i\hbar} [Q, P]$$

$$\rightarrow [Q, P_k] = i\hbar \delta_{jk} \quad , \quad [Q_j, Q_k] = 0 = [P_j, P_k]$$

Idea of derivation:

$$[A, B] \quad , \quad A = A(q), B = B(p)$$

$$[A, B] = i\hbar \frac{\partial A}{\partial q}$$

$$[A, p^2] = [A, p]p + p[A, p] = 2i\hbar \frac{\partial A}{\partial q} p \quad (23)$$

in the limit as  $\hbar \rightarrow 0$ , neglecting order of factors. In the same limit

$$[A(q), B(p)] = i\hbar \frac{\partial A}{\partial q} \frac{\partial B}{\partial p}$$

$$A = A(q, p)$$

$$[A(q, p), B(p)] = [A(p), q] = -i\hbar$$

$$[A, B] = i\hbar \left( \frac{\partial A}{\partial q} \frac{\partial B}{\partial p} - \frac{\partial B}{\partial q} \frac{\partial A}{\partial p} \right) = i\hbar \{A, B\}$$

Consider (23), actually this

$$= i\hbar \left( \frac{\partial A}{\partial q} p + p \frac{\partial A}{\partial q} \right)$$

Symmetric order (always possible for  $A$  and  $B$  = power series in  $q$  and  $p$ ). and result is good to 1st powers in  $\hbar \rightarrow$  limit as  $\hbar \rightarrow 0$  for reduction to 1st powers in  $\hbar$  result.

any two canonically conjugate variables have  $[\dots] = i\hbar$

any two non-canonically conjugate variables have  $[\dots] = 0 \rightarrow$  they commute.

### Hamiltonian in the Electromagnetic Field

Using Gaussian units

$$\vec{E} = -\nabla\phi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \quad , \quad \vec{B} = \nabla \times \vec{A}$$

$$\vec{F} = q \left[ \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right] \quad (\text{Lorentz force})$$

$$H = \frac{1}{2m} \left( \underbrace{\vec{p} - \frac{e}{c} \vec{A}}_{m\vec{v}} \right)^2 + e\phi$$

Classical Proof:

$$\frac{dx}{dt} = \frac{\partial H}{\partial p_x} = \frac{1}{m} \left( p_x - \frac{e}{c} A_x \right)$$

$$\frac{dp_x}{dt} = \frac{\partial H}{\partial x} = \frac{e}{c} \frac{\partial \vec{A}}{\partial x} \cdot \vec{v} - e \frac{\partial \phi}{\partial x}$$

Therefore

$$m \frac{d^2 x}{dt^2} = \frac{dp_x}{dt} - \left( \frac{e}{c} \frac{\partial A_x}{\partial t} + \vec{v} \cdot \nabla A_x \right) = \text{Lorentz force}$$

or in general

$$m\vec{\ddot{r}} = e \left[ \vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right] \quad QED$$

Schrödinger's equation:

$$\frac{1}{2m} \left( -i\hbar \nabla - \frac{e}{c} \vec{A} \right)^2 \psi + e\phi\psi = i\hbar \frac{\partial \psi}{\partial t}$$

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + \frac{e}{mc} i\hbar \vec{A} \cdot \nabla \psi + \frac{e^2}{2mc^2} A^2 \psi + \frac{i\hbar e}{2mc} \nabla \cdot \vec{A} \psi + e\phi\psi = i\hbar \frac{\partial \psi}{\partial t}$$

We can assume  $\nabla \cdot \vec{A} = 0 \rightarrow \nabla \cdot \vec{A}$  term = 0. Now consider  $\vec{B} = B\hat{k} =$  a constant. This implies that

$$A_x = -\frac{1}{2}By \quad , \quad A_y = \frac{1}{2}Bx$$

$$\nabla \times \vec{A} = B\hat{k} \rightarrow i\hbar \frac{e}{mc} \vec{A} \cdot \nabla \psi = \frac{i\hbar e}{2mc} B \left( \underbrace{x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}}_{\frac{\partial}{\partial \varphi}} \right) \psi$$

$$\frac{e^2}{2mc^2} A^2 \psi = \frac{e^2}{8mc^2} B^2 (x^2 + y^2) \psi$$

For  $B$  small we neglect the  $B^2$  terms. Now if

$$\psi e^{-iEt/\hbar} u$$

we get the time-independent equation

$$Eu = -\frac{\hbar^2}{2m} \nabla^2 u + Vu + \frac{i\hbar e}{2mc} B \frac{\partial u}{\partial \varphi}$$

where  $V = \phi$ . We assume that  $V$  is spherically symmetric and separate in spherical-polar coordinates

$$u = R(r) P_\ell^{m'}(\theta) e^{im'\varphi}$$

$$\frac{\partial u}{\partial \varphi} = K u \quad K = \text{constant}$$

$\rightarrow$  RHS changes by the addition of a constant  $\rightarrow$

$$E = E_0 - \frac{e\hbar}{2mc} B m' \quad E_0 = \text{energy with } B = 0$$

$u$  is unchanged. Thus, in a small magnetic field

1. wave functions remain unchanged
2. energy is changed

### Magnetic Moment in a Field

$$E_{mm} = -B\mu_z$$

Therefore electron behaves as if it had a magnetic moment  $\mu_0 m'$  where  $\mu_0 = \frac{e\hbar}{2mc}$  = Bohr magneton and  $m'$  = magnetic quantum number.

$$M_z = [\vec{r} \times \vec{p}]_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

$$\rightarrow -\frac{e}{2mc} B_z M_z = -\frac{e}{2mc} \vec{B} \cdot \vec{M} \quad (\text{generalized to an arbitrary direction})$$

Therefore

$$\mu = \frac{e}{2mc} M \quad \frac{e}{2mc} = \text{gyromagnetic ratio}$$

Consider now the  $A^2$  term;  $B^2(x^2 + y^2) \rightarrow$  constant change in energy (increase) and negligible change in wave function  $\rightarrow$  diamagnetic properties.  $A^2$  term is also related to scattering of light!

### Constants of the Motion

$$F, \frac{\partial F}{\partial t}$$

$$\frac{dF}{dt} = 0 \text{ if and only if } [F, H] = 0 \text{ i.e., } F \text{ commutes with } H$$

In general the matrix element of an operator is

$$F_{nm} = \underbrace{F_{nm}^0}_{\neq f(t)} e^{-i(E_m - E_n)t/\hbar}$$

If  $[F, H] = 0 \rightarrow E_m = E_n$  or  $F_{nm} = 0$  unless  $E_m = E_n$ .  $H$  is diagonal in the  $E$  representation  $\rightarrow$

$$[F, H] \sim F_{nm} \underbrace{[E_m - E_n]}_{\rightarrow=0} = 0$$

$\rightarrow F$  observable which commutes with  $H$ , has states only between the same energies.

$$F_{ns} = \begin{matrix} n \\ \downarrow \end{matrix} \begin{matrix} 1 \\ a \\ 2 \\ b \\ c \\ d \end{matrix} \begin{matrix} s \rightarrow \\ \left( \begin{matrix} x & & & & \\ & x & x & x & x \\ & x & x & x & x \\ & x & x & x & x \\ & x & x & x & x \\ & & & & \text{etc} \end{matrix} \right) \end{matrix}$$

$$\left. \begin{matrix} n=1 \rightarrow 1 \text{ state} \\ n=2 \rightarrow 4 \text{ states} \\ n=3 \rightarrow 9 \text{ states} \end{matrix} \right\} \text{ same } E$$

Any  $F$  of this type is a constant of the motion!

### Parity Operator

$$PH(\vec{r}_1, \vec{r}_2, \dots) = H(-\vec{r}_1, -\vec{r}_2, \dots) = H(\vec{r}_1, \vec{r}_2, \dots)$$

$$PH\psi = HP\psi$$

$\rightarrow P =$  constant of the motion if  $H$  is invariant under  $P$ .

$$P^2 f = f \rightarrow P^2 = I$$

When  $F$  and  $H$  commute  $\rightarrow$  we can still simultaneously diagonalize  $F$  and  $H$ , and  $P$  can be made simultaneously diagonal with  $H$  and since  $P^2 = I \rightarrow$



elements of  $P$  are (+1 for even) and (-1 for odd). It is also called the inversion operator. Schiff  $\rightarrow$  all  $H$ s are invariant under  $P$ , but in 1957 weak interaction due to  $\beta$ -decay  $\rightarrow$  all  $H$ s not invariant (almost as non-invariant as possible in the  $\beta$ -decay case). Parity invariance holds for E.M. interaction, i.e., Coulomb  $\sim \frac{1}{r_{12}} \rightarrow$  reversal of signs  $\rightarrow$  no chance; nuclear and atomic states conserve parity  $\rightarrow$  aid in description of the systems!

## Angular Momentum - $\vec{M}$

In C.M.

$$\vec{M} = \vec{r} \times \vec{p}$$

Therefore we have

$$\begin{aligned} [M_x, x] &= [(yp_z - zp_y), x] = 0 \\ [M_x, y] &= [(yp_z - zp_y), y] = i\hbar z \quad , \quad [M_x, z] = -i\hbar y \\ [M_x, p_x] &= 0 \quad , \quad [M_x, p_y] = i\hbar p_z \\ [M_x, M_y] &= [M_x, (zp_x - xp_z)] = i\hbar(yp_x - xp_y) = i\hbar M_z \\ [M_x, M_z] &= -i\hbar M_y \\ \rightarrow [M_i, A_j] &= i\hbar A_k \quad A = q, p, M \\ [M_i, A_i] &= 0 \quad i, j, k \rightarrow x, y, z \end{aligned}$$

$R$  = rotation operator; If  $H$  is invariant under rotation  $\rightarrow$

$$RHf = HRf$$

$\rightarrow R$  commutes with  $H$ . Consider an infinitesimal rotation around the  $z$ -axis;  $\phi$  = infinitesimal. Then

$$y \rightarrow y - \phi x \quad , \quad x \rightarrow x + \phi y$$

Therefore

$$f(x, y, z) \rightarrow f(x + \phi y, y - \phi x, z) = f(x, y, z) + \phi y \frac{\partial f}{\partial x} - \phi x \frac{\partial f}{\partial y} = \left(1 + \frac{\phi}{i\hbar} M_z\right) f$$

Superposition of these infinitesimal rotations  $\rightarrow$  any finite rotation.

When  $R$  commutes with  $H \rightarrow M_x, M_y, M_z$  commute with  $H$ .

For an atom with many electrons

$$H = \sum_i T_i + \sum_i \frac{Ze^2}{r_i} + \sum_{i < j} \frac{e^2}{r_{ij}}$$

$\rightarrow$  invariant under rotations!

$$[M_x, M^2] = [M_x, M_x^2 + M_y^2 + M_z^2] = 0 + i\hbar(M_z M_y + M_y M_z) + (-i\hbar)(M_y M_z + M_z M_y) = 0$$

Choose a representation in which  $M^2$  and  $M_z$  are diagonal  $\rightarrow M_x$  and  $M_y$  are not diagonal (i.e., they do not commute with  $M_z$ ), but they do commute with  $M^2$ .

This implies that elements between states of same  $M^2$ , i.e., if  $M_x$  is a non-diagonal matrix which commutes with  $M^2$  then

$$\langle a | [M_x, M^2] | b \rangle = \langle a | M_x | b \rangle M^2(b) - M^2(a) \langle a | M_x | b \rangle = 0$$

This implies that

$$\langle a | M_x | b \rangle = 0 \text{ unless } M^2(a) = M^2(b)$$

or  $M_x$  has elements only between states of the same  $M^2$ !

Consider a sub matrix for which  $M^2$  has a definite eigenvalue, determined by  $j$

Rows and columns of the sub-matrix are labeled by the eigenvalues of  $M_z$  which we call  $\hbar m$

$$L = M_x + iM_y \quad M_x, M_y \text{ hermitian}$$

The hermitian conjugate  $= L^* = M_x - iM_y$ . Then

$$L_{mn} = (M_x)_{mn} + i(M_y)_{mn}$$

$$L_{mn}^* = (M_x)_{mn} - i(M_y)_{mn} = L_{mn}^+$$

$$[M_z, L] = i\hbar(M_y - iM_x) = \hbar L$$

$$[L, L^+] = [M_x + iM_y, M_x - iM_y] = 2\hbar M_z$$

$$M^2 = M_z^2 + \frac{1}{2}(LL^+ + L^+L)$$

Notice that since  $L, L^+$  do not commute they must always appear in a symmetric fashion!! Now since  $M_x$  and hence  $L$  only has elements between states of the same  $M^2$  or “ $j$ ”, we get

$$\begin{aligned} \langle jm | [M_z, L] | j'm' \rangle &= \langle jm | [M_z, L] | jm' \rangle \\ &= (\langle jm | M_z) L | jm' \rangle - \langle jm | L (M_z | jm' \rangle = \hbar(m - m') \langle m | L | m' \rangle \end{aligned} \quad (24)$$

$$= \hbar \langle m | L | m' \rangle \quad (\text{from matrices}) \quad (25)$$

$\rightarrow \langle m | L | m' \rangle = 0$  unless  $m = m' + 1$ . ( $m = m' + 1 \rightarrow (25) \rightarrow (24)$ )  $\rightarrow$  elements only on one side of the diagonal.

$$\begin{aligned} \langle jm | [L, L^+] | jm' \rangle &= \sum_{m''} \langle jm | L | jm'' \rangle \langle jm'' | L^+ | jm' \rangle \\ &\quad - \sum_{m''} \langle jm | L^+ | jm'' \rangle \langle jm'' | L | jm' \rangle \\ &= \sum_{m''} \langle jm | L | jm'' \rangle \langle jm' | L | jm'' \rangle^* \\ &\quad - \sum_{m''} \langle jm'' | L | jm \rangle^* \langle jm'' | L | jm' \rangle \\ &= 2\hbar \langle jm | M_z | jm' \rangle = 2\hbar^2 m \delta_{mm'} \quad (\text{from matrices}) \end{aligned}$$

Let  $m' = m$  and

$$\langle jm' | L | jm \rangle = \begin{cases} \hbar \lambda_m & \text{if } m' = m + 1 \\ 0 & \text{otherwise} \end{cases}$$

$$\text{1st } \sum \text{ above } \left. \begin{array}{l} m'' = m - 1 \\ m'' = m' - 1 \end{array} \right\} \rightarrow m' = m$$

$$\text{2nd } \sum \text{ above } \left. \begin{array}{l} m'' = m + 1 \\ m'' = m' + 1 \end{array} \right\} \rightarrow m' = m$$

Therefore

$$\begin{aligned} \langle jm | [L, L^+] | jm' \rangle &= \hbar^2 |\lambda_{m-1}|^2 - \hbar^2 |\lambda_m|^2 = 2\hbar^2 m \\ &\rightarrow |\lambda_{m-1}|^2 - |\lambda_m|^2 = 2m \\ &\rightarrow |\lambda_m|^2 = c - m(m+1) \\ |\lambda_m|^2 > 0 &\rightarrow m(m+1) < c \quad (\text{for finite } c) \end{aligned}$$

$\rightarrow$  finite max. and min.  $m$ s  $\rightarrow$  finite matrix!

$\lambda_m = 0$  for  $m_1$  and  $m_2 \rightarrow$

$$\langle m_1 + 1 | L | m_1 \rangle = 0 = \langle m_2 + 1 | L | m_2 \rangle$$

where  $m_1$  is the highest  $m$  and  $m_2 + 1$  is the lowest  $m$ . This implies that

$$\begin{aligned} m_{1,2} &= -\frac{1}{2} \pm \sqrt{c + \frac{1}{4}} \\ m_2 + 1 &= -m_1 = j \\ c + \frac{1}{4} &= \left(j + \frac{1}{2}\right)^2 \rightarrow c = j(j+1) \end{aligned}$$

Therefore

$$|\lambda_m|^2 = (j - m)(j + m + 1) = 0 \text{ when } m = j, m = -j - 1$$

$$M^2 = M_z^2 + \frac{1}{2}(LL^+ + L^+L) = \hbar^2 m^2 + \frac{1}{2}\hbar^2(|\lambda_{m-1}|^2 + |\lambda_m|^2) = \hbar^2 j(j+1)$$

where  $-j \leq m \leq j \leftrightarrow m$  changes in integer steps  $\rightarrow 2j = \text{integer}$ . Thus, neglecting  $\hbar$  factors  $\rightarrow$

$$M^2 = \begin{pmatrix} j(j+1) & 0 & \cdots & 0 \\ 0 & j(j+1) & 0 & \cdots \\ & & \ddots & \\ \vdots & & & j(j+1) \end{pmatrix}$$

$$M_z = \begin{pmatrix} j & 0 & \cdots & 0 \\ 0 & j-1 & 0 & \cdots \\ & & \ddots & \\ \vdots & & & -j \end{pmatrix}$$

$$L = \begin{matrix} & m=j & m=j-1 \\ \begin{matrix} m=j \\ m=j-1 \end{matrix} & \begin{pmatrix} 0 & x & 0 & & \\ 0 & 0 & x & 0 & \\ 0 & 0 & 0 & x & 0 \\ 0 & 0 & 0 & 0 & x \\ & & & \ddots & \ddots \end{pmatrix} \end{matrix}$$

where we have used

$$\left\langle \underbrace{m+1}_{\text{row}} \left| L \right| \underbrace{m}_{\text{column}} \right\rangle = \hbar \lambda_m$$

and number of rows = number of columns +1 (labeling is arbitrary).

### Examples:

$$j=0 \rightarrow m=0 \rightarrow M_z = (0) \quad . \quad L = (0) \quad . \quad M^2 = (0) \quad ( \text{ all } 1 \times 1 \text{ matrices } )$$

For any  $j \rightarrow (2j+1) \times (2j+1)$  matrix.

$$j = \frac{1}{2} \quad , \quad M_z = \frac{1}{2}\hbar \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \begin{matrix} \leftarrow m = \frac{1}{2} \\ \leftarrow m = -\frac{1}{2} \end{matrix}$$

$$L = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad , \quad L^+ = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$M_x = \frac{1}{2}\hbar \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{L+L^+}{2} \quad , \quad M_y = \frac{1}{2}\hbar \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{L-L^+}{2}$$

$$M_j = \frac{1}{2}\hbar \sigma_j \quad , \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad , \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Thus the commutation relations become:

$$[\sigma_i, \sigma_j] = 2i\sigma_k$$

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 2\delta_{ij} I$$

$$i=j \rightarrow \sigma_i^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = I$$

Anti-commutation:

$$\sigma_i \sigma_j = -\sigma_j \sigma_i \quad i \neq j$$

These are the Pauli spin matrices. We then have

$$M^2 = \hbar^2 \left( \frac{1}{2} \right) \left( \frac{3}{2} \right) = \frac{3}{4} \hbar^2$$

$$M_x^2 = M_y^2 = M_z^2 = \frac{1}{4} \hbar^2$$

$$j=1 \quad , \quad M_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad , \quad M_x = \frac{\hbar}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$M^2 = 2\hbar^2 \quad \text{and so on}$$

### Eigenfunctions for 1 Particle in Spherically Symmetric Potential

→  $Y_{\ell m}$  such that

$$\left. \begin{aligned} M_z u &= \hbar m u \\ M^2 u &= \hbar^2 \ell(\ell+1) u \end{aligned} \right\} \text{only for } m, \ell = \text{integers}$$

→ diagonal matrices.

But from matrix mechanics we get same formulae but  $m$  and  $j = \frac{1}{2}$  integers also → twice as many solutions and if  $m$  and  $j$  are integers →  $m = m$  and  $j = \ell$  of old system.

$$\rightarrow L = \hbar e^{i\phi} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right]$$

$$LY_{\ell m} = \pm \lambda_m Y_{\ell, m+1}$$

If

$$Y_{\ell m} = P_\ell^{|m|} e^{im\phi}$$

then factor →  $-\lambda_m$  if  $m > 0$  and  $+\lambda_m$  if  $m < 0$ .

$$\left. \begin{aligned} Y_{\ell m} &= (-1)^m P_\ell^{|m|} e^{im\phi} & m > 0 \\ Y_{\ell m} &= (-1)^m P_\ell^{|m|} e^{im\phi} & m < 0 \end{aligned} \right\} \text{notation}$$

→  $+\lambda_m$  always - thanks to Bethe! So

$$LY_{\ell m} = +\lambda_m Y_{\ell, m+1}$$

$\frac{1}{2}$  integer values ( $\vec{M} = \vec{r} \times \vec{p}$  does not imply  $\frac{1}{2}$  integer values), i.e., these are not connect with angular motion → spin.

$$\rightarrow [M_{spin}, r] = [M_{spin}, p] = 0$$

since it is not connected with either. If this is so it will commute with everything →  $M_s^2 = \text{absolute constant of the motion}$  → intrinsic  $j = s$ .

$s = \frac{1}{2}$  for electron, proton, neutron,  $|\lambda|$ ,  $\Sigma$ ,  $\Xi$  particles,  $\mu$ -meson and the neutrino.

$s = 0$  for pi-meson, K-meson.

No  $s > \frac{1}{2}$  for particles with mass (rest), but photon has spin = 1; but it also has  $m_0 = 0$ .

## Perturbation Theory

$$H\psi = W\psi$$

$$H = H_0 + \lambda H'$$

where  $H_0$  represents some solvable problem

$$H_0 u_n = E_n u_n \quad (\text{can be solved})$$

and  $\lambda H'$  is small. The power of  $\lambda \rightarrow$  order of perturbation terms (at the end we set  $\lambda \rightarrow 1$ ).

Assume

$$\psi = \psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \dots$$

$$W = W_0 + \lambda W_1 + \lambda^2 W_2 + \dots$$

Substituting gives

$$(H_0 + \lambda H')(\psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \dots) = (W_0 + \lambda W_1 + \lambda^2 W_2 + \dots)(\psi_0 + \lambda \psi_1 + \lambda^2 \psi_2 + \dots)$$

$$\lambda^0 : \quad H_0 \psi_0 = W_0 \psi_0 \quad \textcircled{0}$$

$$\lambda^1 : \quad H_0 \psi_1 + H' \psi_0 = W_0 \psi_1 + W_1 \psi_0 \quad \textcircled{1}$$

.....

$$\lambda^k : \quad H_0 \psi_k + H' \psi_{k-1} = W_0 \psi_k + W_1 \psi_{k-1} + \dots + W_k \psi_0 \quad \textcircled{k}$$

For total equation to be true all the above equations must be true (for arbitrary  $\lambda$ ).

① equation :  $\psi_0 =$  eigenfunction of original Hamiltonian

$$\psi_0 = u_m \quad (\text{any state - unperturbed}) \quad , \quad W_0 = E_m$$

① equation : Write

$$\psi_1 = \sum_n a_n^{(1)} u_n$$

Substituting gives

$$\sum_n a_n^{(1)} \underbrace{H_0 u_n}_{E_n u_n} + H' u_m = E_m \sum_n a_n^{(1)} u_n + W_1 u_m$$

or

$$H' u_m = \sum_n a_n^{(1)} (E_m - E_n) u_n + W_1 u_m$$

Multiply by  $\bar{u}_k$  and integrate using fact that the  $u_n$  are an orthonormal set.

$$\int \underbrace{\bar{u}_k H' u_m}_{H'_{km}} d\tau = a_k^{(1)} (E_m - E_k) + W_1 \delta_{km}$$

For case  $k = m$  we have

$$W_1 = H'_{mm}$$

which implies that

$$W_0 + W_1 = E_m + H'_{mm}$$

so that

$$H'_{mm} = \text{1st order perturbation on the energy}$$

For case  $k \neq m$  we have

$$a_k^{(1)} = \frac{H'_{km}}{E_m - E_k}$$

In 2nd order we have

$$H_0\psi_2 + H'\psi_1 = W_0\psi^2 + W_1\psi_1 + W_2\psi_0$$

Write

$$\psi_2 = \sum_n a_n^{(2)} u_n$$

Substituting gives

$$\sum_n a_n^{(2)} E_n u_n + \sum_r a_r^{(1)} H' u_r = E_m \sum_n a_n^{(2)} u_n + H'_{mm} \sum_r a_r^{(1)} u_r + W_2 u_n$$

Multiply by  $\bar{u}_k$  and integrate using fact that the  $u_n$  are an orthonormal set. We get

$$\sum_r a_r^{(1)} H'_{kr} = a_k^{(2)} (E_m - E_k) + H'_{mm} a_k^{(1)} + W_2 \delta_{km}$$

For case  $k = m$  we have

$$W_2 = \sum_r a_r^{(1)} H'_{mr} - H'_{mm} a_m^{(1)} = \sum_{r \neq m} a_r^{(1)} H'_{mr}$$

Therefore we finally get

$$W_2 = \sum_{r \neq m} \frac{H'_{mr} H'_{rm}}{E_m - E_r} = \sum_{r \neq m} \frac{|H'_{rm}|^2}{E_m - E_r}$$

Suppose that  $m = \text{lowest state}$ , then  $E_r > E_m \rightarrow W_2 < 0$  for the ground state  $\rightarrow$  2nd order correction is always negative.

### Normalization

$$\psi = \psi_0 + \lambda \psi_1$$

$$\begin{aligned} & \int (\psi_0 + \lambda \psi_1)^* (\psi_0 + \lambda \psi_1) d\tau \\ &= \underbrace{\int |\psi_0|^2 d\tau}_{=1} + \lambda \int (\psi_1^* \psi_0 + \psi_0^* \psi_1) d\tau + O(\lambda^2) \\ &= 1 \end{aligned}$$

This implies that

$$\int (\psi_1^* \psi_0 + \psi_0^* \psi_1) d\tau = 0 \rightarrow a_m^{(1)} + \bar{a}_m^{(1)} = 0$$

This implies that

$$\text{Re } a_m^{(1)} = 0 \quad , \quad \text{Im } a_m^{(1)} = ?$$

We set  $\text{Im } a_m^{(1)} = 0$  for simplicity so that we get  $a_m^{(1)} = 0$ .

### For 2nd Order Normalization

$$\lambda^2 \int (\psi_2^* \psi_0 + \psi_0^* \psi_2 + \psi_1^* \psi_1) d\tau = 0$$

which implies that

$$a_m^{(2)} + \bar{a}_m^{(2)} + \sum_k |a_k^{(1)}|^2 = 0$$

If  $a_m^{(2)}$  is real, this implies that

$$a_m^{(2)} = -\frac{1}{2} \sum_k |a_k^{(1)}|^2$$

**Example - Harmonic Oscillator:**

$$H_0 = \frac{p^2}{2m} + \frac{1}{2} k x^2$$

$$H'_{nm} = \frac{1}{2} b (x^2)_{nm}$$

$$x_{n\ell} = \begin{cases} \frac{1}{\alpha} \sqrt{\frac{n}{2}} & \ell = n-1 \\ \frac{1}{\alpha} \sqrt{\frac{n+1}{2}} & \ell = n+1 \end{cases}$$

$$(x^2)_{nm} \sum_{\ell} x_{n\ell} x_{\ell m} = \frac{1}{2\alpha^2} \begin{cases} \sqrt{(n+2)(n+1)} & m = n-2 \\ 2n+1 & m = n \\ \sqrt{n(n+1)} & m = n+2 \end{cases}$$

where

$$\alpha^2 = \sqrt{\frac{\mu k}{\hbar^2}}$$

$$E_m = \left(m + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}}$$

$$H'_{mm} = \frac{1}{2} b \frac{1}{2\alpha^2} (2m+1) = \left(m + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} \left(\frac{b}{2k}\right)$$

Therefore

$$E_m + H'_{mm} = \left(m + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} \left(1 + \frac{b}{2k}\right)$$



Now

$$\begin{aligned}
W_2 &= \frac{|H'_{m+2,m}|^2}{-2\hbar\sqrt{\frac{k}{\mu}}} + \frac{|H'_{m-2,m}|^2}{+2\hbar\sqrt{\frac{k}{\mu}}} \\
&= \frac{-1}{2\hbar\sqrt{\frac{k}{\mu}}4\alpha^4} [(m+2)(m+1) - m(m-1)] \frac{b^2}{4} \\
&= -\frac{b^2}{8k^2} \hbar \sqrt{\frac{k}{\mu}} \sqrt{1 + \frac{b}{2k}}
\end{aligned}$$

Thus,

$$E_m + H'_{mm} + W_2 = \left(m + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} \left(1 + \frac{b}{2k} - \frac{b^2}{8k^2}\right)$$

and

$$E^{perturbed} = \left(m + \frac{1}{2}\right) \hbar \sqrt{\frac{k}{\mu}} \sqrt{1 + \frac{b}{2k}}$$

### Degeneracies

Suppose that  $E_k = E_m \rightarrow W_2 = \infty$ . For two degenerate statee

$$\begin{pmatrix} H'_{mm} & H'_{mk} \\ H'_{km} & H'_{kk} \end{pmatrix}$$

If diagonal;  $H'_{km} = 0$  and  $H'_{kk} \neq H'_{mm}$  then we have

$$E_m + H'_{mm} \quad \text{and} \quad E_k + H'_{kk}$$

This implies that we want to diagonalize the perturbation (sub)matrix, i.e.,

$$\rightarrow \begin{pmatrix} H'_{mm} & 0 \\ 0 & H'_{kk} \end{pmatrix}$$

where  $H'_{kk}$  and  $H'_{mm}$  are the eigenvalues. This implies that

$$\begin{aligned}
u'_k &= \alpha u_k + \beta u_m \\
u'_m &= \gamma u_k + \delta u_m
\end{aligned}$$

The correct  $u'$  are the eigenvectors of the unitary transformation matrix!

If  $H'_{kk} = H'_{mm}$ ,  $H'_{km} = 0$   $k \neq m \rightarrow k, m \in$  degenerate subspace.

No degeneracy

$$E_m + H'_{mm} + \sum_{r \neq m} \frac{H'_{mr} H'_{rm}}{E_m - E_r}$$

Degeneracy removable

$$E_m + H'_{mm}$$

where  $H'_{mm}$  is an eigenvalue of  $H'$  sub matrix in the degenerate subspace.

Non-removable  $\rightarrow$  construct the matrix

$$H_{km}^{(2)} = \sum_{r \neq k, m} \frac{H'_{kr} H'_{rm}}{E_m - E_r}$$

Then

$$\det \begin{pmatrix} H_{mm}^{(2)} - \lambda & H_{mk}^{(2)} \\ H_{km}^{(2)} & H_{kk}^{(2)} - \lambda \end{pmatrix} = 0$$

$\rightarrow$  the  $\lambda$ s are just the correct second order energies!

### Scattering Problem - Born Approximation

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right) u(r) = E u(r)$$

Asymptotically

$$u(r) \rightarrow e^{ikz} + f(\theta, \varphi) \frac{e^{ikr}}{r}$$

We write

$$u(r) \rightarrow e^{ikz} + \underbrace{v(r)}_{\text{weak}}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad , \quad E = \frac{\hbar^2 k^2}{2\mu} \quad , \quad V(r) = \frac{\hbar^2}{2\mu} U(r)$$

This implies

$$(\nabla^2 + k^2)u(r) = U(r)u(r)$$

or

$$(\nabla^2 + k^2)(e^{ikz} + v(r)) = U(r)(e^{ikz} + \underbrace{v(r)}_{\text{neglect}})$$

$$(\nabla^2 + k^2)v(r) = \underbrace{e^{ikz}U(r)}_{\text{given}} = f(r)$$

Define

$$(\nabla^2 + k^2)G(r, r') = \delta(r - r')$$

Then

$$v(r) = \int G(r, r') f(r') dr'$$

$$(\nabla^2 + k^2)G(\vec{r}) = \delta(\vec{r}) \quad G(\vec{r}) = G(r)$$

$$\nabla^2 = \frac{1}{r} \frac{d^2}{dr^2} r$$

so that

$$\frac{d^2}{dr^2}(rG) + k^2(rG) = r\delta(r) = 0$$

This implies that

$$rG = e^{\pm irk} \quad \text{we choose } +$$

Thus,

$$G = C \frac{e^{ikr}}{r} \quad \text{outgoing waves}$$

Now

$$\begin{aligned} \int_{\text{sphere-radius } r} \nabla G \cdot d\vec{S} &= 4\pi r \frac{dG}{dr} = 1 \\ \rightarrow C &= -\frac{1}{4\pi} \end{aligned}$$

Thus

$$G(\vec{r} - \vec{r}') = -\frac{1}{4\pi} \frac{e^{ik|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|}$$

which implies that

$$\begin{aligned} v(r) &= -\frac{1}{4\pi} \int \frac{e^{ik|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|} U(r') e^{ikz} d\tau' \\ |\vec{r} - \vec{r}'| r - r' \omega &\approx r \\ e^{ik|\vec{r} - \vec{r}'|} &\approx e^{ik(r - r' \omega)} \end{aligned}$$

Hence

$$v(r) = -\frac{1}{4\pi} \frac{e^{ikr}}{r} \int e^{-i \overbrace{kr' \omega}^{\vec{k} \cdot \vec{r}'}} U e^{ikz} d\tau'$$

where

$$\vec{k} = k\vec{r}_0 \quad , \quad \text{vec } r_0 = \text{unit vector in } r \text{ direction}$$

$$\vec{k}_0 = k\vec{z}_0 \quad , \quad \text{vec } z_0 = \text{unit vector in } z \text{ direction}$$

$$v(r) = -\frac{1}{4\pi} \frac{e^{ikr}}{r} \int U(\vec{r}') e^{i\vec{q} \cdot \vec{r}'} d\tau \quad , \quad \vec{q} = \vec{k} - \vec{k}_0$$

and

$$v(r) = \frac{e^{ikr}}{r} f(\theta)$$

Therefore

$$f(\theta) = -\frac{1}{4\pi} \frac{e^{ikr}}{r} \int U(\vec{r}') e^{i\vec{q} \cdot \vec{r}'} d\tau$$

If we choose  $\vec{q}$  along the polar axis, then  $\vec{q} \cdot \vec{r}' = qr' \cos \theta$ . Also note that the  $\varphi$  integral  $\rightarrow 2\pi$ .

This result implies that each volume element contributes

$$\underbrace{U(\vec{r}')}_{\text{weighting factor}} \underbrace{e^{i\vec{q}\cdot\vec{r}'}_{\text{phase factor}}$$

to the scattering amplitude.

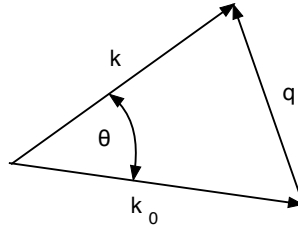
**Example:** Scattering from a system of similar atoms. We can thus calculate  $U(r')$  for one atom  $\rightarrow$  same for all  $\rightarrow$  sum. We thus have

$$\sum_n e^{i\vec{q}\cdot\vec{r}_n} \quad \text{used for x-rays}$$

$f(\theta)$  is the Fourier transform of  $U$ .

$$\sigma(\theta) = |f(\theta)|^2$$

$f(\theta)$  is real if  $U(-\vec{r}') = U(\vec{r}')$  which implies that  $U(\vec{r}') \cos qr' = \text{real}$ . Therefore  $f(\theta) = f(q)$  - see figure



where

$$q = 2k \sin \frac{\theta}{2}$$

and  $\hbar\vec{q}$  = momentum change of scattered particle (momentum transfer)!

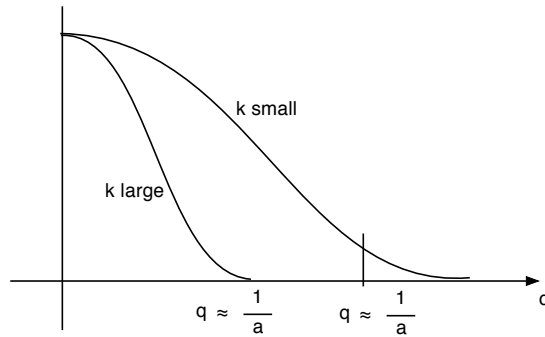
For an isotropic scatterer  $V = V(r)$  and we have

$$f(\theta) = -\frac{1}{q} \int U(r') \sin qr' r' dr'$$

For small  $\theta$  we have

$$q = 2k \sin \frac{\theta}{2} \approx k\theta$$

If  $U(r)$  is small for  $k > a$ , then  $f(\theta)$  is small for  $q \geq \frac{1}{a}$  or  $qa \geq 1$  as shown below



### Spherical Symmetry

$$\sigma_T = 2\pi \int_0^\pi \sigma(\theta) \sin \theta d\theta$$

$$q^2 = 2k^2(1 - \cos \theta)$$

$$\frac{q dq}{k^2} = \sin \theta d\theta$$

$$\theta = 0 \rightarrow q = 0 \quad , \quad \theta = \pi \rightarrow q = 2k$$

$$\rightarrow \sigma_T = \frac{2\pi}{k^2} \int_0^2 k |f(q)|^2 q dq$$

$$\text{for large } k \rightarrow \int_0^\infty$$

$$\sigma_T \sim \frac{2\pi}{k^2} \text{ constant} \sim \frac{1}{E}$$

### Example - Square Well

$$V(r) = \begin{cases} -V_0 & r < a \\ 0 & r > a \end{cases}$$

$$\begin{aligned} f(\theta) &= \frac{2\mu}{\hbar^2} V_0 \int_0^a \frac{\sin qr}{q} r dr \\ &= \frac{2\mu}{\hbar^2} V_0 a^3 \int_0^a \frac{\sin qr}{(qa)^3} d(qr) \\ &= \frac{2\mu}{\hbar^2} V_0 a^3 \left[ \frac{1}{(qa)^3} \underbrace{\int_0^{qa} u \sin u du}_{\sqrt{g(qa)}} \right] \end{aligned}$$

$$\sigma(\theta) = |f(\theta)|^2 \rightarrow V_0 a^3 \dots$$

$$\sigma_T = \frac{2\pi}{k^2} \left( \frac{2\mu}{\hbar^2} V_0 a^3 \right)^2 \frac{1}{a^2} \int_0^{2ka} g(x) x dx$$

→ both  $\sigma_T$  and bound states  $\approx V_0 a^2$ .

$$\frac{\mu V_0 a^2}{\hbar^2} = S \approx \frac{\pi^2}{8} \text{ for the 1st bound state.}$$

For large  $k$

$$\sigma_T \xrightarrow{E \rightarrow \infty} \frac{\pi \mu (V_0 a^2)^2}{\hbar E} = \frac{\pi \hbar^2 S^2}{\mu E} \approx 2\pi \frac{1}{k^2} S^2$$

where

$$\frac{1}{k} \equiv \lambda$$

### Screened Coulomb Potential

$$V(r) = -\frac{Ze^2}{r} e^{-r/a}$$

Thomas-Fermi theory implies

$$a \approx \frac{\hbar^2}{me^2} \frac{1}{\sqrt{Z}} = \frac{a_0}{\sqrt{Z}}$$

$$\begin{aligned} f(\theta) &= \frac{2m}{\hbar^2} \frac{Ze^2}{q} \int_0^\infty \sin qr e^{-r/a} dr \\ &= \frac{2m}{\hbar^2} \frac{Ze^2}{q^2 + \frac{1}{a^2}} \end{aligned}$$

$a \rightarrow \infty \rightarrow$  no screening factor. This implies that

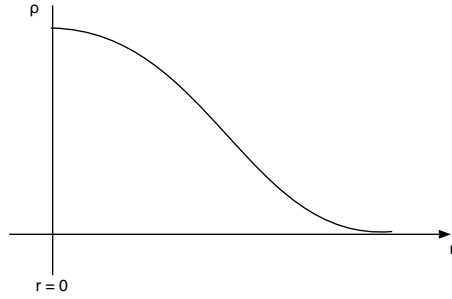
$$f(\theta) \rightarrow \frac{2mZe^2}{\hbar^2 q^2} \rightarrow f(Rutherford)$$

For a given  $a$  if  $q \gg 1/a$ , the scattering looks like Rutherford. But for  $q \rightarrow 0$   $\sigma(\theta)$  = finite.

$$\sigma_T = \frac{16\pi \left( \frac{mZe^2 a^2}{\hbar^2} \right)^2}{4k^2 a^2 + 1}$$

For large  $a$ ,  $\sigma_T \sim a^2$ .

If  $\rho(r)$  = electron density around nucleus as shown below



then

$$U(r) = \frac{2m}{\hbar^2} e^2 \left[ -\frac{Z}{r} + \underbrace{\int \frac{\rho(r'')}{|r - r''|} d^3 r''}_{\text{effect on } r \text{ due to all other charges}} \right]$$

$$\nabla^2 U(r) = -\frac{2m}{\hbar^2} e^2 4\pi [Z\delta(r) - \rho(r)]$$

$$\begin{aligned} f(\theta) &= \frac{1}{4\pi} \int U(r) \frac{1}{q^2} [\nabla^2 e^{i\vec{q}\cdot\vec{r}}] d^3 r \\ &= \frac{1}{4\pi q^2} \int (\nabla^2 U(r)) e^{i\vec{q}\cdot\vec{r}} d^3 r \\ &= \frac{2}{a_0 q^2} \int [Z\delta(r) - \rho(r)] e^{i\vec{q}\cdot\vec{r}} d^3 r \\ &= \frac{2}{a_0 q^2} [Z - F(q)] \end{aligned}$$

where  $F(q)$  = form factor.

### Born Approximation for Partial Waves

$$u_\ell'' + \left[ k^2 - \frac{\ell(\ell+1)}{r^2} - U(r) \right] u_\ell = 0 \quad \textcircled{1}$$

$$j_\ell'' + \left[ k^2 - \frac{\ell(\ell+1)}{r^2} \right] j_\ell = 0 \quad \textcircled{2}$$

where  $j_\ell(x) = x J_\ell(x)$ . Now multiply ① by  $j_\ell$  and ② by  $u_\ell$  and add to get

$$(j_\ell u_\ell'' - u_\ell j_\ell'') = j_\ell(r) U(r) u_\ell(r)$$

Now taking

$$\int_0^R ( ) dr \rightarrow$$

$$\left[ \underbrace{j_\ell u'_\ell - u_\ell j'_\ell}_{j_\ell(r=0)=u_\ell(r=0)=0} \right]_0^R = \int_0^R j_\ell(r) U(r) u_\ell(r) dr \quad (\text{this is exact})$$

Let  $R \rightarrow \infty \rightarrow$

$$\begin{aligned} j_\ell &\rightarrow \sin(kr - \ell\pi/2) \\ u_\ell &\rightarrow \sin(kr - \ell\pi/2 + \delta_\ell) \\ &\rightarrow k \sin(-\delta_\ell) = \int_0^{R \rightarrow \infty} \\ &\rightarrow \sin \delta_\ell = -\frac{1}{k} \int_0^\infty j_\ell(r) U(r) u_\ell(r) dr \quad (\text{this is exact}) \end{aligned}$$

The integral is the matrix element of the potential between perturbed and unperturbed states. Now replace  $u_\ell$  by the unperturbed wave  $j_\ell$  which implies the 1st approximation

$$\begin{aligned} u_\ell &\rightarrow j_\ell - \tan \delta_\ell n_\ell \\ &\rightarrow \delta_\ell \approx -\frac{1}{k} \int_0^\infty U(r) j_\ell^2(r) dr \\ &\approx -k \underbrace{\int_0^\infty U(r) j_\ell^2(r) r^2 dr}_{\text{leading term!}} \end{aligned}$$

For  $\vec{r} \gg \vec{r}'$

$$f = -\frac{1}{4\pi} \int U(r) e^{i\vec{q} \cdot \vec{r}} d\tau$$

which is not always sufficiently accurate.

$$f \sim e^{2i\delta} - 1$$

Born approximation  $\rightarrow 2i\delta_\ell$  (for large  $\delta_\ell$  this is not accurate).

Idea is to use Born approximation for  $\delta_\ell$  for large  $\ell$  and calculate  $\delta_\ell$  for small  $\ell$  by solution of Schrödinger's equation. Since

$$\delta_\ell \sim k \int j_\ell u_\ell U dr$$

small  $\delta_\ell \rightarrow u_\ell \rightarrow j_\ell$ , which implies that

$$f(\theta) = \frac{1}{k} \sum_\ell (2\ell + 1) \delta_\ell P_\ell$$

Now

$$e^{i\vec{k} \cdot \vec{r}} = \frac{1}{k} \sum_\ell (2\ell + 1) i^\ell j_\ell(kr) P_\ell(\alpha)$$



where  $\alpha$  = angle between  $\vec{k}$  and  $\vec{r}$ . Then

$$e^{i\vec{k}_0 \cdot \vec{r}} = \frac{1}{k_0} \sum_{\ell'} (2\ell' + 1) i^{\ell'} j_{\ell'}(k_0 r) P_{\ell'}(\beta)$$

where  $\beta$  = angle between  $\vec{k}_0$  and  $\vec{r}$ . Now take complex conjugate of  $e^{i\vec{k} \cdot \vec{r}}$  and multiply which implies that

$$e^{i\vec{q} \cdot \vec{r}} \text{ contains terms like } i^{\ell-\ell'} j_{\ell} j_{\ell'} P_{\ell}(\alpha) P_{\ell'}(\beta)$$

Using the addition theorem for spherical harmonics

$$\int P_{\ell} P_{\ell'} d\Omega = P_{\ell}(\theta) \delta_{\ell\ell'}$$

where  $\theta$  = angle between  $\vec{k}$  and  $\vec{k}_0$ . These results  $\rightarrow f \rightarrow \delta_{\ell}$ .

### Validity of the Born Approximation

$$v(r) = -\frac{1}{4\pi} \int U(\vec{r}') \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} e^{ikz'} d\tau'$$

We assume that perturbation is largest at center of the scatterer. Calculate  $v(0)$ .

If  $v(0) \ll e^{ik_0} = 1$ , then we can be satisfied with the Born approximation which neglects  $v(r)$ .

$$v(0) = -\frac{1}{4\pi} \int U(\vec{r}') \frac{e^{ikr'} r' e^{ik \overbrace{r' \cos \theta = z'}^{\omega'}}}{r} dr' d\omega' 2\pi$$

Integrate over  $d\omega'$

$$v(0) = -\frac{2\pi}{4\pi k} \int \frac{2\mu}{\hbar^2} V(r') (e^{ikr'} - 1) dr'$$

Thus,

$$|v(0)| = \frac{\mu}{\hbar^2 k} \int V(r') (e^{ikr'} - 1)' dr' = \frac{1}{\hbar v} \int V(r') (e^{ikr'} - 1)' dr'$$

Case I:

$$ka \ll 1 \rightarrow \text{expand } e^{2ikr'}$$

$$|v(0)| = \frac{1}{\hbar v} 2ik \int V(r') dr'$$

Consider a square well

$$|v(0)| = \frac{2\mu|i|}{\hbar^2} \frac{1}{2} V_0 a^2 = \frac{\mu V_0 a^2}{\hbar^2} \quad \text{same as bound state expression}$$

Therefore

$$v(0) \ll 1 \text{ or } \frac{\mu V_0 a^2}{\hbar^2} \ll 1$$

But 1st bound state where

$$\begin{aligned} \frac{\mu V_0 a^2}{\hbar^2} &\approx \frac{\pi^2}{8} \rightarrow \text{good scattering approximation} \\ &\rightarrow \underbrace{\int V(r') r' dr'}_{\text{always true}} \text{ for small } ka \end{aligned}$$

Born approximation is valid if the potential is much weaker than required for a bound states!

Case II: large  $ka$

$e^{2ikr'}$  is wildly oscillating function and  $V(r')$  is slowly varying

$$\int (\text{slowly varying})(\text{oscillating}) \rightarrow \text{small contribution}$$

But  $V(r')$  may have a singularity at  $r' = 0$  (which is cancelled by the factor  $e^{2ikr'} - 1$ )  $\rightarrow$  we must keep it or

$$\int_{kr=1}^{\infty} V(r) dr \ll \hbar v$$

where we assume cancellation below the limit  $kr = 1$  for good approximation

Only useful for  $V$ s  $\rightarrow$  convergence, i.e., not Coulomb potential.

In non-relativistic theory, large enough  $v$  can always be found to satisfy condition.

For relativistic theory  $v_{max} = c$ . Therefore for arbitrary  $V$

$$\int V dr \ll \hbar c$$

must hold if Born approximation is to hold at some point. Consider the screened Coulomb potential

$$\begin{aligned} V &= -\frac{Ze^2}{r} e^{-r/a} \\ \int_{kr=1}^{\infty} V(r) dr &\approx Ze^2 \int_{1/k}^a \frac{dr}{r} = Ze^2 \ln ka \end{aligned}$$

Therefore,  $\hbar c \gg Ze^2 \ln ka$  or

$$\frac{Ze^2}{\hbar c} \ln ka \ll 1 \rightarrow \frac{Z}{137} \ln ka \ll 1$$

→  $Z \ll 137$  (dropping  $\ln ka$  which often causes trouble).

→ good Born approximation

or  $\hbar v / Ze^2 \gg 1$  (never works for heavy atoms).

Born approximation is velocity dependent but not momentum dependent. Proton scattering versus electron scattering requires higher  $E$ s for good Born approximation.

### Variational Method

Arbitrary  $\psi = \sum_E A_E u_E$  (energy eigenfunctions). Calculate

$$\int \psi^* H \psi d\tau = \sum_E |A_E|^2 E \geq E_0 \sum_E |A_E|^2$$

For normalized  $\psi$ , we have

$$\sum_E |A_E|^2 = 1 = \int \psi^* \psi d\tau$$

Therefore

$$\frac{\int \psi^* H \psi d\tau}{\int \psi^* \psi d\tau} \geq E_0 \quad \text{for any arbitrary } \psi$$

Guess approximate wave function → upper limit. (Rayleigh-Ritz method).

Example: He-Atom

$$H = \underbrace{-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2)}_{\text{electron KE}} - \underbrace{2e^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right)}_{\text{electron-nucleus interaction}} + \underbrace{\frac{e^2}{r_{12}}}_{\text{electron-electron interaction}}$$

Assume

$$\psi \sim e^{-Zr_1/a} e^{-Zr_2/a}$$

but we should take  $Z = 2 - \delta$  due to repulsive(screening) effects. Therefore assume the trial function

$$\psi = \left( \frac{Z^3}{\pi a^3} \right) e^{-Z(r_1+r_2)/a} \quad (\text{normalized})$$

$$\text{KE} \sim Z^2 \sim \frac{e^2}{2a} Z^2 \cdot 2 \quad (2 = \text{number of electrons})$$

$$\text{PE(nucleus + electron)} - \frac{2e^2}{a} 2Z$$

Effect of  $Z \rightarrow$  shrinking of wave function, i.e.,

$$K(a) \leftrightarrow K\left(\frac{a}{Z}\right)$$

$$\frac{1}{r_{12}} = \frac{1}{r_1} \sum_n \left( \frac{r_2}{r_1} \right)^n P_n(\cos \theta)$$

where  $\theta$  = angle between  $\vec{r}_1$  and  $\vec{r}_2$ . Then if  $r_2 \leq r_1$  we have

$$e^2 \left\langle \frac{1}{r_{12}} \right\rangle = \int d\tau_1 d\tau_2 \underbrace{e^{-2Z(r_1+r_2)/a}}_{|\psi|^2} \frac{1}{r_1} \sum_n \left( \frac{r_2}{r_1} \right)^n P_n(\cos \theta)$$

Keep  $\hat{r}_1$  fixed,  $|r_1|, |r_2|$  fixed and integrate over all directions of  $r_2 \rightarrow$  polar axis in  $r_2$ - space direction of  $r_1 \rightarrow$  no contribution unless  $n = 0 \rightarrow 4\pi$ .

This implies  $1/r_1$  or  $1/r_2$ , whichever is larger. Integrate over  $\vec{r}_1 \rightarrow$

$$e^2 \left\langle \frac{1}{r_{12}} \right\rangle = (4\pi)^2 \int r_1^2 dr_1 r_2^2 dr_2 e^{-2Z(r_1+r_2)/a} \frac{1}{r_{larger}}$$

Finally we get

$$e^2 \left\langle \frac{1}{r_{12}} \right\rangle = \frac{5}{8} \frac{e^2 Z}{a}$$

Therefore

$$\langle H \rangle = \frac{e^2}{a} \left[ Z^2 - 4Z + \frac{5}{8} Z \right] = \frac{e^2}{a} \left[ Z^2 - \frac{27}{8} Z \right]$$

Best  $E_0$  is the minimum of  $\langle H \rangle \rightarrow Z_{min} = 27/16 = 1.69 \rightarrow$  best value for this trial function. Then

$$\langle H \rangle = -\frac{e^2}{a} \left( \frac{27}{16} \right)^2 > E_0$$

This implies that

$$-2.85 \frac{e^2}{a} > E_0$$

Actually

$$E_0 = -2.902 \frac{e^2}{a}$$

$$He^+ = -4 Ry = -2 \frac{e^2}{a} \rightarrow E_{diff} = 0.90 \frac{e^2}{a} = 1.804 Ry$$

Using perturbation theory:  $Z = 2$  (ignoring electron interactions)

$$\rightarrow \langle H \rangle = -2.75 \frac{e^2}{a}$$

Hylleraas used 6 parameter trial function  $\rightarrow$  accuracy of 1 part in 10000.

Kinoshita used 38 parameter trial function - theory =  $198310.41 \text{ cm}^{-1}$  and experiment gives  $198310.5 \pm 1$ . What about higher energy levels?

$[H, M] = 0 \rightarrow$  eigenfunction of  $H$  is an eigenfunction of  $M$  and vice versa. Trial function corresponding to eigenvalue of  $M^2 = L(L+1)$   $L = 1 \rightarrow$  p-state.

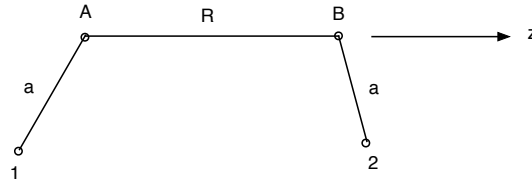
$H$  is invariant under interchange of  $r_1$  and  $r_2$ ; some eigenfunctions change under this transformation  $\rightarrow$  antisymmetric; others do not under this transformation  $\rightarrow$  symmetric. Antisymmetric trial function  $\rightarrow$  orthogonal to the ground state eigenfunction  $\rightarrow$  lowest antisymmetric state ( $\Sigma$  does not contain  $E_0$ ).

For 2nd state,  $\ell = 0$ , symmetric  $\rightarrow$  trial function must be orthogonal to the ground state wave function, then  $A_0 = 0$  and then

$$\sum_E |A_E|^2 E > E_1 \sum_E |A_E|^2$$

Hylleraas: any trial function  $\rightarrow E \rightarrow H = H(\alpha_1, \dots)$ . Variational principle  $\rightarrow$  multi-variable minimization process  $\rightarrow n$  parameters gives  $n$  linear equations  $\rightarrow n$  solutions. The lowest solution corresponds to the answer!

### Interaction between Two Hydrogen Atoms



We have

$$H = H_0 + H'$$

$$H_0 = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{r_{A1}} - \frac{e^2}{r_{B2}}$$

$$H' = e^2 \left( \frac{1}{R} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} + \frac{1}{r_{12}} \right)$$

For  $R \gg a$

$$\frac{1}{r_{A2}} = \frac{1}{\sqrt{R^2 - 2Rz_2 + r_2^2}} = \frac{1}{R} \left( 1 + \frac{z_2^2}{R^2} + O\left(\frac{1}{R^2}\right) + \dots \right)$$

Therefore

$$H' = \frac{e^2}{R^3} \left( x_1 x_2 + y_1 y_2 - 2z_1 z_2 + O\left(\frac{1}{R^4}\right) \right)$$

where  $x_1 \equiv x_{A1}$ , etc. This has the form of the interaction of two dipoles at A and B.

$H'_{00}$  = perturbation in ground state energy (1st order)

$$\langle x_1 \rangle = 0 \rightarrow H'_{00} = 0$$

2nd-order perturbation:

$$\sum_{n \neq 0} \frac{|H'_{0n}|^2}{E_0 - E_n}$$

Find minimum of  $E_0 - E_n$  and replace denominator by minimum  $\rightarrow$  overestimate.

$$H'_{0n} = \underbrace{\langle x_1 \rangle_{0n}}_{\neq 0 \text{ only for } n \geq 1} \langle x_2 \rangle_{0n} + \dots$$

Therefore

$$\begin{aligned} E_n - E_0 &\geq 2 \left( \underbrace{-\frac{e^2}{2a} \frac{1}{4}}_{\text{1st excited level}} + \underbrace{\frac{e^2}{2a}}_{\text{ground state}} \right) = \frac{3}{4} \frac{e^2}{a} \\ &= W = - \sum_{n \neq 0} \frac{|H'_{0n}|^2}{E_0 - E_n} < \frac{\sum_{n \neq 0} |H'_{0n}|^2}{\frac{3}{4} \frac{e^2}{a}} \\ &< \frac{\sum_n H'_{0n} H'_{n0}}{\frac{3}{4} \frac{e^2}{a}} = \frac{(H'^2)_{00}}{\frac{3}{4} \frac{e^2}{a}} \end{aligned}$$

We can calculate  $(H'^2)$  easily.

$$(H'^2) = \frac{e^4}{R^6} (x_1^2 x_2^2 + y_1^2 y_2^2 + 4z_1^2 z_2^2 + \text{mixed terms})$$

Now mixed terms imply

$$\int xy u_0^2(r) d\tau_1 = 0$$

and quadratic terms imply

$$\begin{aligned} \int x_1^2 u_0^2 d\tau_1 &= \frac{1}{3} \int r_1^2 u_0^2 d\tau_1 \quad (\text{because } u_0^2 \text{ is spherically symmetric}) \\ &= \frac{1}{3} \int r_1^2 \frac{1}{\pi a_0^2} e^{-2r_1/a_0} 4\pi r_1^2 dr_1 = a_0^2 \frac{4}{3} \frac{4!}{2^5} = a_0^2 \end{aligned}$$

Therefore

$$\langle x^2 \rangle = a_0^2 \quad \text{for ground state of } H_2$$

Therefore

$$\begin{aligned} (H'^2)_{00} &= \frac{6e^4 a_0^4}{R^6} \\ &\rightarrow -W < \frac{8e^4 a_0^5}{R^6} \end{aligned}$$

This is not a perturbation calculation. Doing this explicitly would be a tough job; in this particular case we get a good result, but usually not. Result depends on  $H'_{0n}$  decreasing with increasing  $E_n$ .

Another way of looking at it:

$$\sum_n |x_{mn}|^2 |E_m - E_n| = \frac{\hbar^2}{2m} \quad (\text{deals with 1 atom})$$

$$\sum_n (x_{mn})^2 = (x^2)_{mm}$$

This gives average for

$$\langle E_m - E_n \rangle = \frac{e^2}{a_0} \quad (\text{for 1 atom})$$

For two atom - average excitation energy =  $e^2/a_0$ , but we do not want arithmetic average - want harmonic mean. Arithmetic mean gives a poor estimate.

Overestimate if we put in  $e^2/a_0 \rightarrow$

$$-W > \frac{6e^2 a_0^5}{R^6} \quad (\text{previously underestimated})$$

(this is precisely the same result as in Schiff - different method). Often a related average will help in a problem where we cannot calculate the average. Actually

$$-W = 6.5 \frac{e^2 a_0^5}{R^6}$$

The upper and lower bounds are so close together here because  $E_0 \gg E_1$

Now use trial function

$$u_0(r_1)u_0(r_2)(1 + AH') \quad (\text{not normalized})$$

This is generally applicable  $\rightarrow$  unperturbed wave function gets a correction  $\sim H'$ . Insert this into the variation expression:

$$E_0 + W \leq \frac{\int u_0(1 + AH')(H_0 + H')u_0(1 + AH')d\tau}{\int u_0^2(1 + AH')^2d\tau}$$

Fortunately  $H'$  contains no differential operators. The

$$\langle H' \rangle_{00} = 0 = \langle H'^3 \rangle \quad (\text{for any odd powers of } H')$$

$$\int u_0 H' H_0 H' u_0 d\tau = 0 \quad (\text{accidental simplification})$$

$$\rightarrow W = (H'^2)_{00} (2A - E_0 A^2)$$

$\rightarrow$  perturbation energy is a quadratic function of  $A$  (a parameter), Minimum  $\rightarrow$

$$A = \frac{1}{E_0} \quad E_0 < 0 \rightarrow A < 0 \quad \text{etc ...}$$

Various perturbation methods treated in this section have precise applications:

- (1) Stationary state : emphasis on perturbed energy levels (all)
- (2) Born approximation: scattered amplitude for arbitrary potential
- (3) Variation principle: extremely accurate for low levels

The final approximation scheme is The WKB method (Wentzel-Kramers-Brillouin). Here the emphasis is on obtaining the wave function under general conditions (approximation is only moderate). (Bethe does not like approximation as  $\hbar \rightarrow 0$  that Schiff uses!).

Solving

$$u'' + k^2(x)u > 0 \quad k^2 > 0 \quad \text{for the moment} \quad k \text{ real}$$

We have  $k=f(x)$ .

If  $k^2$  did not depend on  $x \rightarrow e^{ikx}$

If  $k^2$  changes slowly:  $e^{ikx}$  is still pretty good.

Assume that  $k^2$  is a slowly varying function of  $x$ . Assume that  $u$  can be written as  $e^{iS}$ . Thus,

$$u' = iS' e^{iS}, \quad u'' = e^{iS}(-S'^2 + iS'')$$

Reduces differential equation to the form

$$-S'^2 + iS'' + k^2 = 0 \quad (\text{no approximations so far})$$

$\rightarrow$  2nd-order linear in  $u$ , i.e.,

$$S' = y \rightarrow -y^2 + iy' + k^2 = 0$$

Now assume that  $k^2$  is slowly varying  $\rightarrow y' \ll y^2$ , thus, in 1st approximation  $y = \pm k$ , i.e., we write  $gy_1 = \pm k$ . The second approximation is written  $y = y_1 + y_2$  which implies

$$y_1^2 = k^2, \quad y_2 = \frac{iy_1'}{y_1}$$

To investigate accuracy we have to evaluate  $y_2^2 + y_2'$ :

$$y = S' = \pm k + \frac{ik'}{2k}$$

$$S = \pm \int k dx + \frac{i}{2} \log k + \text{constant}$$

$$u = e^{iS} = A \exp \left[ \pm i \int k dx - \frac{1}{2} \log k \right]$$

$$u = Ak^{1/2} \exp \left[ \pm i \int k dx \right]$$



This is the WKB approximation to the original equation.

Slowly varying condition: For a good approximation

$$\left(\frac{k'}{2k}\right)^2 - \frac{k''}{2k} + \frac{k'^2}{2k} = \frac{3}{4} \left(\frac{k'}{k}\right)^2 - \frac{k''}{2k} \ll k^2$$

or

$$\frac{k'}{2k} \ll k$$

$$\frac{1}{2k} \frac{d \log k}{dx} = \frac{\lambda}{4\pi} \frac{d \log k}{dx} \ll 1$$

or the  $\log k$  must change only slightly over a distance  $\lambda/4\pi$ .

Consider

$$-V_0 e^{-x/a}$$

For  $ka \gg 1$ , WKB is OK.

$$\log k \approx \log k' = \log (E + V_0 e^{-x/a})$$

If  $E \gg V_0 \rightarrow$  always OK, or

$$\frac{d}{dx} \log k^2 = \frac{V_0 e^{-x/a}}{E + V_0 e^{-x/a}} \frac{1}{a} \ll \sqrt{\frac{2m}{\hbar^2}} \sqrt{E + V_0 e^{-x/a}}$$

In Born approximation valid for

$$\frac{1}{\hbar v} \int V dr \ll 1$$

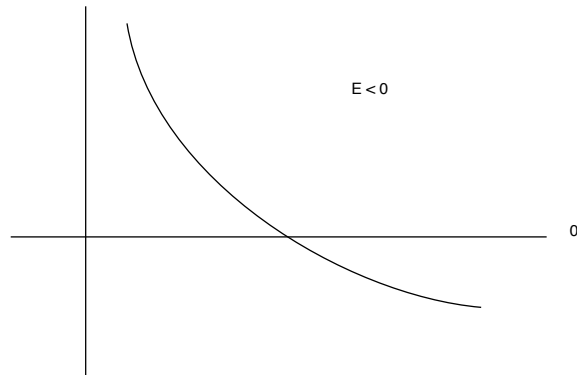
WKB - no rapidly changing potential; always valid at high energies.

Both can be applied to the same problem. WKB good for heavy particle  $\rightarrow$  large  $k$

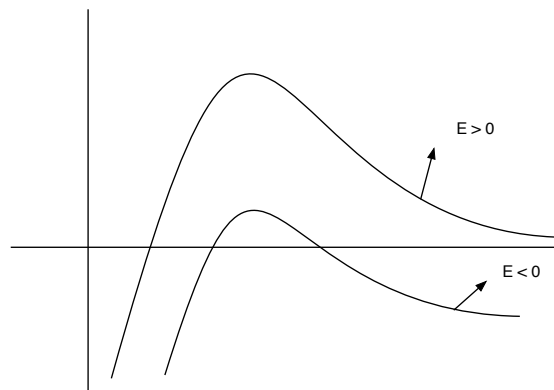
$$k = \frac{p}{\hbar} \quad \text{small } \hbar \rightarrow \text{WKB better for same } p$$

In the classical limit ( $\hbar \rightarrow 0$ ) it is very good!

Consider  $E - V$  plot below:



$E - V = 0 \rightarrow$  classical turning point; we must join WKB solution at this point!

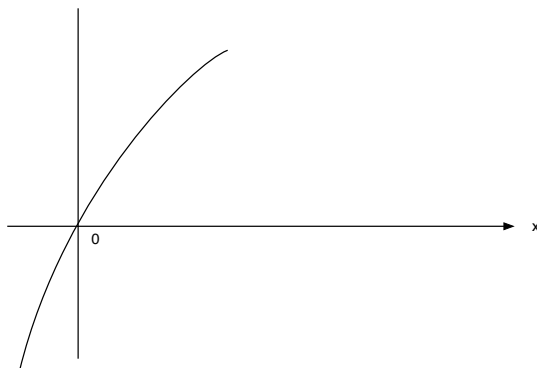


$E - V > 0 \rightarrow$  WKB solution valid  $\rightarrow$  oscillatory (this corresponds to the region of classical motion).

$E - V < 0 \rightarrow$  classically forbidden  $\rightarrow$  exponential

$$u = k^{-1/2} \exp \pm \int^x k(x') dx'$$

at the turning point  $k^2 = 0 \rightarrow$  conditions are not valid!



$k^2(x) = Cx$  at the turning point only. Let

$$\xi = \int_0^x k \, dx$$

If  $k^2 \sim x \rightarrow$  solution  $J_{1/3}(\xi) \rightarrow$  solution for all  $x$ .

Exactly:  $\rightarrow$  trial solution

$$u = A \sqrt{\frac{\xi}{k}} J_{\pm 1/3}(\xi)$$

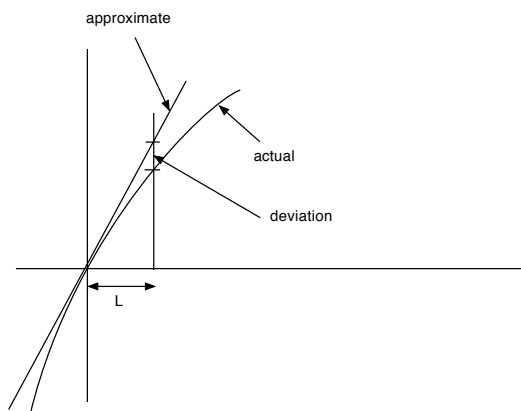
Asymptotic behavior is the same as previous solutions! This function solves the equation

$$u'' + (k^2 - \theta)u = 0$$

$$\theta = \frac{3}{4} \frac{k'^2}{k^2} - \frac{1}{2} \frac{k''}{k} - \frac{5}{36} \frac{k^2}{\xi^2}$$

for large  $x \rightarrow$  OK.

But for small  $x \rightarrow$  use  $k^2 = Cx(1 + ax + bx^2)$



where

$$a \sim \frac{1}{L} \quad , \quad b \sim \frac{1}{L^2}$$

For small  $x$ ,

$$\theta = 0.26a^2 - 0.43b \sim \frac{1}{L^2}$$

Theory is good at a point if  $k^2 L^2 \gg 1$  !! On the right side of the turning point

$$k^2 > 0 \quad , \quad u = A \sqrt{\frac{\xi_1}{k}} J_{\pm 1/3}(\xi_1)$$

On the left side

$$k^2 < 0 \quad , \quad u = A \sqrt{\frac{\xi_2}{k}} I_{\pm 1/3}(\xi_2)$$

where

$$\xi_2 > 0 \quad , \quad \xi_2 = \int_0 k d|x|$$

We want to join the solutions. Therefore we need behavior for small arguments.

$$J_n(x) \sim x^n$$

$$J_{\pm 1/3}(\xi) \sim \xi^{\pm 1/3} \sim x^{\pm 1/2}$$

$$u_+^1 \sim x$$

$$u_+ \sim \text{constant}$$

$$u_+^2 \sim |x| = -x$$

$u_+^1$  and  $u_+^2$  must join smoothly. Therefore

$$I_{-1/3} \rightarrow J_{-1/3}$$

$$I_{+1/3} \rightarrow -J_{+1/3}$$

### Bessel Functions

$$J_\rho(x) = \frac{\left(\frac{x}{2}\right)^\rho}{\rho!0!} - \frac{\left(\frac{x}{2}\right)^{\rho+2}}{(\rho+1)!1!} + \dots$$

Let  $x = ix'$ . Then first two terms look like

$$i^\rho x'^\rho + i^\rho x'^{\rho+2}$$

$$\rightarrow I_\rho(x) = i^{-\rho} J_\rho(ix)$$

Continuity requires that

$$I_{-1/3} \rightarrow J_{-1/3} \quad , \quad I_{1/3} \rightarrow -J_{1/3}$$

Asymptotically

$$I_{-1/3} - I_{1/3} \rightarrow \frac{2}{\sqrt{\frac{\pi \xi_2}{2}}} \sin \frac{\pi}{3} \frac{1}{\sqrt{\frac{\pi \xi_2}{2}}} e^{-\xi_2}$$

$$J_{-1/3} + J_{1/3} \rightarrow \frac{2}{\sqrt{\frac{\pi\xi_1}{2}}} \sin \frac{\pi}{3} \cos \left( \xi_1 - \frac{\pi}{4} \right)$$

$$I_{-1/3} + I_{1/3} \rightarrow \frac{1}{\sqrt{\frac{\pi\xi_2}{2}}} e^{\xi_2}$$

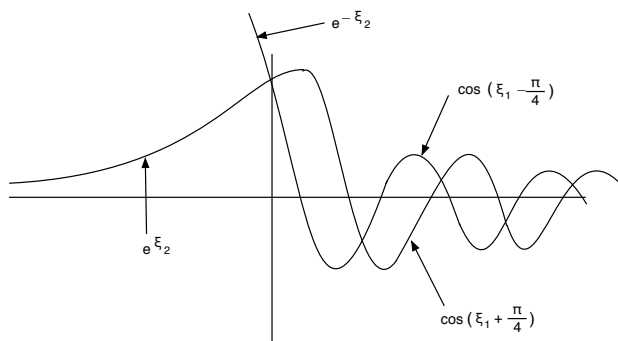
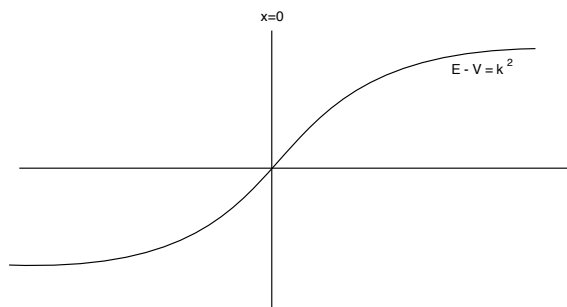
$$J_{-1/3} - J_{1/3} \rightarrow \frac{1}{\sqrt{\frac{\pi\xi_1}{2}}} \cos \left( \xi_1 + \frac{\pi}{4} \right)$$

$$J_n(\xi) \rightarrow \frac{1}{\sqrt{\frac{\pi\xi_1}{2}}} \cos \left( \xi_1 + \frac{\pi}{4} - \frac{n\pi}{2} \right)$$

These imply that

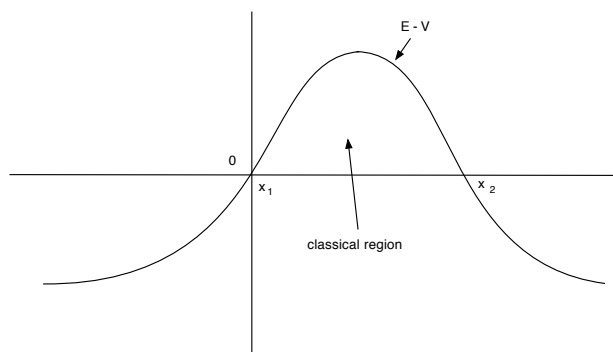
$$\frac{1}{2} k^{-1/2} e^{-\xi_2} \xrightarrow[\text{join smoothly}]{} k^{-1/2} \cos \left( \xi_1 - \frac{\pi}{4} \right)$$

$$k^{-1/2} e^{\xi_2} \xleftarrow[\text{join smoothly}]{} k^{-1/2} \cos \left( \xi_1 + \frac{\pi}{4} \right)$$



$-\pi/4 \rightarrow$  phase for a function which naturally joins an exponentially decaying function!

### Energy Levels



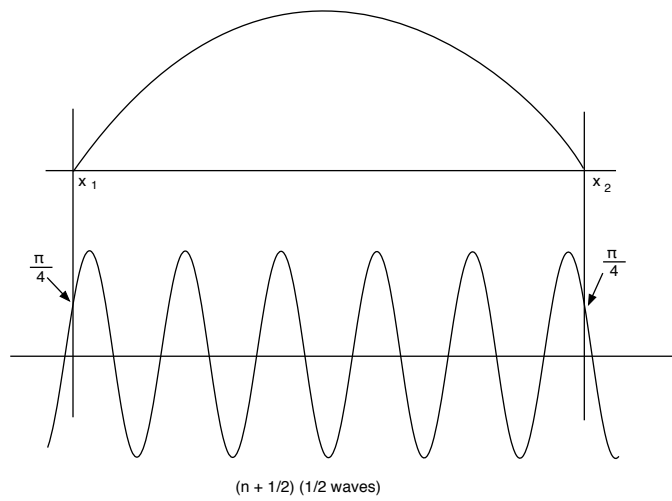
In classical region  $\rightarrow$  wave function oscillatory. In outside region  $\rightarrow$  wave function is exponentially decaying.

$$\begin{aligned} \cos\left(\int_{x_1}^{x_2} k(x') dx' - \frac{\pi}{4}\right) & \text{ possible wave function} \\ &= \pm \cos\left(\int_{x_1}^{x_2} k(x') dx' - \frac{\pi}{4}\right) \\ &= \pm \cos\left(\int_{x_1}^{x_2} k(x') dx' + \frac{\pi}{4}\right) \\ & -\frac{\pi}{4} + \int_{x_1}^{x_2} = \int_{x_2}^{x_1} + \frac{\pi}{4} + n\pi \end{aligned}$$

or

$$\int_{x_1}^{x_2} = \left(n + \frac{1}{2}\right)\pi \rightarrow \text{existence of bound state}$$

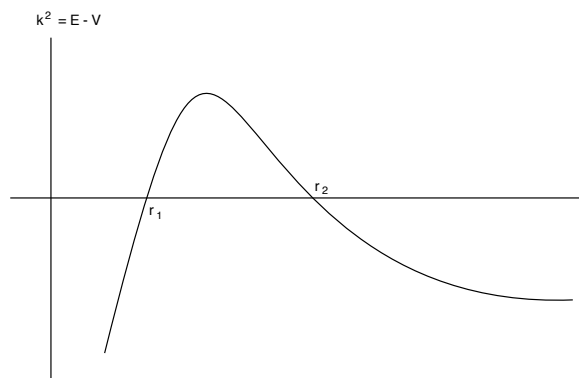
i.e., find  $x_1, x_2$ , calculate  $\int \rightarrow$  must  $= (n + 1/2)\pi$  for a bound state to exist.



Oscillator → works exactly.

H-atom:

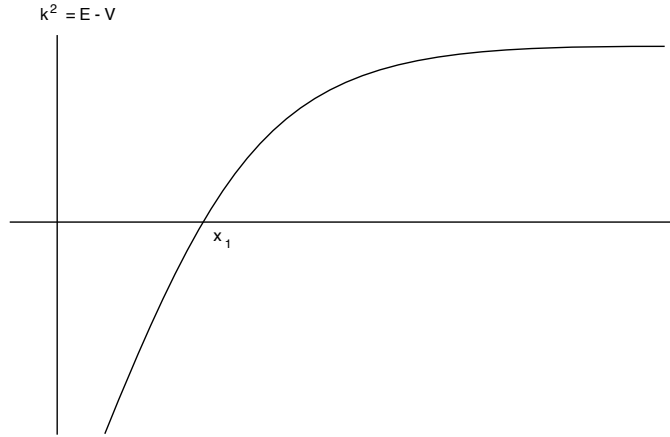
$$k^2 = -\frac{\ell(\ell+1)}{r^2} + \frac{2me^2}{\hbar^2 r} - \frac{2m|E|}{\hbar^2}$$



**Free Particle**

$$u = j_\ell(k_0 r)$$

$$E > 0 \quad , \quad k^2(r) = k_0^2 - \frac{\ell(\ell+1)}{r^2}$$



so that

$$\cos\left(\int_{x_1}^r k dr' - \frac{\pi}{4}\right) \rightarrow$$

phase of wave function for all  $r \rightarrow$  asymptotic form of Bessel function

$$\cos\left(k_0 r - (\ell + 1)\frac{\pi}{2}\right)$$

but we get

$$\cos\left(k_0 r - (\sqrt{\ell(\ell + 1)} + 1/2)\frac{\pi}{2}\right)$$

We can make this correct by replacing  $\ell(\ell + 1) \rightarrow (\ell + 1/2)^2$ ; this gives exact results here.  $\rightarrow$  suggest that we replace same quantities in H-atom problem  $\rightarrow$  exactly correct energy levels!

### Phase Shifts

$$U - \frac{2\mu}{\hbar^2} V$$

WKB wave function for large  $r$

$$\cos\left(\int_{r_1}^r \sqrt{k_0^2 - U - \frac{(\ell + 1/2)^2}{r'^2}} dr' - \frac{\pi}{4}\right)$$

(free particle  $\rightarrow$  no  $U$  term). Then compare phases of cosines  $\rightarrow$  phase shift (as we have defined it) or

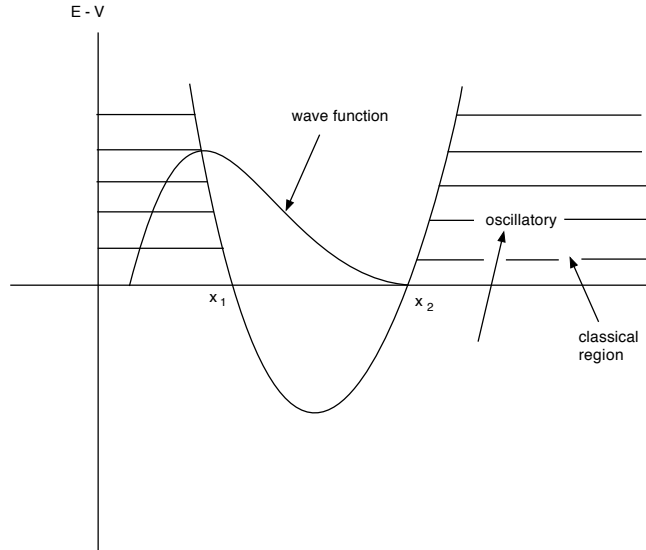
$$\delta_\ell = \lim_{r \rightarrow \infty} \left[ \int_{r_1}^r \sqrt{k_0^2 - U - \frac{(\ell + 1/2)^2}{r'^2}} dr' - \int_{r_0}^r \sqrt{k_0^2 - \frac{(\ell + 1/2)^2}{r'^2}} dr' \right]$$

i.e., the two terms have different turning points with and without  $U$ .



For large  $\delta_\ell \rightarrow$  always good or  $ka \gg 1$  (i.e., when Rayleigh series cannot be summed). Not good for small phase shifts, i.e.,  $\ell > k_0 a$ .

### Potential Barrier



We have for the barrier

$$A = \frac{\text{Amplitude}(x > x_2)}{\text{Amplitude}(x < x_1)} = \frac{1}{2} \exp - \int_{x_1}^{x_2} k(x') dx'$$

and transmission coefficient of the barrier is given by  $T = |A|^2$ .

### Connection with Classical Theory

Consider the stationary state conditions with  $k = p/\hbar$ .

Classical motion is oscillator between  $x_1$  and  $x_2$ . The full period is

$$2 \int_{x_1}^{x_2} p dx = \left(n + \frac{1}{2}\right) \hbar = \text{Bohr-Sommerfeld quantum condition}$$

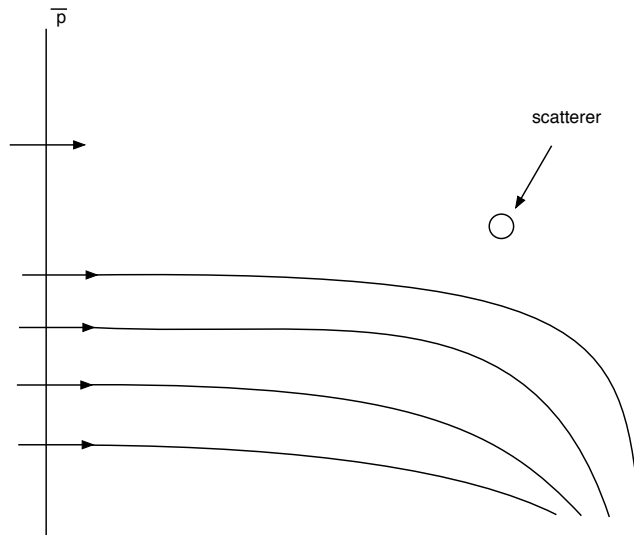
except for the factor of  $1/2!$

3-Dimensions:

$$\psi = e^{-iEt/\hbar + iS/\hbar}$$

$$\frac{1}{2m} (\nabla S)^2 - (E - V(r)) - \frac{i\hbar}{2m} \nabla^2 S = 0$$

Limit  $\hbar \rightarrow 0$  neglecting last term  $\rightarrow$  classical Hamilton-Jacobi equation where  $\nabla S = \vec{p}$ .



We can calculate  $S$  by integrating along trajectories  $\rightarrow$  phases everywhere (good for high energies, slight deflections and non-crossing trajectories). We know phases as particles pass nucleus  $\rightarrow$  construction of a new wave front, not of constant phase  $\rightarrow$  use of Kirchoff's theorem!

### Time-Dependent Perturbations

$$H = H_0 + H'(t)$$

$$\psi = \sum_n a_n(t) u_n e^{-iE_n t/\hbar}$$

Insert in Schrödinger's equation  $\rightarrow$

$$i\hbar \dot{\psi} = (H_0 + H')\psi$$

$$\begin{aligned} i\hbar \sum_n (\dot{a}_n + E_n a_n) u_n e^{-iE_n t/\hbar} \\ = \sum_n (a_n \underbrace{H_0 u_n}_{E_n u_n} + a_n H' u_n) e^{-iE_n t/\hbar} \end{aligned}$$

Using orthogonality

$$i\hbar \dot{a}_k = \sum_n a_n H'_{kn} e^{-i\omega_{kn} t}$$

$$\omega_{kn} = \frac{E_k - E_n}{\hbar}$$

$$H'_{kn} = \int u_k^* H' u_n d\tau$$

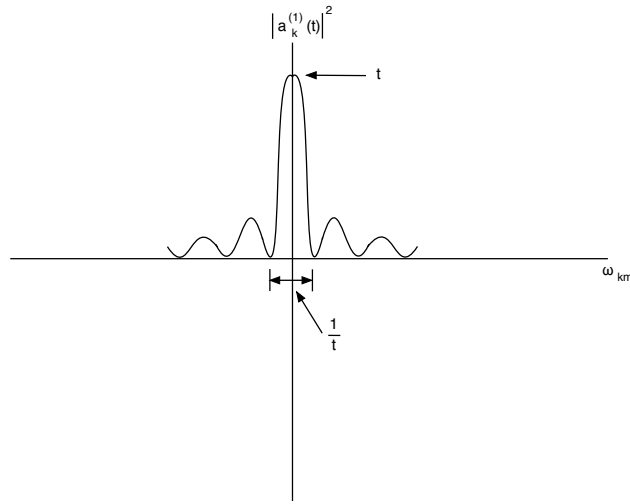
This implies a set of linear differential equations. They are completely equivalent to the original Schrödinger equation (exactly), i.e., if solved exactly!

Usual approximation:  $a_n$  is expanded in a power series in  $H'$ .

$$\begin{aligned}\dot{a}_k^{(0)} &= 0 \quad , \quad a_k^{(0)} = \text{constant} \\ \dot{a}_m^{(0)} &= 1 \quad \text{all others} = 0 \\ \dot{a}_k^{(1)} &= \frac{1}{i\hbar} H'_{km} e^{i\omega_{km}t} \quad , \quad H'_{km} \neq f(t) \\ \rightarrow a_k^{(1)}(t) &= \frac{-1}{\hbar\omega_{km}} H'_{km} (e^{i\omega_{km}t} - 1)\end{aligned}$$

The last factor insures that  $a_k^{(1)}(0) = 0$ .

$$\left| a_k^{(1)}(t) \right|^2 = \frac{1}{(\hbar\omega_{km})^2} |H'_{km}|^2 \left( 4 \sin^2 \frac{1}{2} \omega_{km} t \right)$$



Therefore, after long times we get  $a_k$  substantially different from 0 only when  $\omega_{km} \approx 0$  or  $E_k \approx E_n$ . For when  $\omega_{kn}$  not near 0  $\rightarrow$  rapid decay of the state. All this  $\rightarrow$  that good results come from work in the continuous spectrum.

$$\rho(k) = \text{density of states} \propto E_k (\rightarrow \text{energy interval})$$

$$\begin{aligned}\omega = \text{transition probability} &= \frac{1}{t} \int_{E_m - \epsilon}^{E_m + \epsilon} |A_k(t)|^2 \rho(k) dE_k \quad \left( \sim \left( t^2 \frac{1}{t} \right) \frac{1}{t} \right) \\ &= \frac{2\pi}{\hbar} |H'_{km}|^2 \rho(E_k)\end{aligned}$$

This is Fermi's "Golden Rule".

Application:

Scattering in a box of side  $L \rightarrow$

$$k_x = \frac{2\pi}{L} n_x$$

$\rightarrow$  essentially a continuum of states for a very large  $L$ ! The number of state is given by

$$\left(\frac{L}{2\pi}\right)^3 dk_x dk_y dk_z$$

where

$$dk_x dk_y dk_z = k^2 dk d\Omega \rightarrow \text{volume element in } k\text{-space}$$

The number of states per unit energy  $= \rho(E_k)$  and is given by

$$\rho(E_k) = \left(\frac{L}{2\pi}\right)^3 \frac{k^2 dk}{dE_k} d\Omega$$

In classical mechanics

$$\frac{dE}{dp} = v$$

Then

$$p = \hbar k \rightarrow \rho(E_k) = \left(\frac{L}{2\pi}\right)^3 \frac{1}{\hbar} \frac{k^2}{v} d\Omega$$

Here  $k$  and  $v$  refer to the final state of the system, i.e., after the perturbation has been applied.

Incident flux:

$$\psi_{incident} = L^{-3/2} e^{i\vec{k} \cdot \vec{r}}$$

$$\text{incident flux} = L^{-3} v_0 \quad v_0 = \text{velocity of incident particle}$$

$$\sigma = \frac{\omega}{L^{-3} v_0} = \frac{2\pi}{\hbar^2} L^6 \frac{1}{(2\pi)^3} \frac{k^2}{v v_0} |H'_{km}|^2 d\Omega$$

$$H'_{km} \leftrightarrow \psi \text{ with } L^{-3/2} \text{ factors}$$

Therefore put  $L^3$  term with  $H'_{km}$  term

$$\sigma = \left(\frac{k}{2\pi\hbar}\right)^2 \frac{d\Omega}{v v_0} |L^3 H'_{km}|^2$$

Since

$$\int \psi^* H' \psi d\tau = L^{-3}$$

$\rightarrow$  cancellation of  $L \rightarrow$  no  $L$  dependence as indeed should happen!

$\sigma$  is symmetric in  $v, v_0$  and  $H'_{km}$ , but is not symmetric in  $k^2$ . Therefore

$$\frac{\sigma_{forward}}{\sigma_{reverse}} = \frac{\sigma_{m \rightarrow k}}{\sigma_{k \rightarrow m}} = \frac{k_k^2}{k_m^2} = \frac{k_k^2}{k_0^2} = \frac{p_k^2}{p_0^2}$$

The principle of detailed balancing

$$\rightarrow = \frac{\lambda_0^2}{\lambda_k^2}$$

Example:

$$h\nu + DP + N$$

is easily observable and reversible. This implies if we know cross-sections one way, then can predict for other way. Now

$$\frac{k}{v} = \frac{m}{\hbar}$$

Thus, in Born approximation

$$\sigma = \left( \frac{m}{2\pi\hbar^2} \right)^2 \frac{v}{v_0} d\Omega |L^3 H'_{km}|^2$$

**Perturbation by a Time-dependent Potential -  $A \sin \omega t$**

$$H'_{km} = H'^{(0)}_{km} \sin \omega t$$

This implies that

$$a_k(t) = \frac{i}{2\hbar} H'^{(0)}_{km} \left[ \frac{e^{i(\omega_{km} + \omega)t} - 1}{\omega_{km} + \omega} - \frac{e^{i(\omega_{km} - \omega)t} - 1}{\omega_{km} - \omega} \right]$$

Thus, there are two kinds of transitions. Therefore, for large  $t$ ,  $\omega_{km} = \pm\omega$  or  $E_k - E_m = \pm\hbar\omega$ .

Atom interacting with a light wave

$$eFz \sin \omega t \quad (\text{polarized in the } z\text{-direction})$$

$\rightarrow$  induced transitions  $\pm\hbar\omega \rightarrow$  Bohr frequency condition

We started by assuming deBroglie wavelength. We assumed particle could be represented by wave function  $\rightarrow$  can construct wave packet!

These alone enabled us to determine the time dependence of the wave function, i.e., that under perturbation as given we must get Bohr relation (not exact, since high probability of existence for small spread in  $\omega$ ). Therefore, we never assume it! Now

$$|H'^{(0)}_{km}|^2 \sim F^2 |z_{km}|^2$$

→ optical transitions (caused by light) ~ in intensity to the square of the matrix element between the initial and final states (sum rules) → stimulated emission - i.e., due to presence of light waves.

2nd-order perturbation: (as in Schiff) - time independent perturbation

$$a_k^{(2)} = \frac{1}{\hbar^2} \sum_n \frac{H'_{kn} H'_{nm}}{\omega_{nm}} \left[ \frac{e^{i\omega_{km}t} - 1}{\omega_{km}} - \underbrace{\frac{e^{i\omega_{kn}t} - 1}{\omega_{kn}}}_{\text{term (A)}} \right]$$

Term (A) does not satisfy conservation of energy due to the fact that we have turned on the perturbation sharply at  $t = 0$  and since it is well-defined in time → breakdown in energy relations (Heisenberg principle) (this is purely mathematical!!!).

In an experiment perturbation is applied gradually, i.e., over many periods of natural motion of the atom.

Case I:  $H'$  - no energy conserving transitions →  $\omega_{nm}$  is never small → forget second term. We thus get old formula

$$H'_{km} \rightarrow \sum_n \frac{H'_{kn} H'_{nm}}{\omega_{nm}}$$

It is possible that  $H'$  causes an energy conserving transition in 2nd order (no need to worry about degeneracy);  $n$  = is an intermediate state;  $m$  is the initial state;  $k$  is the final state.

Case II: energy conserving transitions exist

$$\int \frac{H'_{kn} H'_{nm}}{\omega_{nm} - i\epsilon} \rho(n) dE_n$$

where

$$\rho(n) = \frac{\text{number of states}}{\text{unit energy}}, \quad \epsilon > 0, \text{ small, real}$$

$$a_k^{(2)} = \frac{1}{\hbar^2} \sum_n \frac{H'_{kn} H'_{nm}}{\omega_{nm}} \left[ \frac{e^{i\omega_{km}t} - 1}{\omega_{km}} - \frac{e^{i\omega_{kn}t} - 1}{\omega_{kn}} \right]$$

$\rho(n)$  = number of states per unit energy.

$$\sum_n \rightarrow \int \rho(n) d\omega_{nm} \hbar$$

Make assumption

$$\frac{E_m t}{\hbar} \gg 1$$

Then

$$\begin{aligned}\omega_{km} &= \frac{E_k - E_m}{\hbar} \sim \frac{1}{t} \rightarrow \text{condition for factor to be large} \\ &\rightarrow E_k - E_m \ll E_m \\ &\int_{-c/t}^{c/t} d\omega_{nm} + \underbrace{\left( \int_{-\infty}^{-c/t} + \int_{c/t}^{\infty} \right)}_{f'}\end{aligned}$$

$f' \rightarrow$  contains all but infinitesimal amount of energy spectrum = principal value ( $c \gg 1$ ). Thus,

$$\frac{c}{t} \ll \frac{E_m}{\hbar}$$

Therefore

$$1 \ll c \leq \frac{E_m t}{\hbar}$$

$\omega_{kn}$  term  $\frac{1}{c}$  1st term  $\rightarrow$  neglect in  $f'$

$$\int_{-c/t}^{c/t} d\omega_{nm} \text{ has no singularity at } \omega_{nm} = 0$$

$E_n, \rho(n)$  change very little in this interval from condition

$$\frac{c}{t} \ll \frac{E_m}{\hbar}$$

and same for the matrix elements. Therefore all factors not containing  $\omega_{nm}$  can be considered constant wrt terms with  $\omega_{nm}$  !! Therefore

$$\int_{-c/t}^{c/t} d\omega_{nm} = \frac{\rho(n)}{\hbar^2} H'_{kn} H'_{nm} \int_{-c/t}^{c/t} \frac{d\omega_{nm}}{\omega_{nm}} \left[ \underbrace{\frac{e^{i\omega_{km}t} - 1}{\omega_{km}}}_{\text{constant wrt } \omega_{nm}} - \underbrace{\frac{e^{i\omega_{kn}t} - 1}{\omega_{kn}}}_{\text{neglect}} \right]$$

We replace the integral with an integral around contour - on semicircle as shown

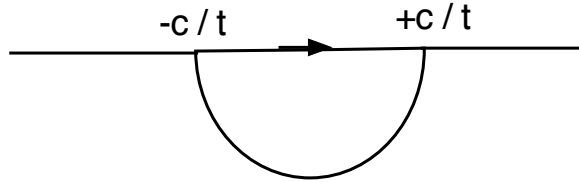
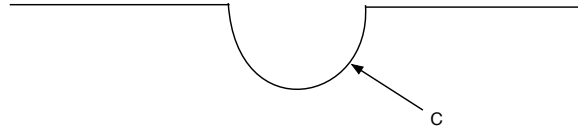


Figure 1: A

hence

$$\int_{\text{semi}} \frac{d\omega_{nm}}{\omega_{nm}} = \pi i$$

Therefore  $H'_{km} = \text{principal value} + \pi i$  (integrand for  $\omega_{nm} = 0$ ). This is the same result as if we integrated entire integrand on contour below.



Therefore

$$H'_{km}(2) = \int_C \frac{d\omega_{nm}}{\omega_{nm}} \rho(n) H'_{kn} H'_{nm}$$

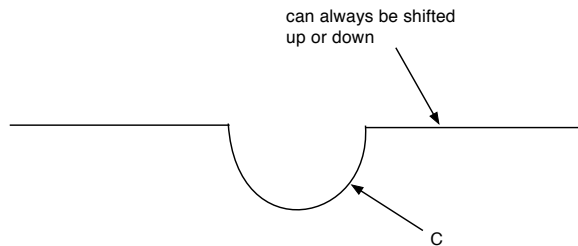
which is the same as ordinary 2nd order perturbation theory!

$$\frac{dE_n}{E_n - E_m} \rightarrow \frac{dE_n}{E_n - E_m - i\epsilon}$$

since we want the denominator to be negative imaginary where usual denominator vanishes; we get same result in ordinary perturbation theory if we replace  $E_m$  by  $E_m + i\epsilon$ .

The principal value expression

$$PV \int f(z) \frac{dz}{z} + i\pi f(0) = \int_C f(z) \frac{dz}{z} \quad , \quad z = z' - i\epsilon, z' \text{ real}$$



$m$  state in the past  $\rightarrow k$  state in the future. Mathematical theory for any perturbation if we replace  $E_m$  by  $E_m + i\epsilon$ !

**Inelastic Scattering** - Electron scattered by electron in H-atom.

$$H_0 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{r_2}$$



where  $r_1 \rightarrow$  incident electron;  $r_2 \rightarrow$  electron in H-atom.

$$H' = \frac{e^2}{r_{12}} - \frac{e^2}{r_1}$$

$$L^{-3/2} e^{i\vec{k}_0 \cdot \vec{r}_1} u_{100}(\vec{r}_2)$$

$$L^{-3/2} e^{i\vec{k} \cdot \vec{r}_1} u_n(\vec{r}_2)$$

Energy conservation  $\rightarrow$

$$k^2 = k_0^2 - \frac{2m}{\hbar^2} [E_n - E_1]$$

$$H'_{km} = L^{-3} \int u_n^*(\vec{r}_2) e^{-i\vec{k} \cdot \vec{r}_1} \left( \frac{e^2}{r_{12}} - \frac{e^2}{r_1} \right) e^{i\vec{k}_0 \cdot \vec{r}_1} u_1(\vec{r}_2) d\tau_1 d\tau_2$$

The exponential terms combine into

$$e^{i\vec{q} \cdot \vec{r}_1} \quad \vec{q} = \vec{k}_0 - \vec{k}$$

and the  $e^2/r_1$  term gives no contribution due to the orthonormal  $u$ s. Then

$$\sigma(\theta) = \frac{k}{k_0} |L^3 H'_{km}|^2 \left( \frac{m}{2\pi\hbar^2} \right)^2$$

$$\begin{aligned} L^3 H'_{km} &= \int u_n^*(\vec{r}_2) u_1(\vec{r}_2) e^{i\vec{q} \cdot \vec{r}_1} V(r_{12}) d\tau_1 d\tau_2 \\ &= \int \underbrace{e^{i\vec{q} \cdot (\vec{r}_1 - \vec{r}_2)} V(r_{12})}_{\text{Fourier transformation}} d\tau_{12} e^{i\vec{q} \cdot \vec{r}_2} u_n^*(\vec{r}_2) u_1(\vec{r}_2) d\tau_2 \end{aligned}$$

$$\tilde{V}(q) = \int V(r) e^{i\vec{q} \cdot \vec{r}} d\tau = \text{Fourier transformation}$$

$$L^3 H'_{km} = \tilde{V}(q) \underbrace{\int e^{i\vec{q} \cdot \vec{r}_2} u_n^*(\vec{r}_2) u_1(\vec{r}_2) d\tau_2}_{F_{1n}(q) = \text{form factor}}$$

If

$$V(r) = \frac{e^2}{r} \rightarrow \tilde{V}(q) = \frac{4\pi e^2}{q^2}$$

$$\sigma(\theta) = \frac{k}{k_0} \left( \frac{m}{2\pi\hbar^2} \frac{4\pi e^2}{q^2} \right)^2 |F_{1n}(q)|^2 = \underbrace{\frac{4k}{k_0 a_0^3 q^4}}_{\text{Rutherford factor}} |F_{1n}(q)|^2$$

$$q^2 = k_0^2 - k^2 - 2k_0 k \cos \theta$$

$$q_{min} = k_0 - k \quad , \quad q_{max} = k_0 + k$$

$$k_0 \gg \frac{2m}{\hbar^2} (E_n - E_1) \rightarrow q_{max} \approx 2k_0$$

$$q_{min} = \frac{k_0^2 - k^2}{k_0 + k} \approx \frac{\frac{2m}{\hbar^2} \Delta E}{2k_0} = \frac{\Delta E}{\hbar v_0}$$

$$q dq = k_0 k \sin \theta d\theta$$

$$2\pi\sigma(\theta) \sin \theta d\theta = \frac{8\pi k q dq}{k_0^2 k q^4 a_0^2} |F_{1n}(q)|^2$$

$F_{in}$ : For small  $q$

$$1 + iqx_2 - O(q^2) \rightarrow F_{in}(q) = iq\langle x \rangle_{n1} + O(q^2)$$

For large  $q$ :  $F_{1n}$  small wrt 1 when  $qa > 1$ . Thus,

$$\begin{aligned} \sigma_T &= \int \sigma(\theta) d\Omega = \frac{8\pi}{k_0^2 a_0^2} \int_{q_{min}}^{1/a} \frac{q dq}{q^4} (q^2 |x_{n1}|^2) \\ &= \frac{8\pi}{k_0^2 a_0^2} |x_{n1}|^2 \ln \frac{1}{aq_{min}} \\ &= \frac{8\pi}{k_0^2 a_0^2} |x_{n1}|^2 \ln \frac{\hbar v_0}{a_0 \Delta E} \end{aligned}$$

where

$$\Delta E = \frac{e^2}{2a_0}$$

Thus,

$$\sigma_T = \frac{8\pi}{k_0^2 a_0^2} |x_{n1}|^2 \ln \frac{2\hbar v_0}{e^2} = \frac{8\pi}{k_0^2 a_0^2} |x_{n1}|^2 \ln 274\beta$$

with

$$\frac{|x_{21}|^2}{a_0^2} = \frac{2^{18}}{3^{12}} \approx \frac{1}{2}$$

$H'(t)$  is slowly varying;

$$\begin{aligned} &E_n(t); e^{-i \int^t E_n(t') dt' / \hbar} \\ \dot{a}_k &= - \sum_n a_n e^{i \int \omega_{kn}(t') dt'} \int \underbrace{u_k^* \frac{\partial u_n}{\partial t}}_{-\frac{1}{\hbar \omega_{kn}} \left( \frac{\partial H}{\partial t} \right)_{kn}} d\tau \end{aligned}$$

Transition probability

$$= |a_k|^2 \sim \frac{1}{\omega_{kn}} \frac{\left( \frac{\partial H}{\partial t} \right)_{kn}}{E_k - E_n} \rightarrow \frac{\text{change of } H \text{ during 1 period}}{\text{energy difference}}$$

**Instantaneous Changes**

$$\begin{aligned} &H_1 \rightarrow H_2 \\ E_m^{(1)} u_m^{(1)} &= \sum_n b_n u_n^{(2)} e^{-i E_n^{(2)} t / \hbar} \\ b_n &= \int u_n^{(2)} u_m^{(1)} d\tau \\ \text{example: } &H^3 \rightarrow H e^3 + \beta \end{aligned}$$