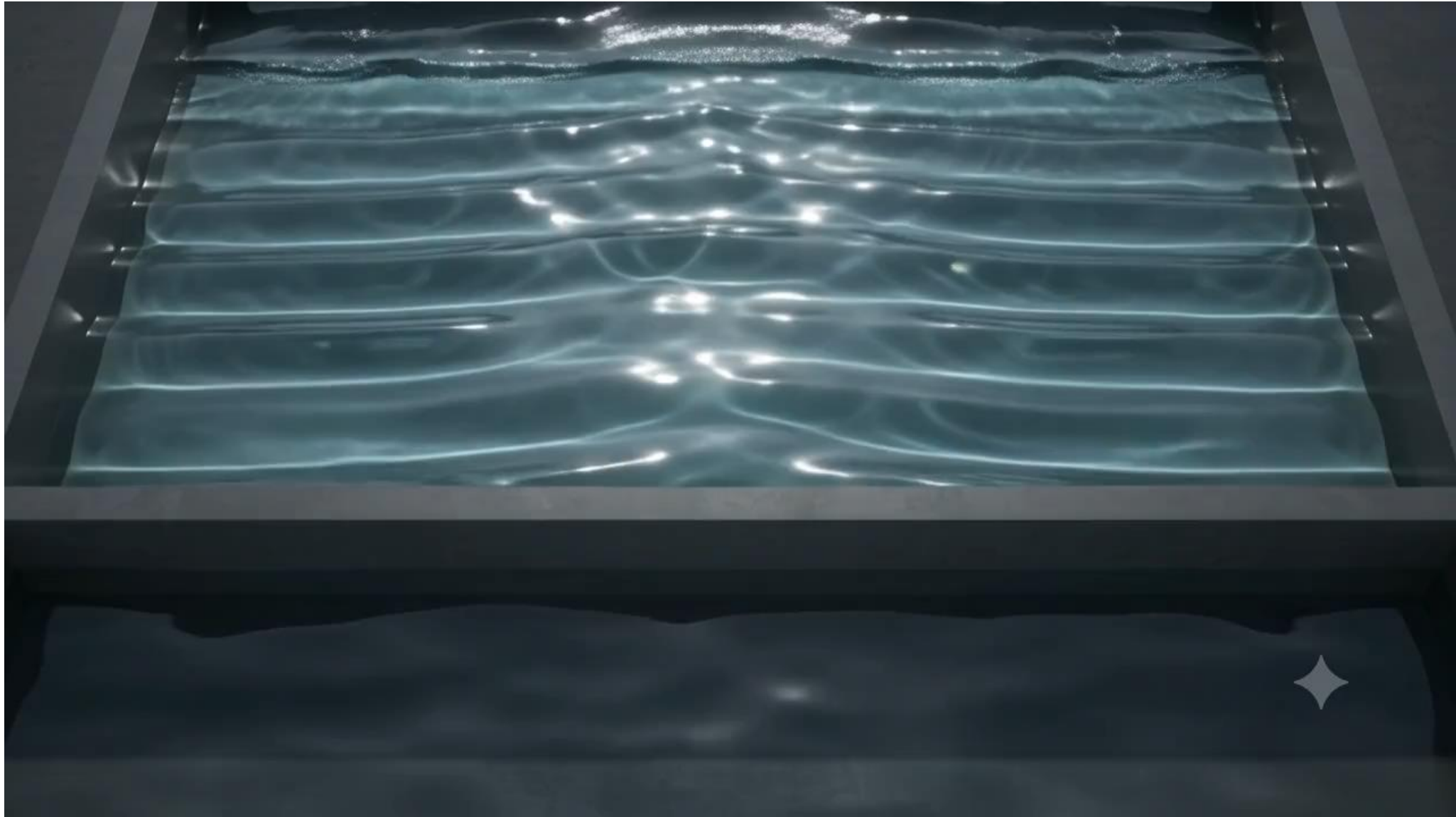


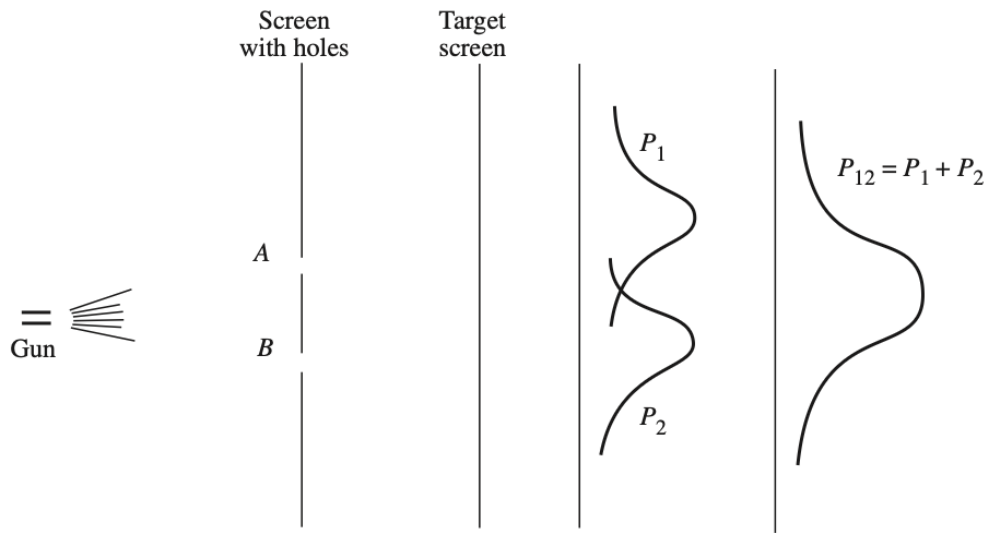
Electrons as Waves



Physical description of a wave

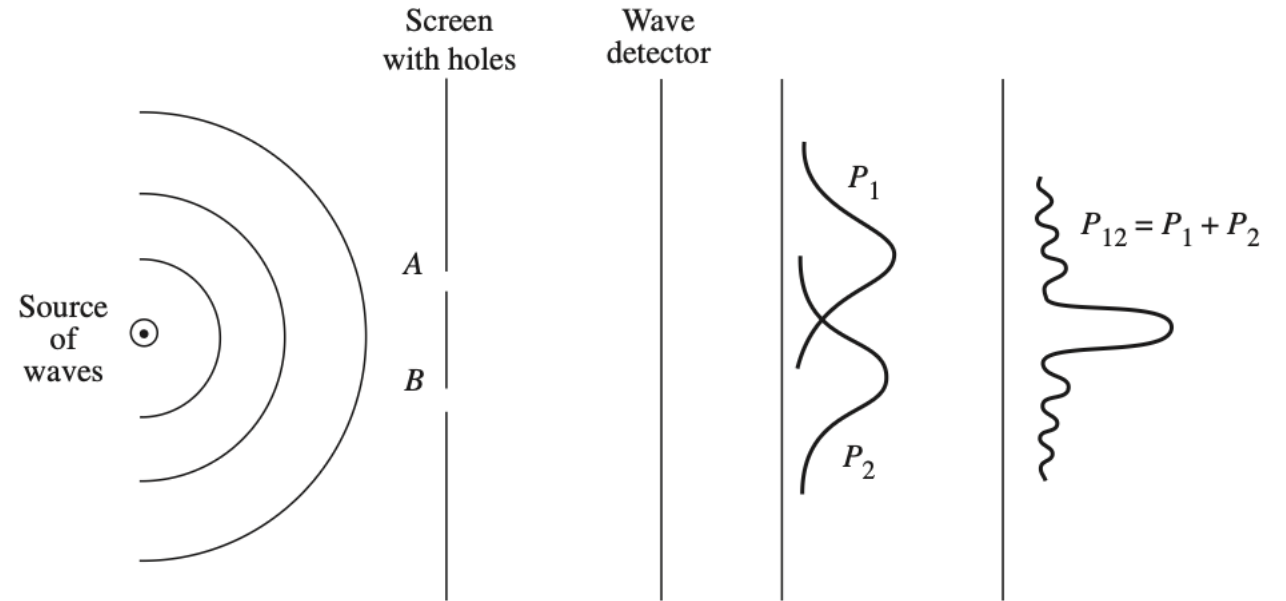
- Waves are described by a function $F(r, t)$ that maps the value (scalar) or a vector at each point in space and time.
 - Vibrations in a solid
 - Amplitude of water oscillations
 - Electromagnetic field oscillations
- Lets take an example of heat propagating in a solid:

Properties of particles and waves



Particles shot from gun

$$P = P_1 + P_2$$



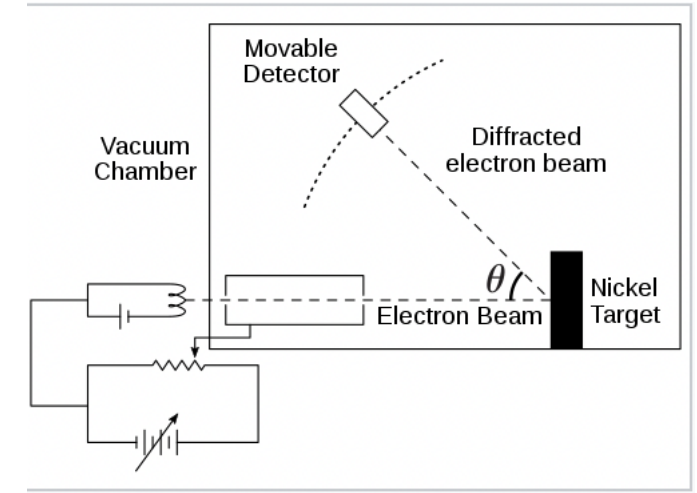
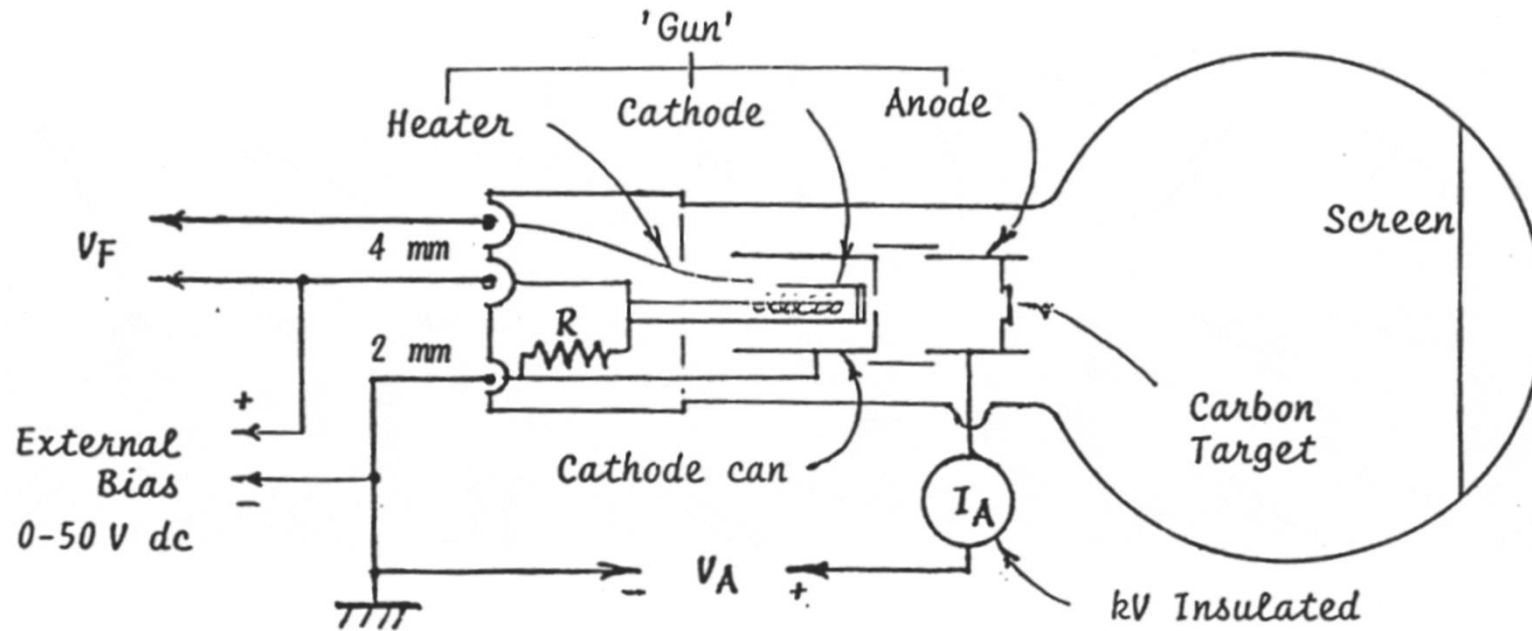
Water waves in a tub

$$P_1 = |h_1|^2 \quad \text{and} \quad P_2 = |h_2|^2$$

$$P = |h_1 + h_2|^2 \neq P_1 + P_2$$

$$P = |h_1|^2 + |h_2|^2 + 2|h_1||h_2|\cos\delta$$

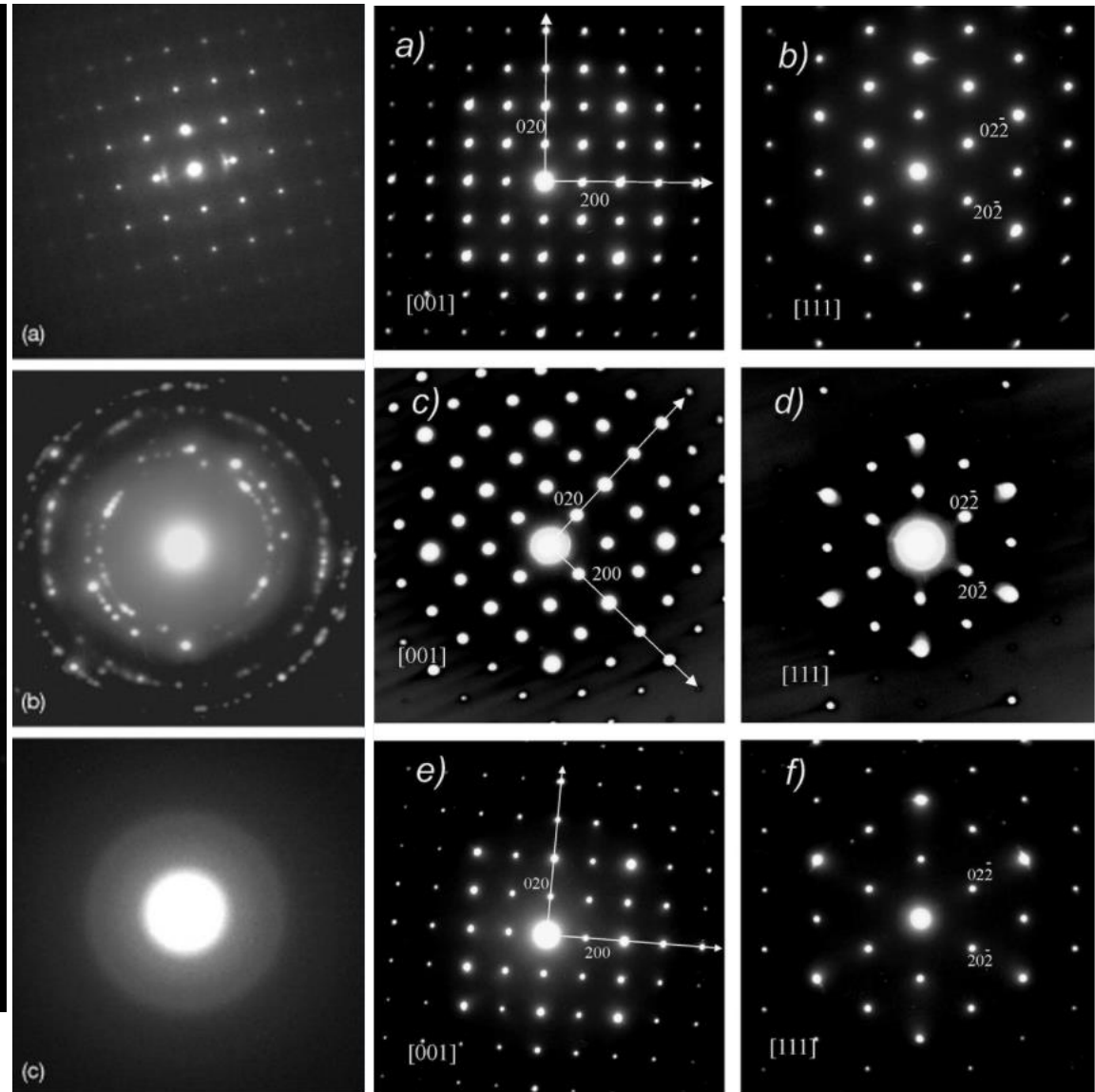
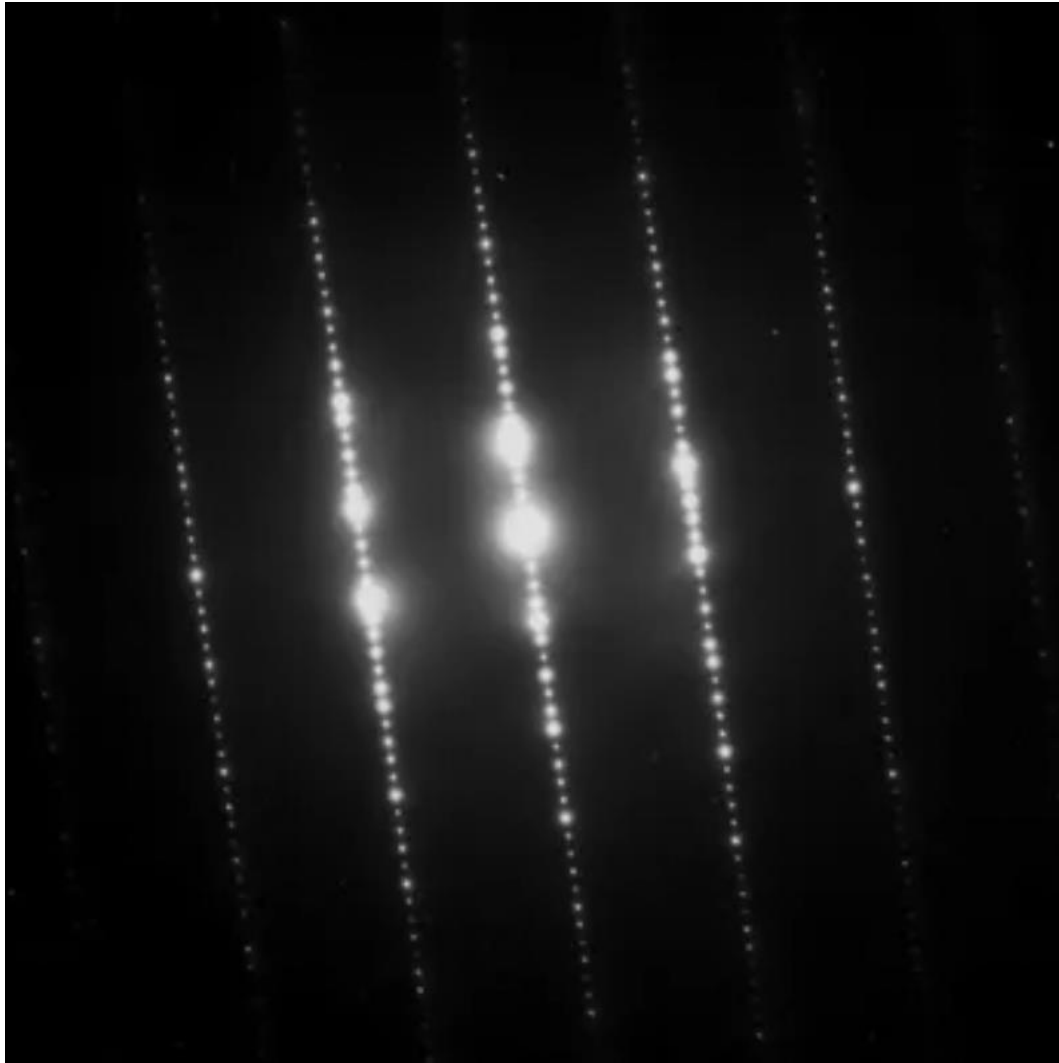
Is electron a particle or a wave ?



Davisson and Germer

What do you see on the screen ?

Electrons are definitely waves!



But, wait a minute!

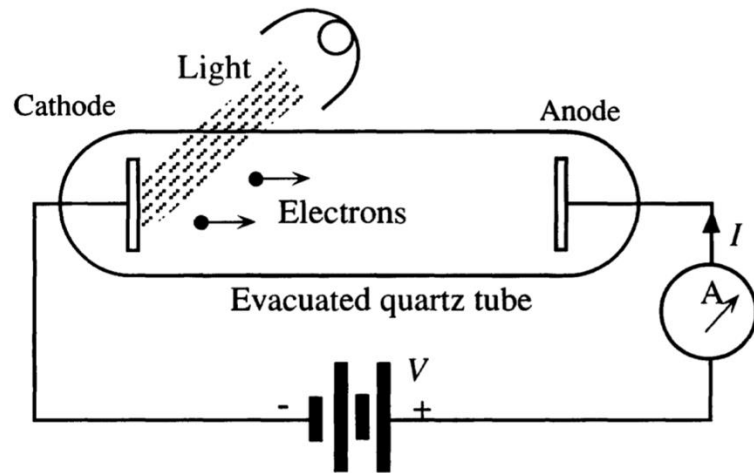
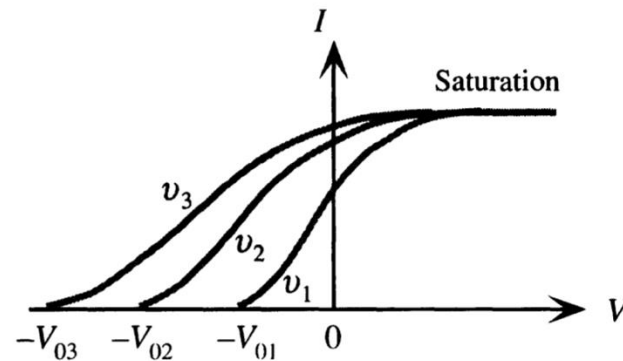
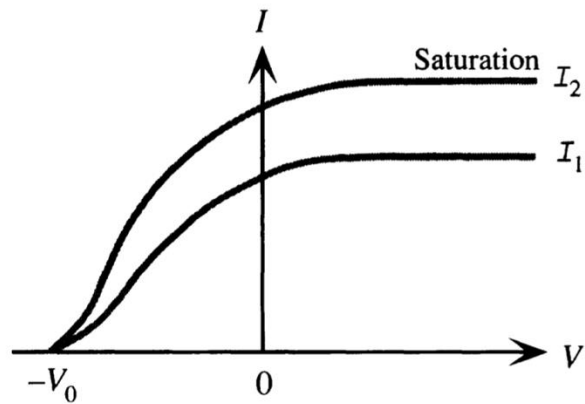
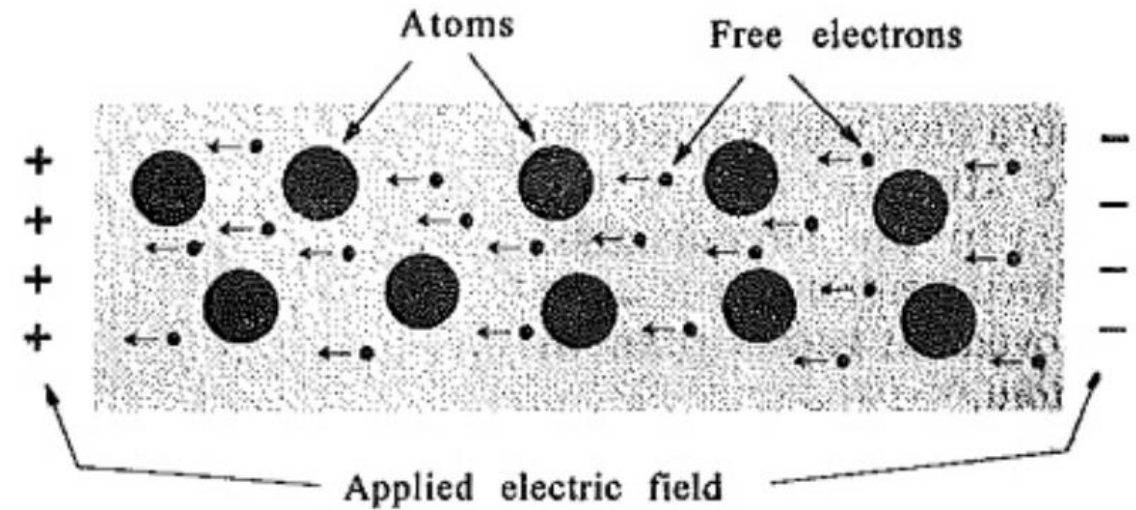


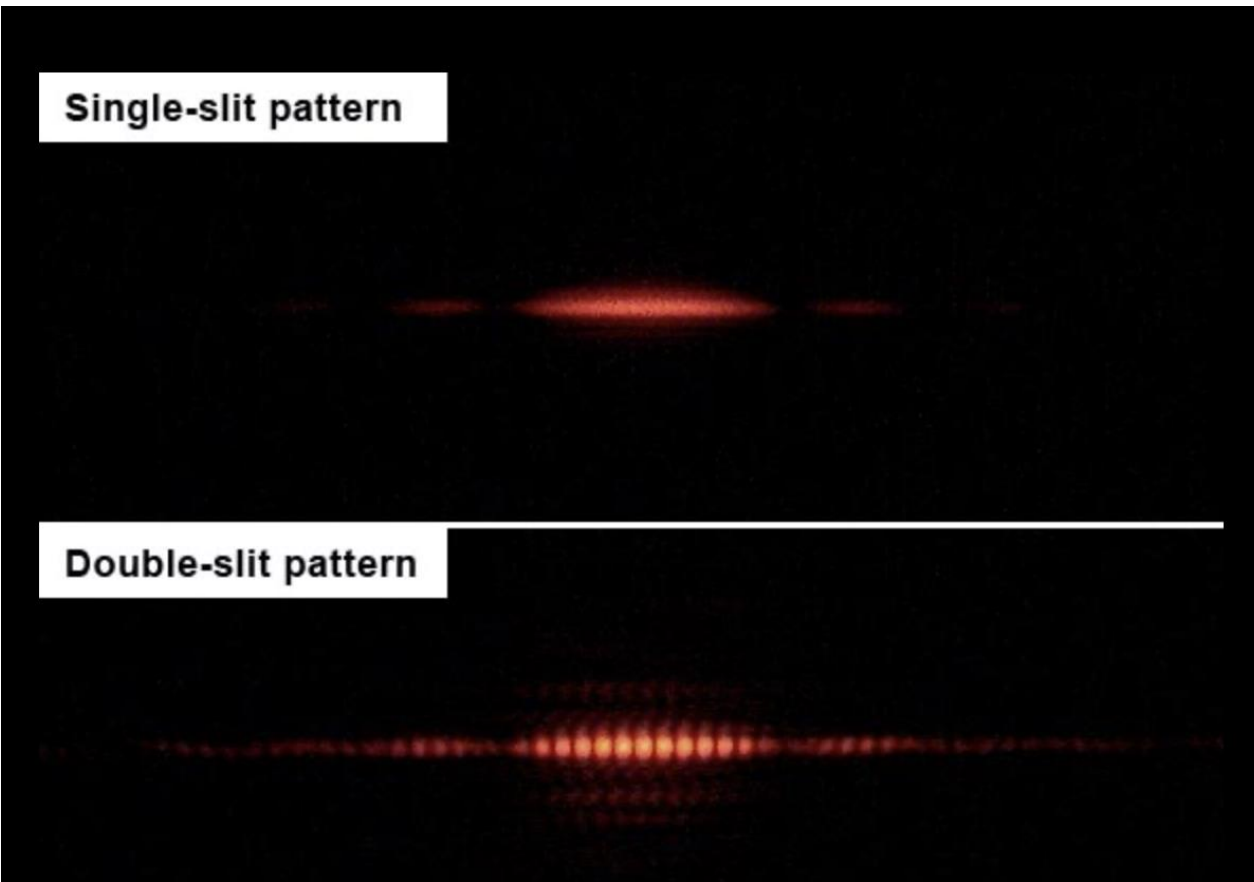
Figure 3.4 The photoelectric effect.



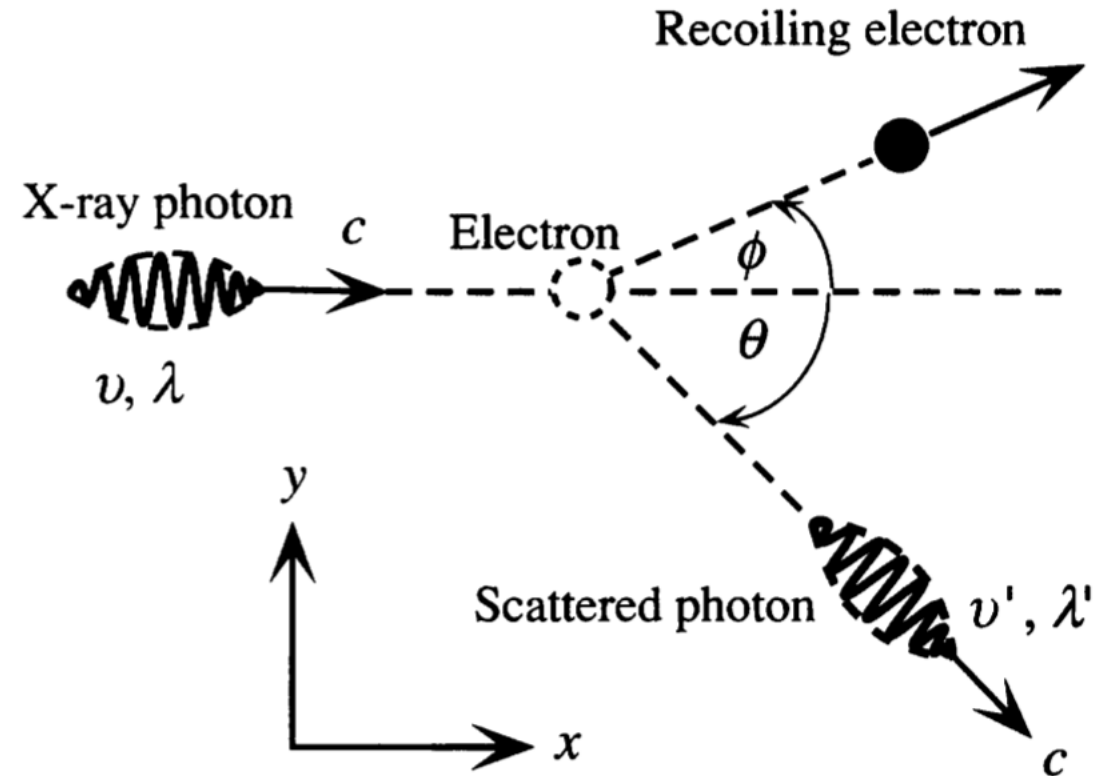
It is a particle! As well

Duality of light

Young's double slit



Compton scattering (1924)



$$\lambda - \lambda' = \frac{h}{m_e c} (1 - \cos \theta)$$

R. Feynman: "All of quantum mechanics can be gleaned by thinking through this single experiment"

De Broglie Correlation

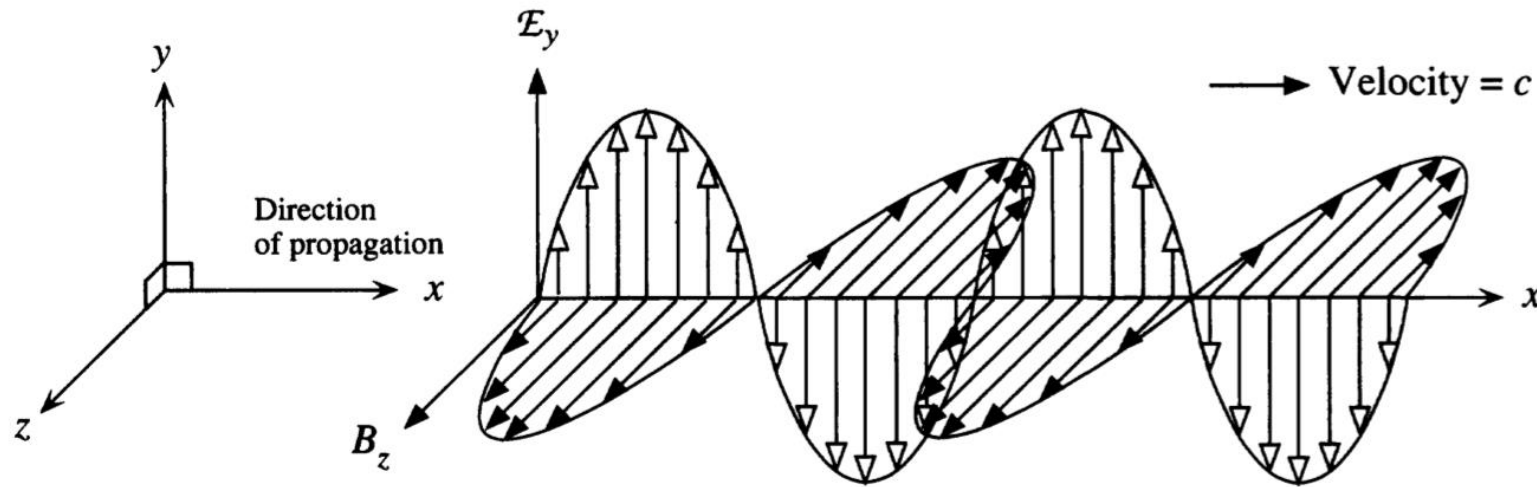
Any particle moving with a momentum P has a wavelength

$$\lambda = \frac{h}{p}$$

What is the wavelength of a 50 g ball travelling at 20m/s ? $6.6 \times 10^{-34} \text{ m}$

What is the wavelength of proton (1.6×10^{-27}) moving at 2200 m/s ? 0.18 nm

Classical view of wave propagation



$$E(x, t) = E_0 e^{i(\omega t - kx)}$$

The velocity at which the phase moves (phase velocity) $v_p = \frac{\partial x}{\partial t} = \frac{\omega}{k} = v\lambda$

Power transferred per unit area Time average intensity = $\frac{1}{2} c \epsilon E_0^2$

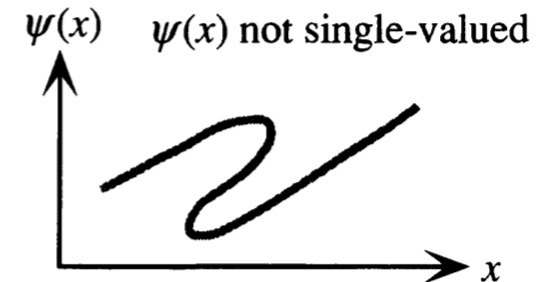
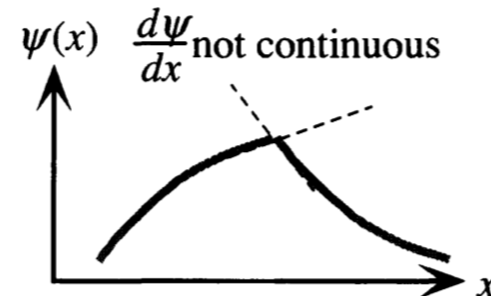
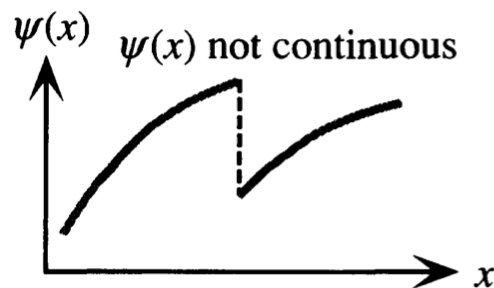
Born Interpretation (1926)

Similar to the wave description $E(x, t) = E_0 \sin(\omega t - kx)$

Whose intensity is proportional to E_0^2

We assume there exists a function $\psi(x, t)$ such that

- $|\psi(x, y, z, t)|^2$ is the probability to find the particle at x,y,z at any time t
- ψ is a complex quantity and carries no physical meaning.
- ψ and $\frac{d\psi}{dx}$ is continuous everywhere
- ψ is single valued everywhere



Erwin Schrodinger (1925-26)

Suppose an electron is in a potential field (V) facing a force

$$F = -\frac{dV}{dx}$$

If the potential is time independent;

Say, it only varies on x Example : $V(x) = -\frac{e^2}{4\pi\epsilon x}$

The electron position probabilities does not change with time!

$|\psi|^2$ is only a function of x

Then $\psi(x, t) = \psi(x) * \psi(t)$, where $\psi(t) = e^{-i\omega t}$

The time-independent SE

The spatial function is then obtained by solving

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

A simple example:

A completely free electron

$V = 0$ everywhere

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

A Free Particle

Ψ = wavefunction
for electron

$$\Psi = A \cos\left(\frac{2\pi}{\lambda}x - \omega t\right)$$

Using the deBroglie relationship

$$\frac{2\pi}{\lambda} = \frac{2\pi p}{h} = k \quad p = \text{electron momentum}$$

Using the Planck relationship

$$\omega = \frac{E}{\hbar} = \frac{E}{h/2\pi} \quad E = \text{electron energy}$$

Particle In a Box

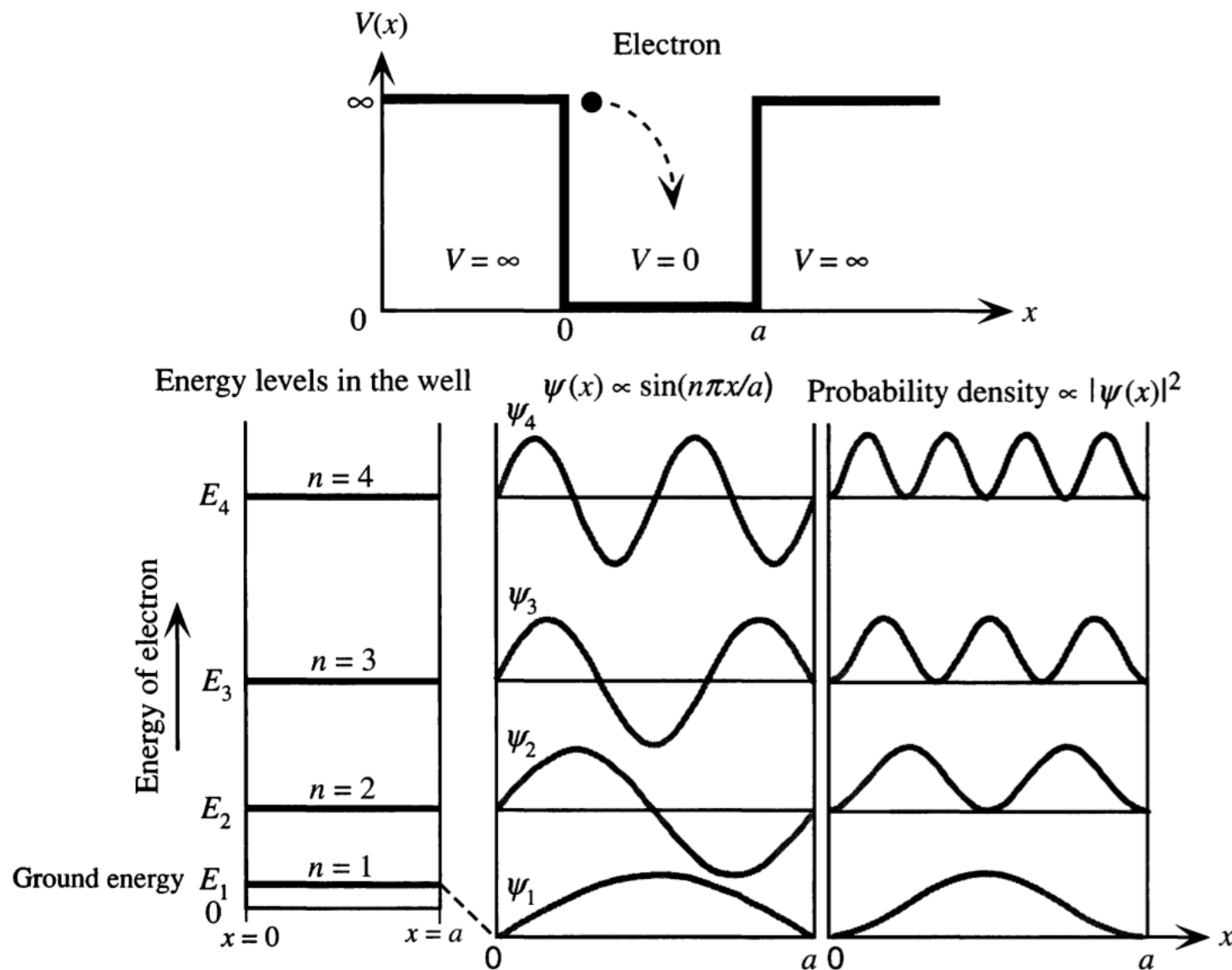
$$\psi(x) = 2Aj \sin kx$$

$$k = \frac{2\pi n}{a}$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{h^2 n^2}{8ma}$$

Normalization leads:
[HW]

$$A = \frac{1}{\sqrt{2a}}$$



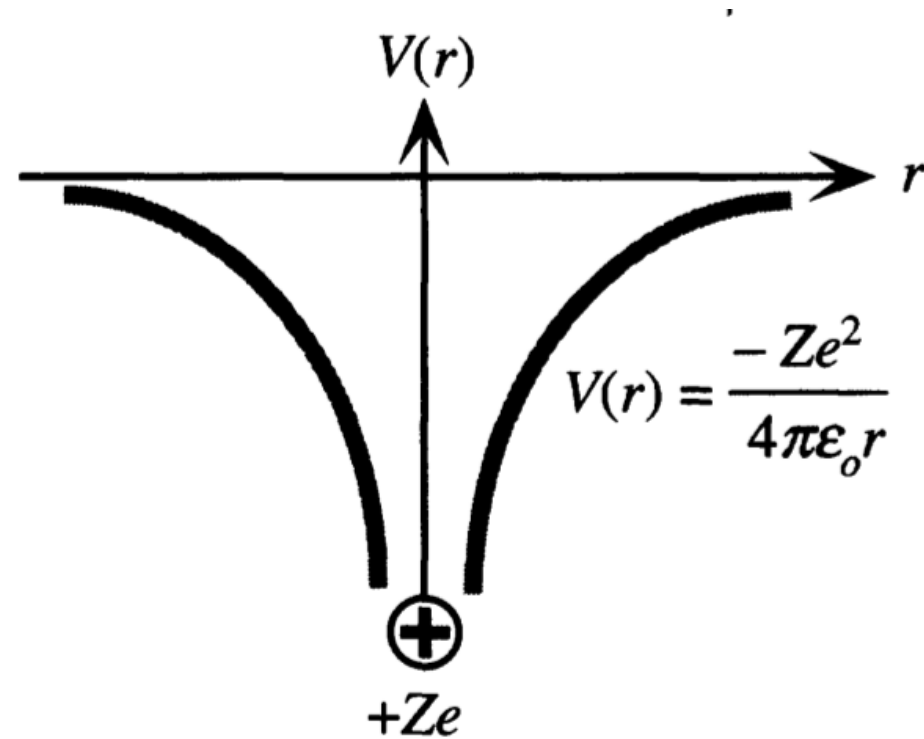
Some important consequences:

- Upon confinement, the particle wave-vectors and energies cannot take arbitrary values and are allowed only discrete values.
- At each discrete energy levels, the corresponding wavefunctions are ortho-normal. [HW2]
- For an electron inside the well $\Delta x = a$ [it can be anywhere in the well].
- If it has energy E , it can have two possible wave-vectors ($k, -k$).

$$\Delta p = 2\hbar k$$

- There exists a relationship: $\Delta x \Delta p = a \cdot \hbar \cdot \frac{2\pi n}{a} = h$

Hydrogen Atom



- An electron facing an attractive potential from nuclei.
- Potential: Spherically symmetric
- The wavefunction then has the form
$$\psi(r, \theta, \phi)$$
- Univalued at all points in space!

$$\psi(r, \theta, \phi) = \psi(r, \theta, \phi + 2\pi) = \psi(r, \theta + 2\pi, \phi)$$

As $r \rightarrow \infty$, $\psi \rightarrow 0$

Schrodinger's equation in three dimensions:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{where} \quad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In spherical coordinates

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

Due to the symmetry of the potential, the solution can be split:

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

Where $R(x,y,z)$ is the radial function, dependent on position x,y,z

$Y(\theta, \phi)$ is called a spherical harmonic function

If we substitute to the S.E. a solution that is variable separated

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

We get two radial equations

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

$$\Phi(\phi) = e^{im\phi}$$

$$\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + [l(l+1)\sin^2\theta - m^2]\Theta = 0$$

Solutions are associated Legendre's functions

$$p_l^m(x) = (1-x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx} \right)^{|m|} p_l(x)$$

$$P_0 = 1$$

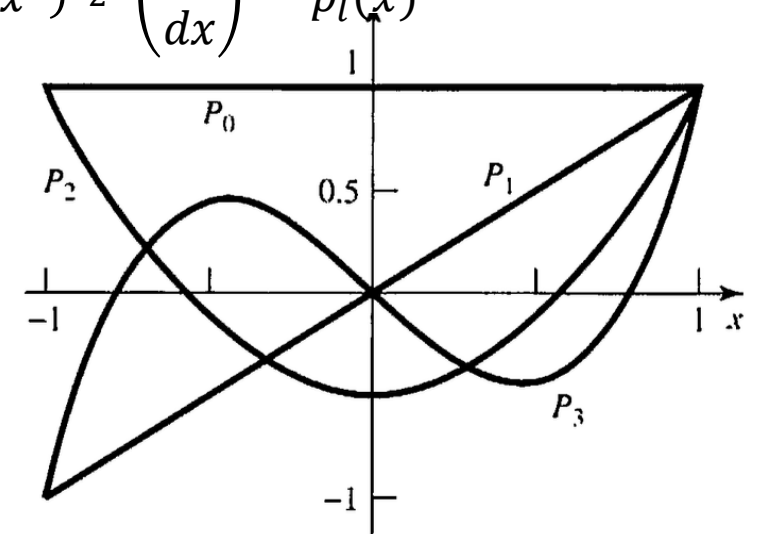
$$P_1 = x$$

$$P_2 = \frac{1}{2}(3x^2 - 1)$$

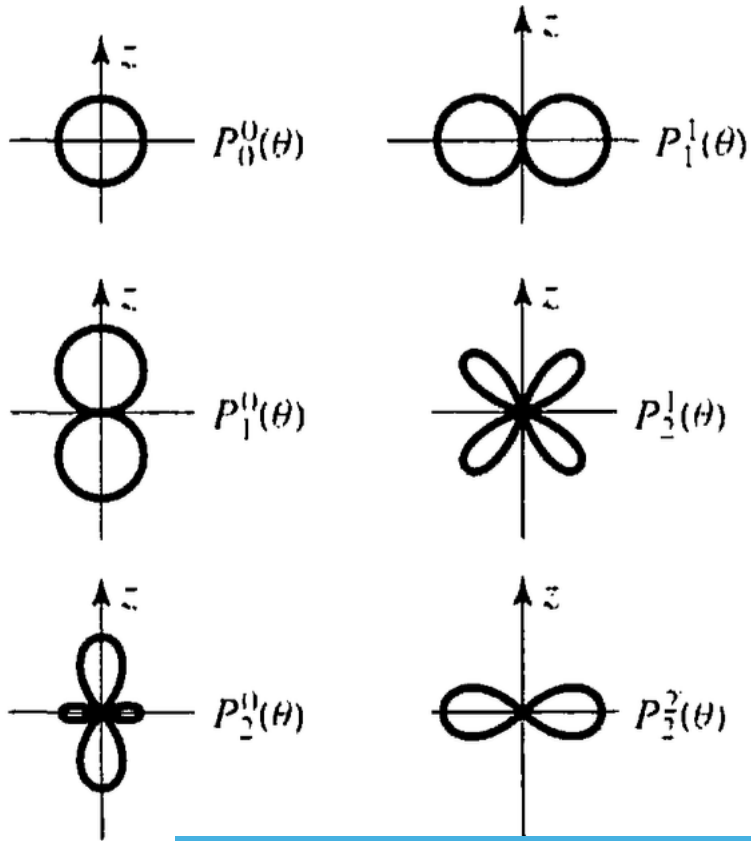
$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$



Associated Legendre's functionals P_l^m



- There are two quantum numbers l, m
- P_l^m is zero for negative l values. Therefore $l = 0, 1, 2, 3, \dots$
- m – mathematically can take all integer values $(0, \pm 1, \pm 2, \dots)$
- However, $P_l^m = 0$ for $|m| > l$
- Increasing an integer in either adds a node in the angular distribution

l is called azimuthal quantum number and m is called as magnetic quantum number

Radial

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = l(l+1)R$$

Introduce a new variable $u = rR$

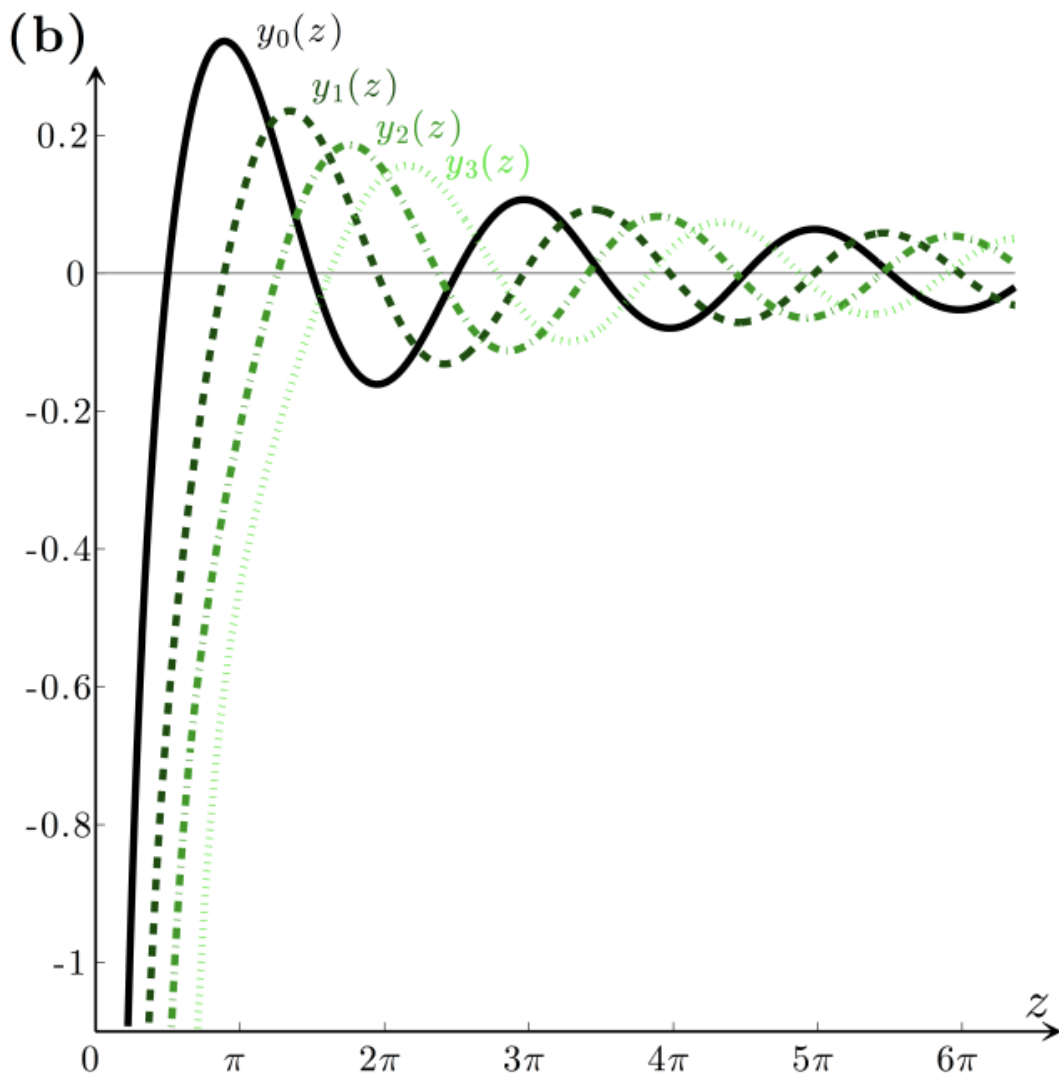
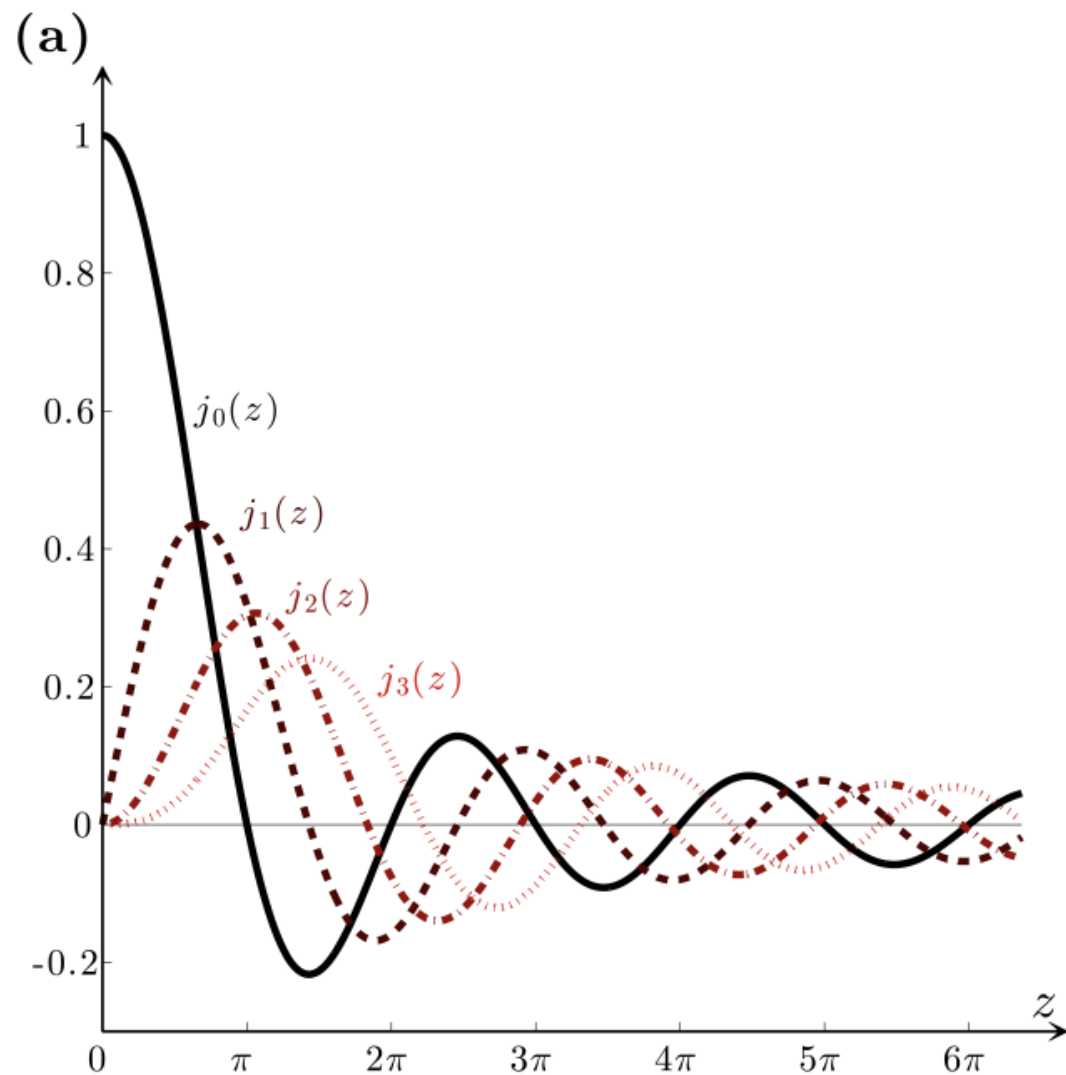
$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$

Solutions are simpler, when there is a spherical barrier.

$$u(r) = A r j_l(kr) + B r n_l(kr)$$

Spherical Bessel's function J_l and Spherical Newman's functions (n_l)

Spherical Bessel's and Newmann



Radial – True Hydrogen atom

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} [V(r) - E] R = l(l+1)R$$

Introduce a new variable $u = rR$

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$

This looks like, In addition to the Coulombic potential, there is a centrifugal term, that pushes the electron out.

When $r \rightarrow \infty$, The solutions, look like plane waves.
And when $r \rightarrow 0$, the centrifugal force dominates!

- The solutions are polynomial solutions:

$$R_{n,l} = \frac{1}{r} \rho^{l+1} e^{-\rho} v(\rho)$$

Where, $\rho = \frac{r}{an}$, where a is called as $a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$ Bohr radius

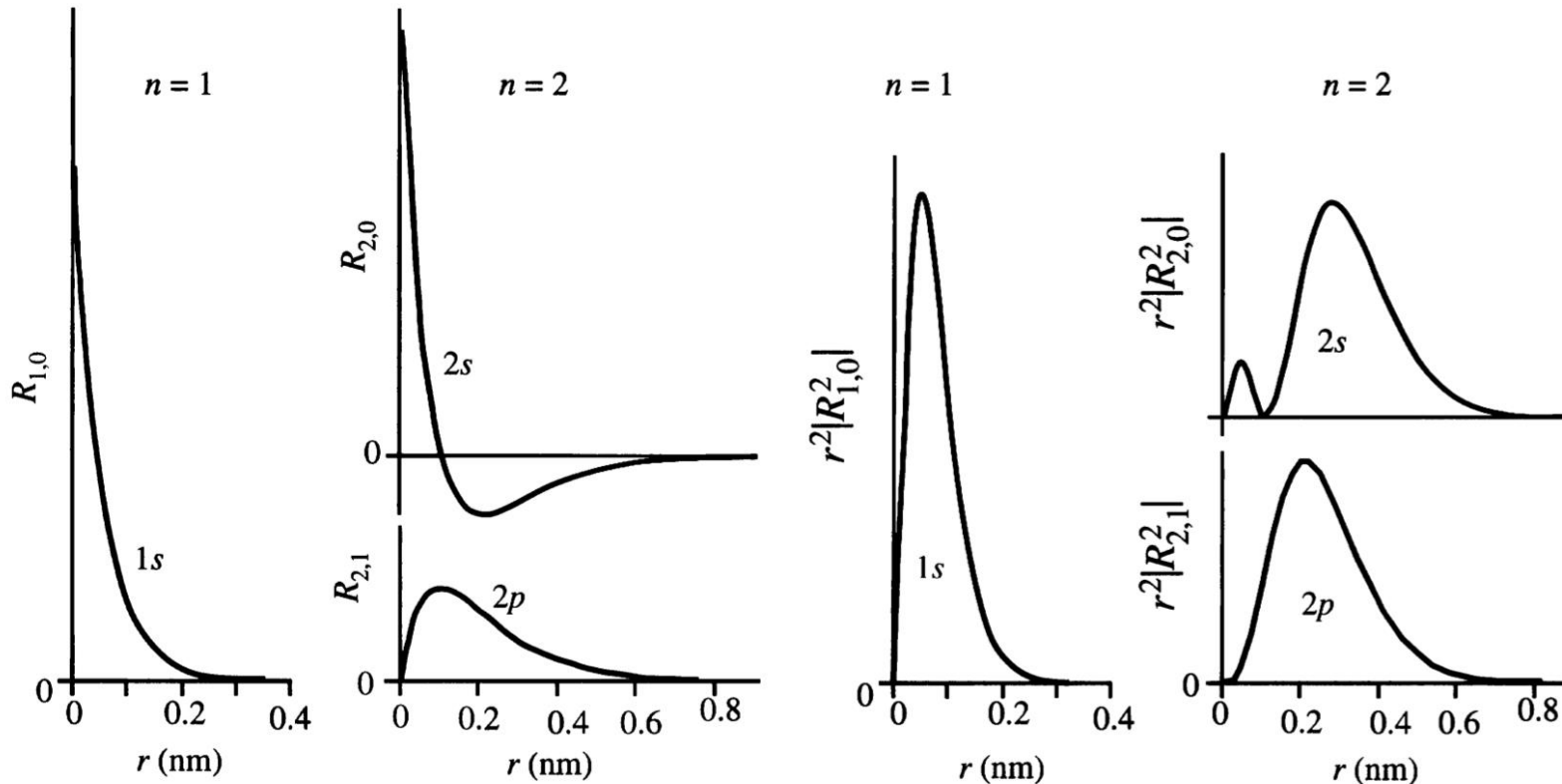
$$a = 0.529 \text{ \AA}$$

$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$ called associated Laguerre's polynomial.

$$L_{q-p}^p(x) = (-1)^p \left(\frac{d}{dx} \right)^p \left[e^x \left(\frac{d}{dx} \right)^q e^{-x} x^q \right]$$

The polynomial is of degree $j_{max} = n - l - 1$

Radial wavefunctions



$$R_{10} = 2a^{-3/2} \exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}} a^{-3/2} \left(1 - \frac{1}{2} \frac{r}{a} \right) \exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}} a^{-3/2} \frac{r}{a} \exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}} a^{-3/2} \left(1 - \frac{2}{3} \frac{r}{a} + \frac{2}{27} \left(\frac{r}{a} \right)^2 \right) \exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}} a^{-3/2} \left(1 - \frac{1}{6} \frac{r}{a} \right) \left(\frac{r}{a} \right) \exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}} a^{-3/2} \left(\frac{r}{a} \right)^2 \exp(-r/3a)$$

$$R_{40} = \frac{1}{4} a^{-3/2} \left(1 - \frac{3}{4} \frac{r}{a} + \frac{1}{8} \left(\frac{r}{a} \right)^2 - \frac{1}{192} \left(\frac{r}{a} \right)^3 \right) \exp(-r/4a)$$

$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}} a^{-3/2} \left(1 - \frac{1}{4} \frac{r}{a} + \frac{1}{80} \left(\frac{r}{a} \right)^2 \right) \frac{r}{a} \exp(-r/4a)$$

$$R_{42} = \frac{1}{64\sqrt{5}} a^{-3/2} \left(1 - \frac{1}{12} \frac{r}{a} \right) \left(\frac{r}{a} \right)^2 \exp(-r/4a)$$

$$R_{43} = \frac{1}{768\sqrt{35}} a^{-3/2} \left(\frac{r}{a} \right)^3 \exp(-r/4a)$$

- Similar to the particle in a box, Every function has increasing number of nodes!
- No. of nodes = $n-1$, where n – principle quantum number!

Energy Levels (Radially Quantized)

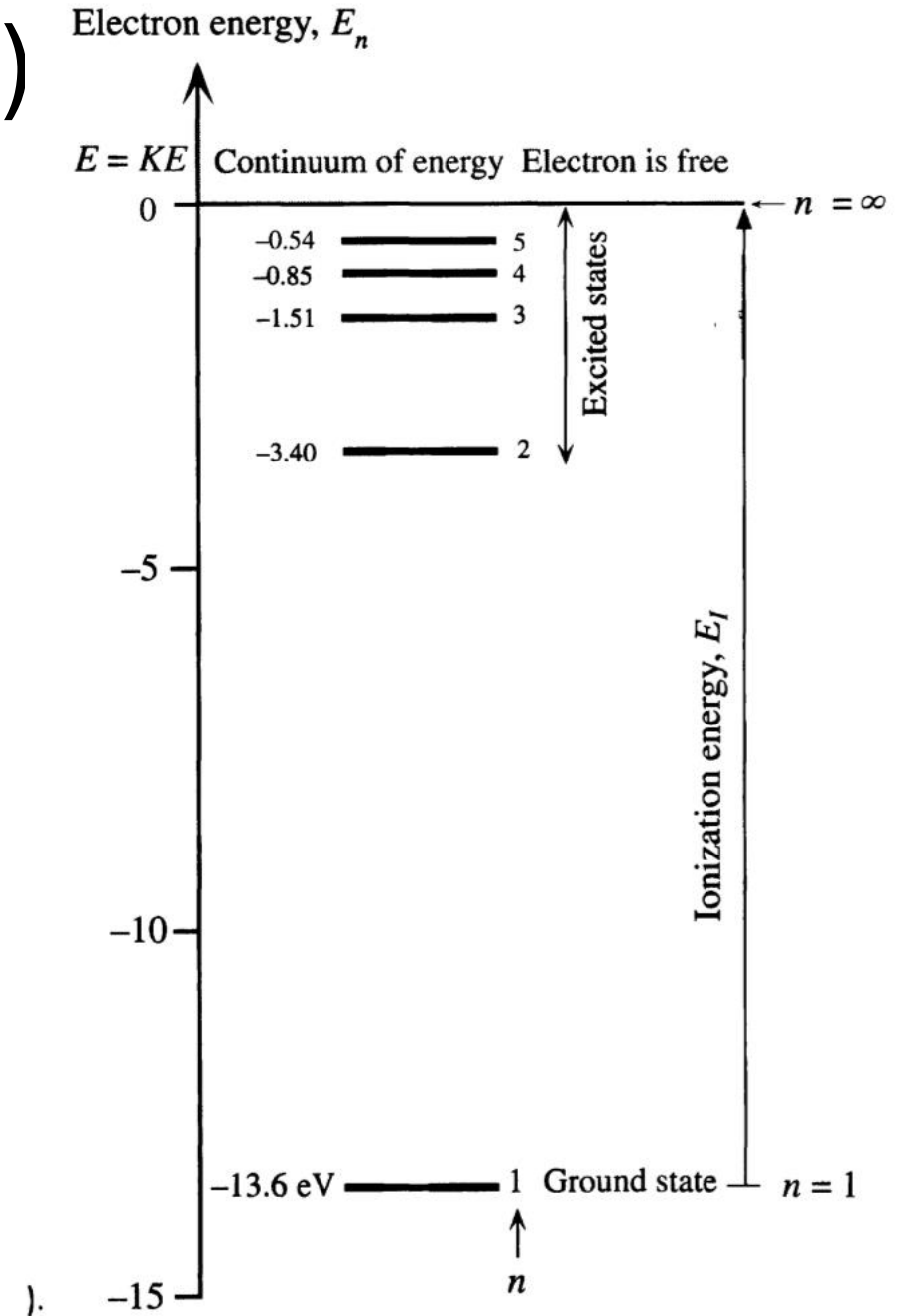
- Only radial dependence!

- $E_n = -\frac{Z^2 E_l}{n^2}$

- $E_l = \frac{me^4}{8\epsilon^2 h^2} = 13.6 \text{ eV}$

Any state (wavefunction) is defined by three quantum numbers,
Its energy is defined here with just the principal quantum number

$$H\psi_{n,l,m} = E_n \psi_{n,l,m}$$



Angular Momentum

- Orbital Angular momentum L

Classically, $L = I\omega$

$$\mathcal{L}\psi_{n,l,m} = L\psi_{n,l,m}$$

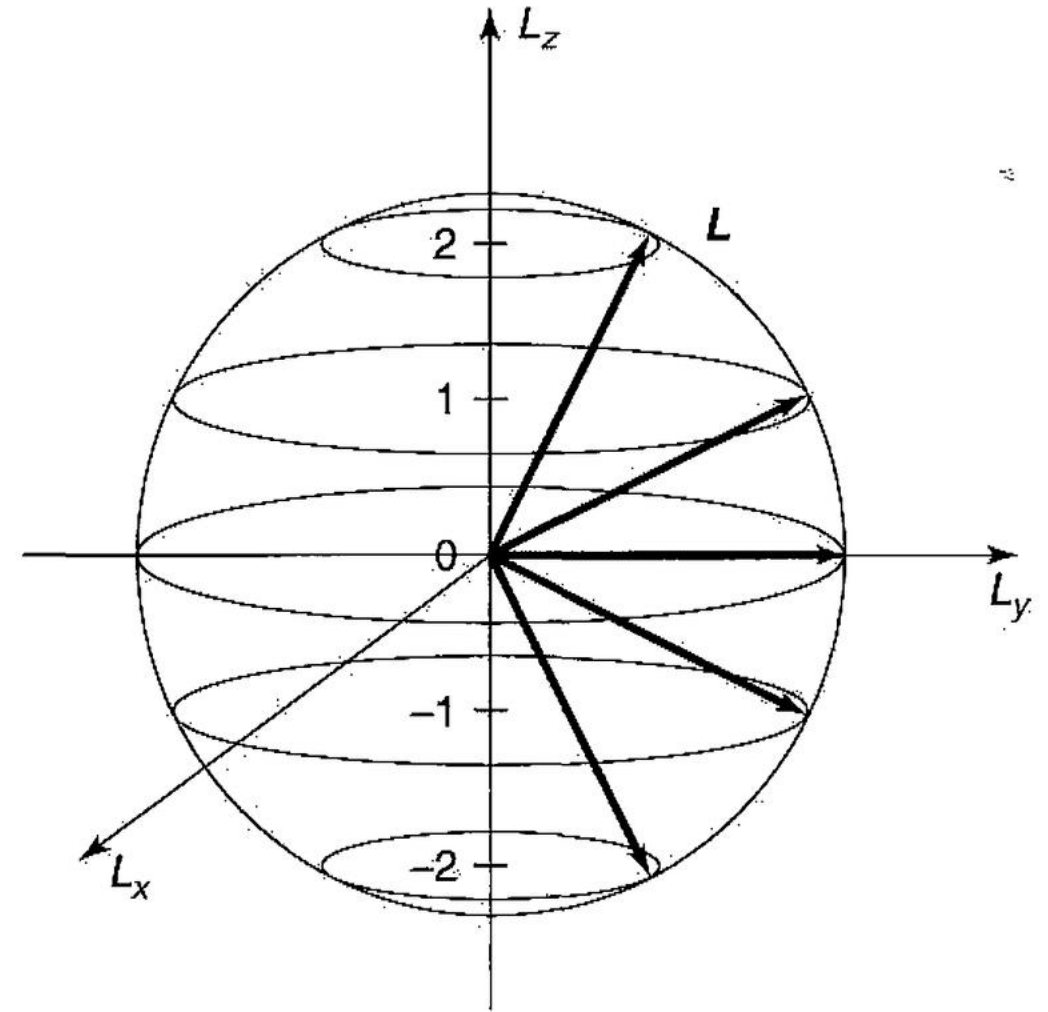
$$L = \hbar\sqrt{l(l+1)}$$

1. Since l is quantized, L is also quantized.

2. $l = 0, 1, 2, \dots$, so in ground state, $L=0$

that is in an 's' orbital, orbital angular momentum = 0. The electrons do not orbit!

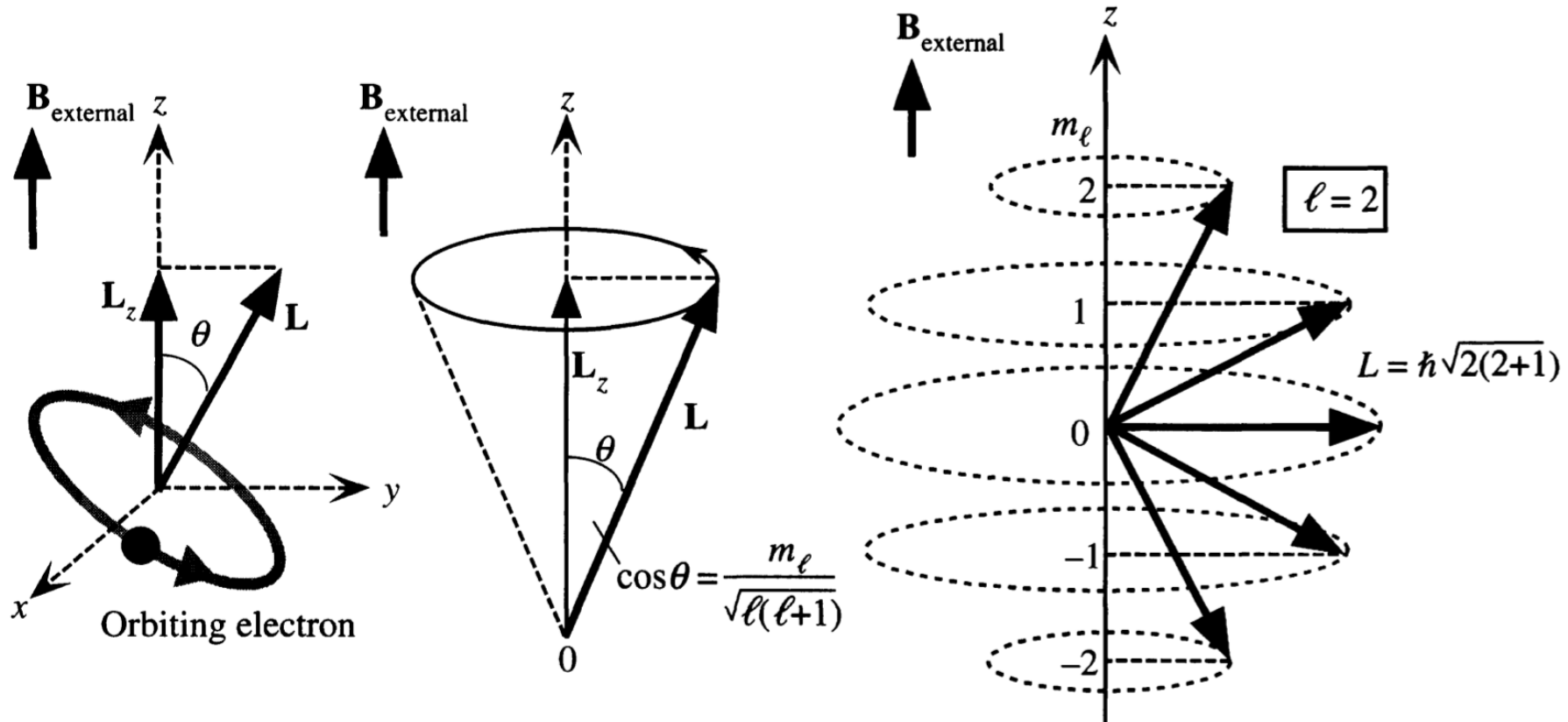
3. $l < n$



Magnetic Quantum Number

Assume a non zero (L) ie. $L \neq 0$.

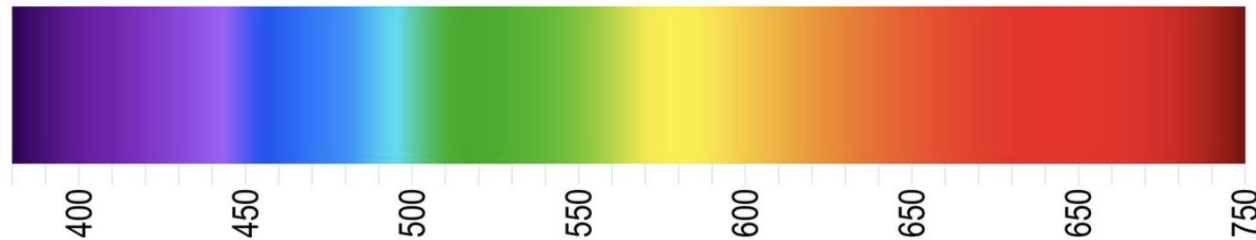
L – have both direction and magnitude!



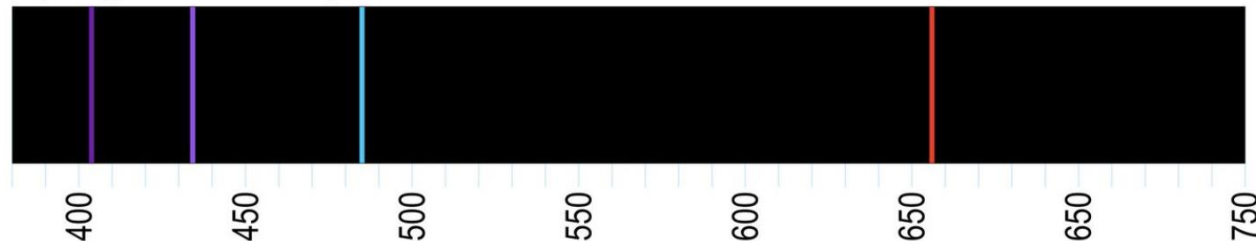
Hydrogen atom spectra

- Photon energy $E = \hbar\nu$
- Photon angular momentum $\hbar$

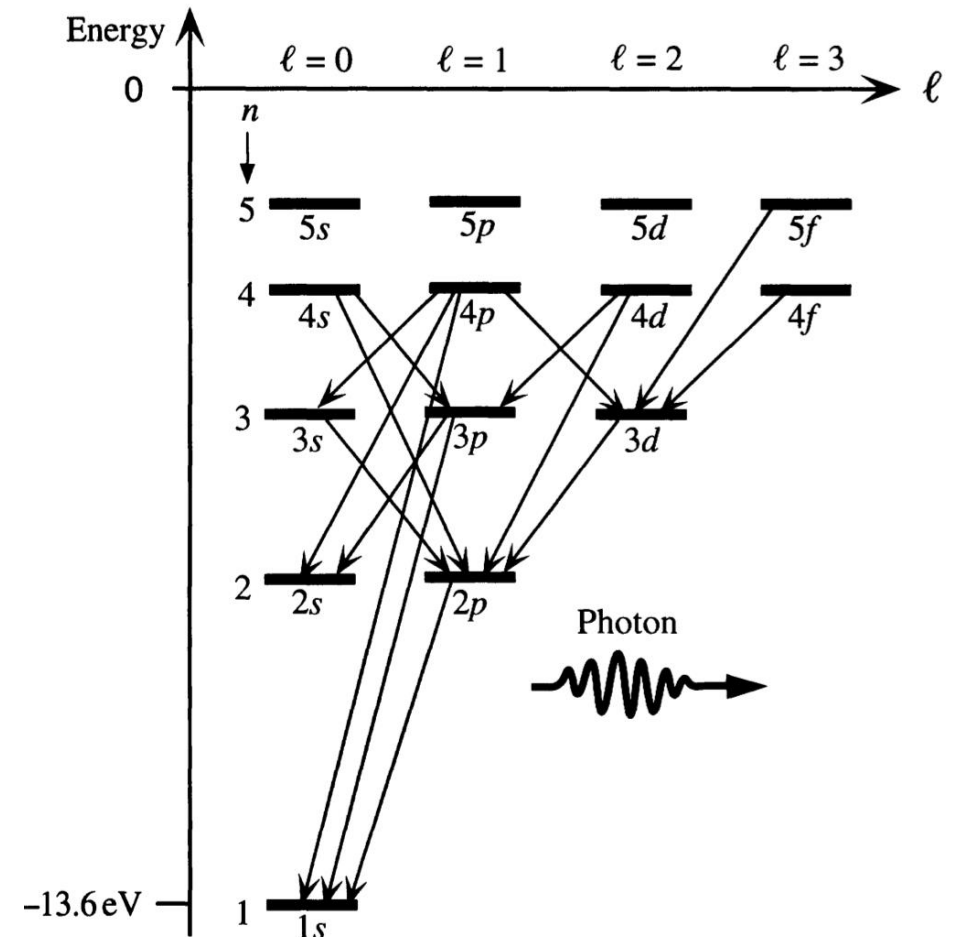
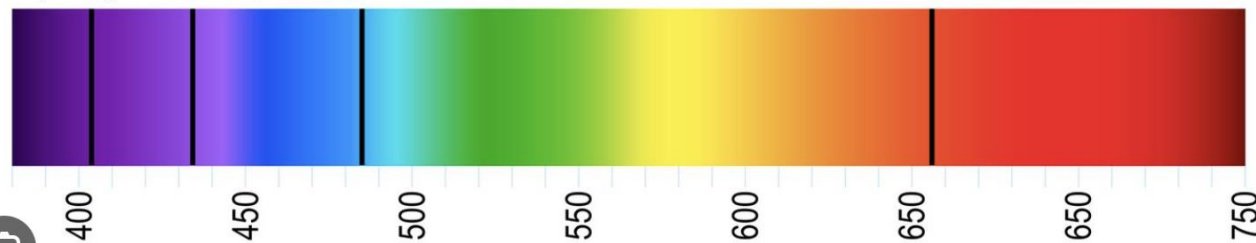
Continuous spectrum



Hydrogen Emission spectrum



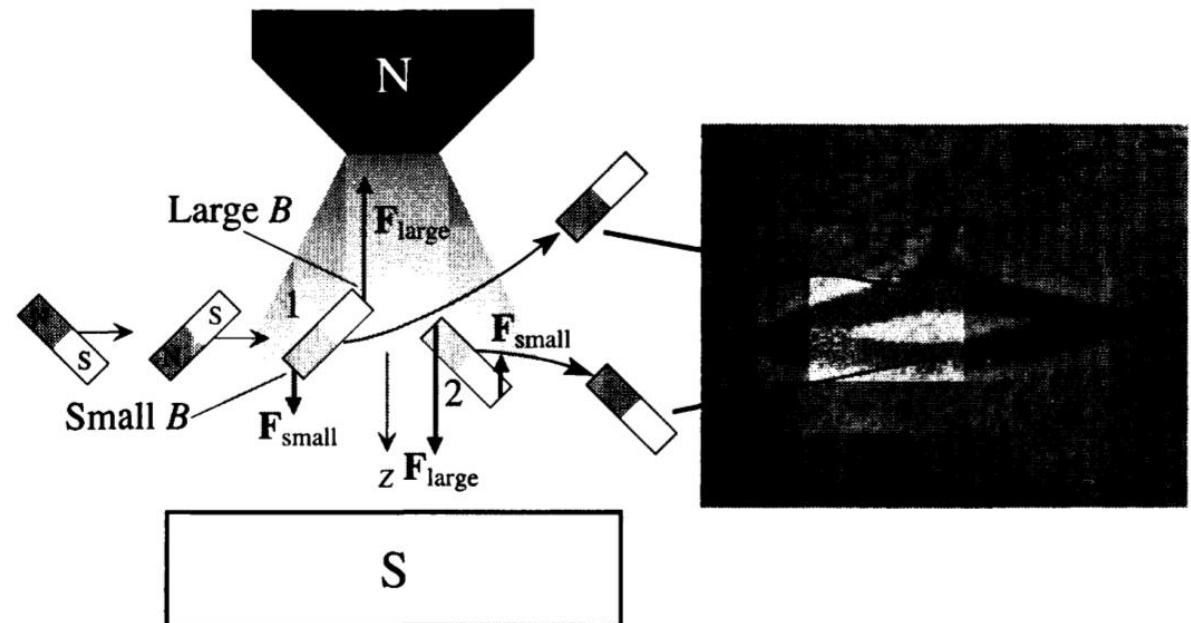
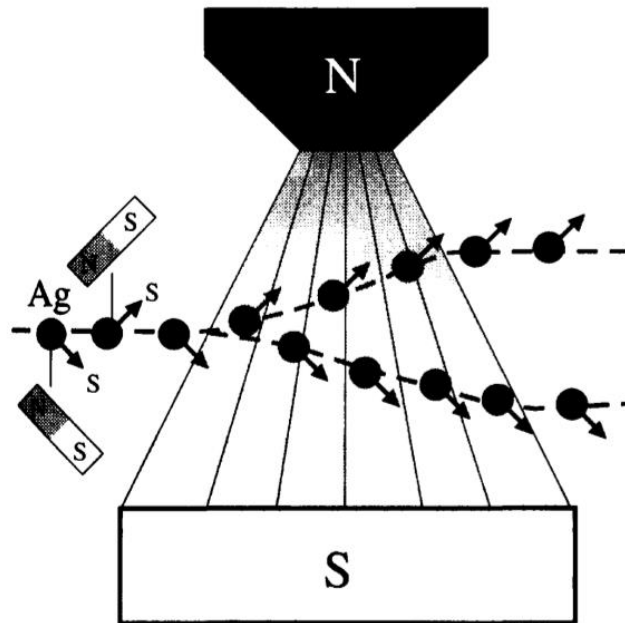
Hydrogen Absorption spectrum



Stern-Gerlach Experiment

- When a stream of Silver atoms were made to pass through a magnet
- Ag – L=0
no orbital angular momentum

‘Open Lips’
Are observed!



Only two quantized moments!
Intrinsic moment!

$$\mu_{spin} = -\frac{e\hbar}{m_e} m_s$$

Spin

- Spin is name for intrinsic angular momentum of a particle.
- It is quantized!
- Two kinds of particles:
 - Half integer particles: $S = \pm \frac{1}{2}, \pm \frac{3}{2}$ called Fermions
 - Integer particles : $S = 1, 2, 3$ (Bosons)
- There are $2S + 1$ possible states.
 - Electrons have 2 possible states (Spin-up and Spin down)
 - Photons have 3 states ($\hbar, 0, -\hbar$)

Pauli's Exclusion

- While several states in an atom
 - Why not have all the electrons in the lowest state ?
- Atoms with even number of electrons are more stable
- Chemical bonding seem to indicate a tendency to have even number of electrons in each state!
- No two Fermions (half-integer spin particles) can have all the quantum numbers the same!