ELEC 315:
Quantum Mechanics for Atoms and Electrons

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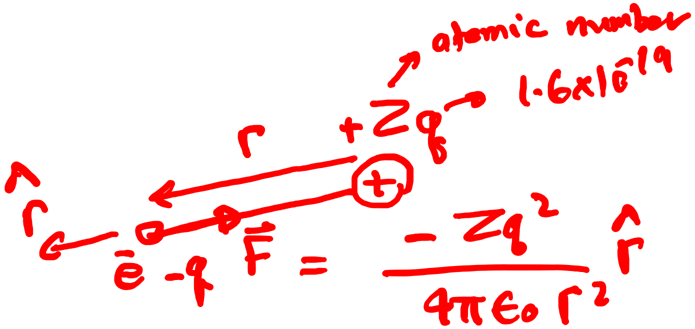
Outline

- Photoelectric effect
- Wave nature of electrons
- Quantum mechanics
- The Schrödinger Equation
- 1D and 2D potential well
- Hydrogen atom orbitals

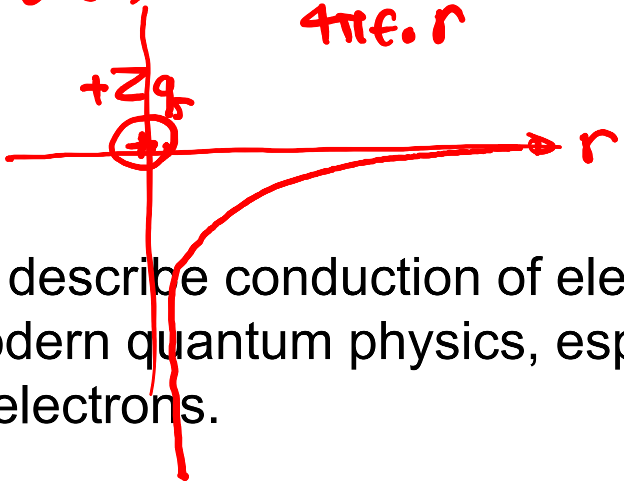
Electrons in Matter

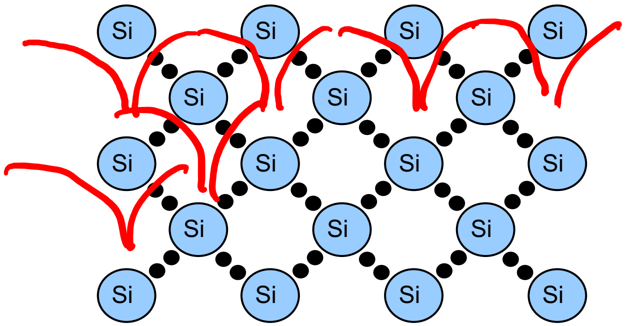
- Coulomb's attraction is present between electrons and protons of the nucleus in a solid. Some electrons take part in forming bonds and some are free to move.



$$\vec{F} = \frac{-Zq^2}{4\pi\varepsilon_0 r^2}\hat{r}$$

$$U(\vec{r}) = -\frac{Zq}{4\pi\varepsilon_0 r}$$

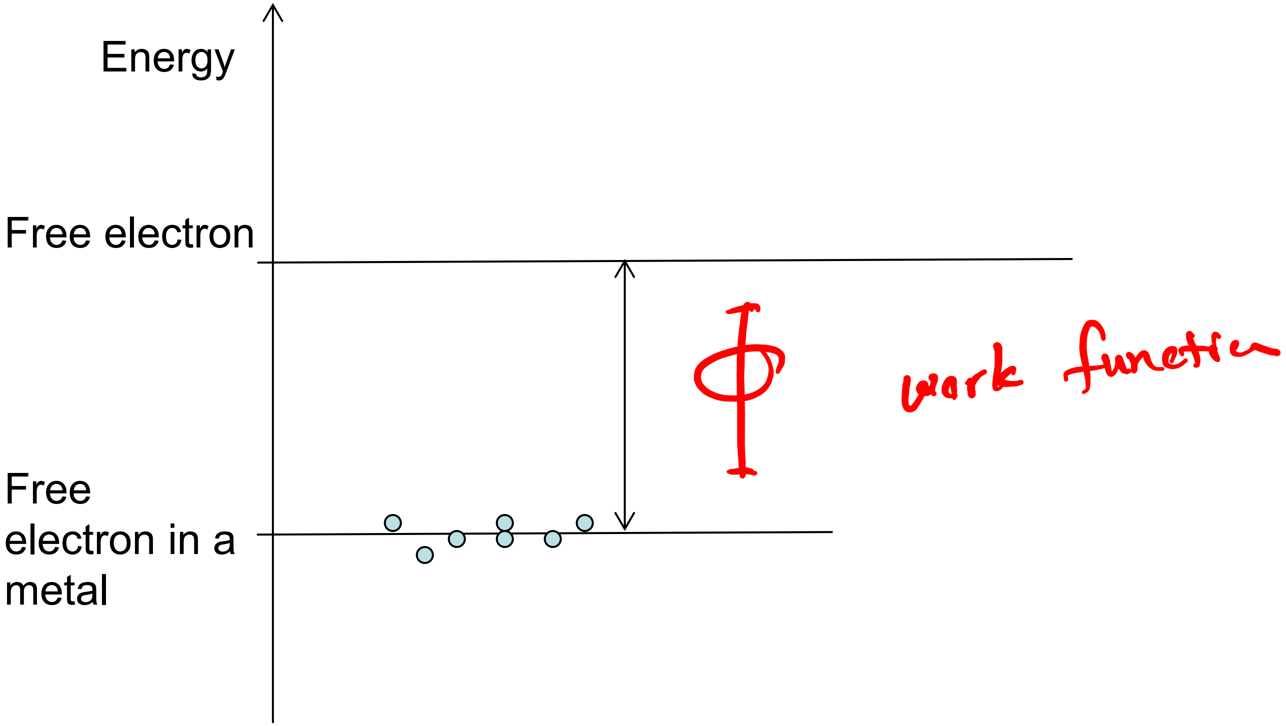




- To describe conduction of electrons in solids, we need to use modern quantum physics, especially dual wave and particle nature of electrons.

Free Electrons in Metal

- Free electrons inside a metal:



Energy

Free electron

Free electron in a metal

Φ work function

The Photoelectric Effect

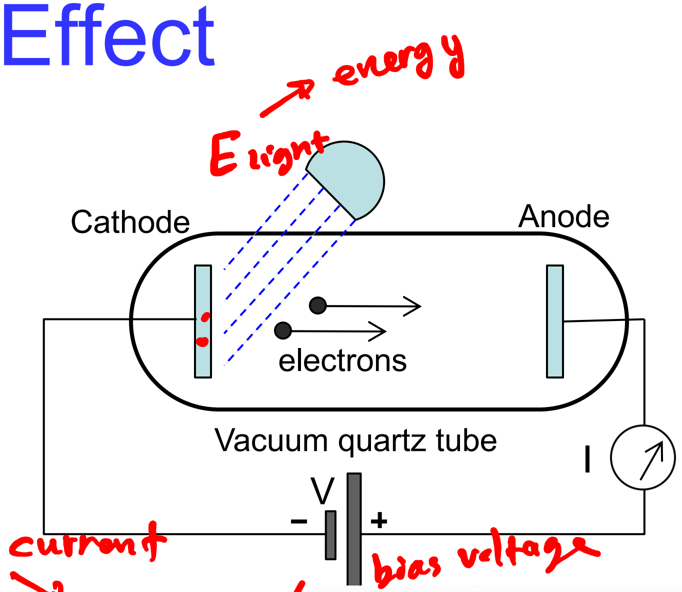
- Einstein's photoelectric experiment in 1905 is the first experiment showing particle nature for light, which was believed to be a wave only.
- He observed that for each light frequency there is a negative voltage $-V_0$ that "stops the photocurrent". This voltage, again, is not a function of light intensity.
- This "stopping voltage" actually shows the maximum kinetic energy (KE) of electrons emitted from the cathode:

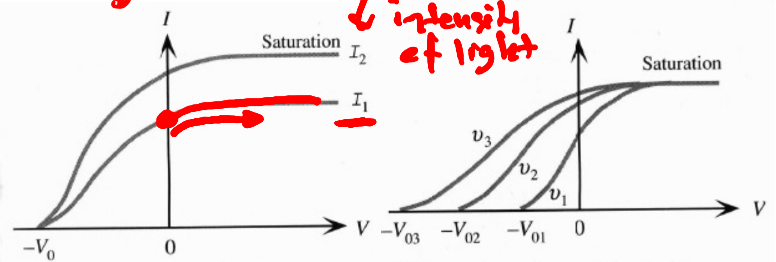
potential energy of cathode = $-\phi + qV$

$$qV_0 = KE_{\max} = \frac{1}{2} m v_e^{\,2}$$

$KE = E_{light} - \phi + qV$

↑
kinetic energy of electrons





(a) Photoelectric current versus voltage when the cathode is illuminated with light of identical wavelength but different intensities (I). The saturation current is proportional to the light intensity.

(b) The stopping voltage and therefore the maximum kinetic energy of the emitted electron increases with the frequency of light, υ. (The light intensity is not the same; it is adjusted to keep the saturation current the same.)

$-V_0$ stopping voltage

Kasap

Planck’s Constant and Work Function

$y = ax + b$

$KE_{max} = h\nu - \Phi$

- Plotting the maximum energy for different light frequencies show a linear curve:

$$KE_{max} = E_{photon} - \Phi + qV = h\nu - \Phi + qV$$

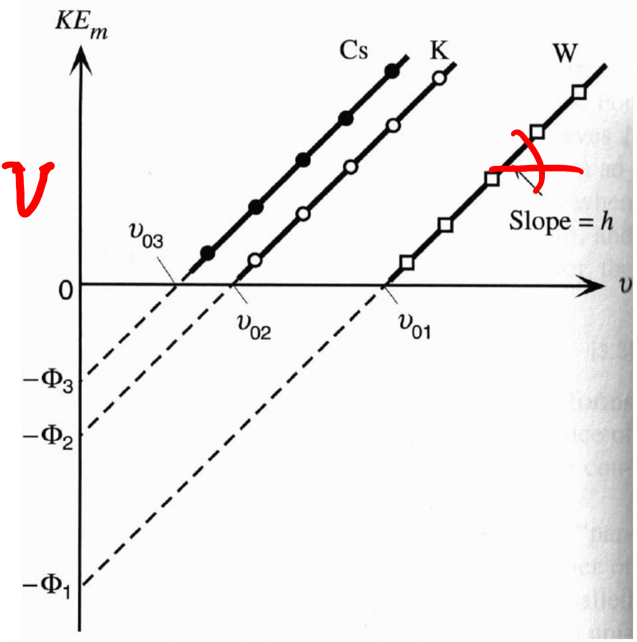
- The slope of this line is the main quantum coefficient known as Planck’s constant:

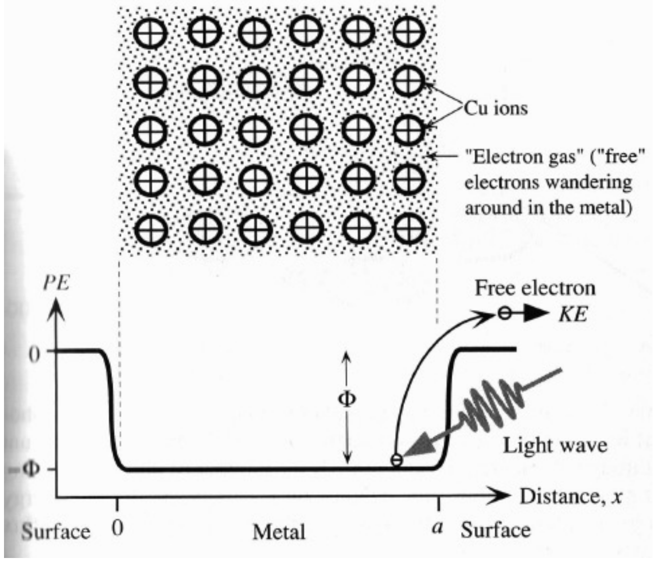
$h = 6.626 \times 10^{-34}$ J-s

- We call this energy particle photons.
- The potential energy (PE) for electrons in a metal is called work function and is given by:

$$PE = \Phi =$$

- Work functions:
  - Tungsten (W):
  - Platinum (Pt):
  - Cesium (Cs):

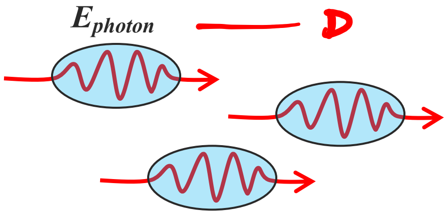




Light as Wave and Particle

- **Photons:** packet of light with energy $E_{photon} = h\nu$

$p = h/\lambda$



number of photons @ ν

$I = N h\nu$

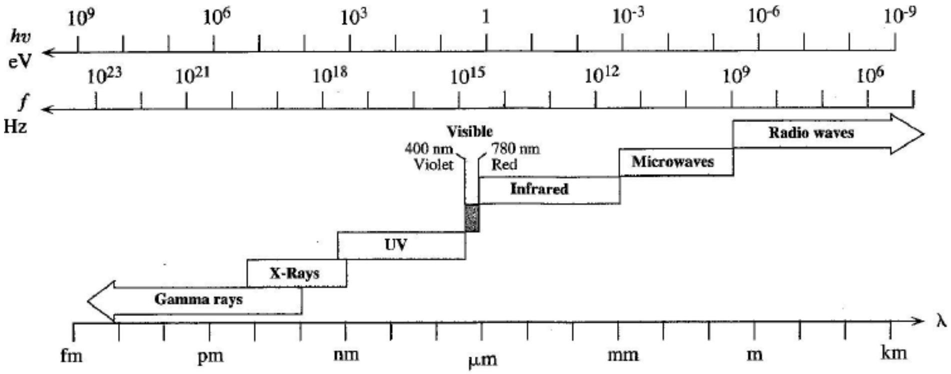
intensity

Planck's constant

- Momentum $p = h / \lambda$, where λ is wavelength
- Visible photons λ = 400 nm to 780 nm
  - $\nu = c / \lambda$
  - $E_{photon} = h\nu = h c / \lambda = 5 \times 10^{-19}$ J to 2.8×10^{-19} J
  - In electron volts (divide energy by charge of an electron): 3.1 eV, visible range ~ 3.1 to 1.75 eV.

1.6×10^{-19} J = 1 eV

$c = \lambda\nu$



The electromagnetic spectrum and conventional designations

Example:

- We use a platinum cathode $\Phi = 4.09$ eV, what is the retarding voltage for having zero photocurrent if the wavelength is 244 nm?

$$E_{ph} = h\frac{c}{\lambda} = 6.626\times10^{-34} \times \frac{3\times10^{8}}{244\times10^{-9}}$$

$$= 8.15\times10^{-19}\ \text{J}$$

$$= 5.1\ \text{eV}$$

$$KE_{max} = E_{ph} - \phi + qV = 0 \longrightarrow$$

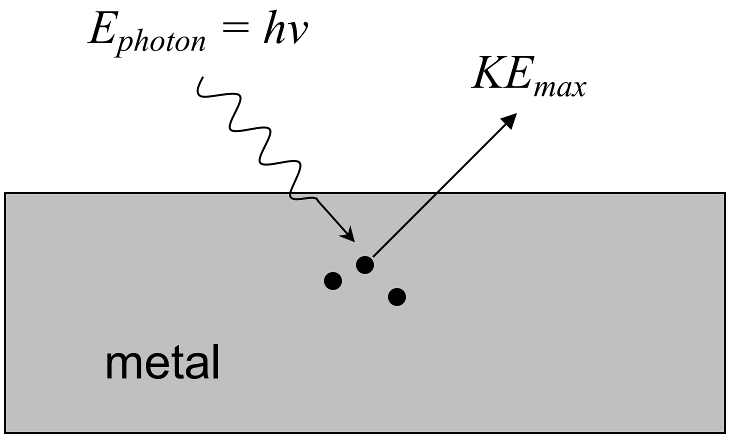
$$qV = -(E_{ph} - \phi)$$

$$= -\left(h\frac{c}{\lambda} - 4.09\ \text{eV}\right)$$

$$= -(5.1\ \text{eV} - 4.09\ \text{eV})$$

$$= -1.01\ \text{eV}$$

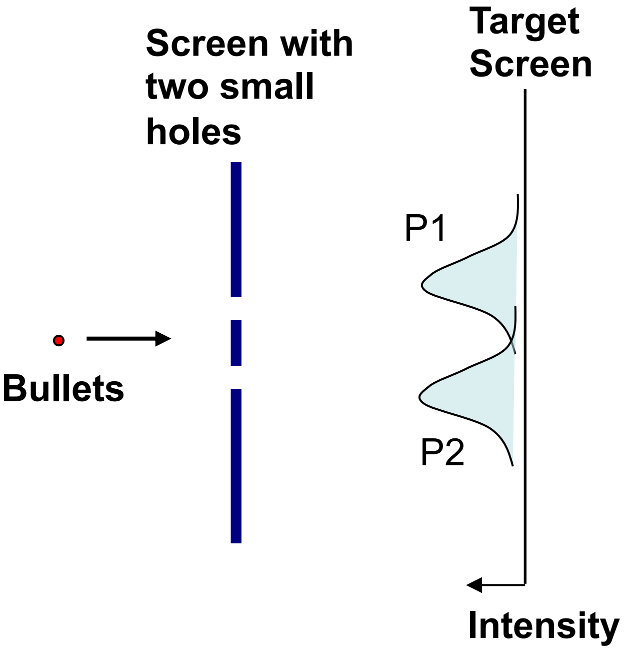
$$V_{stopping} = -1.01\ \text{V}$$



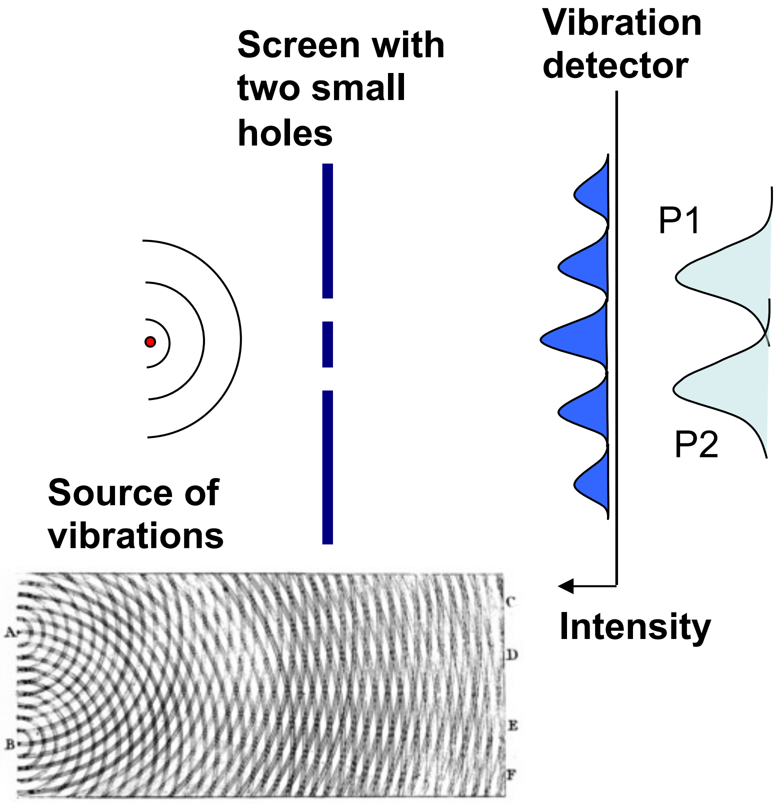
Electron diffraction experiment

- Davisson and Germer in 1927 performed diffraction experiments on electron that showed the wave nature of electrons.
- The difference in diffraction experiment for particles and waves can be understood by assuming two cases: i) we are firing bullets through a screen with two holes. ii) we are generating vibrations on the surface of water in a tank and use a screen with two holes.

Case (i)



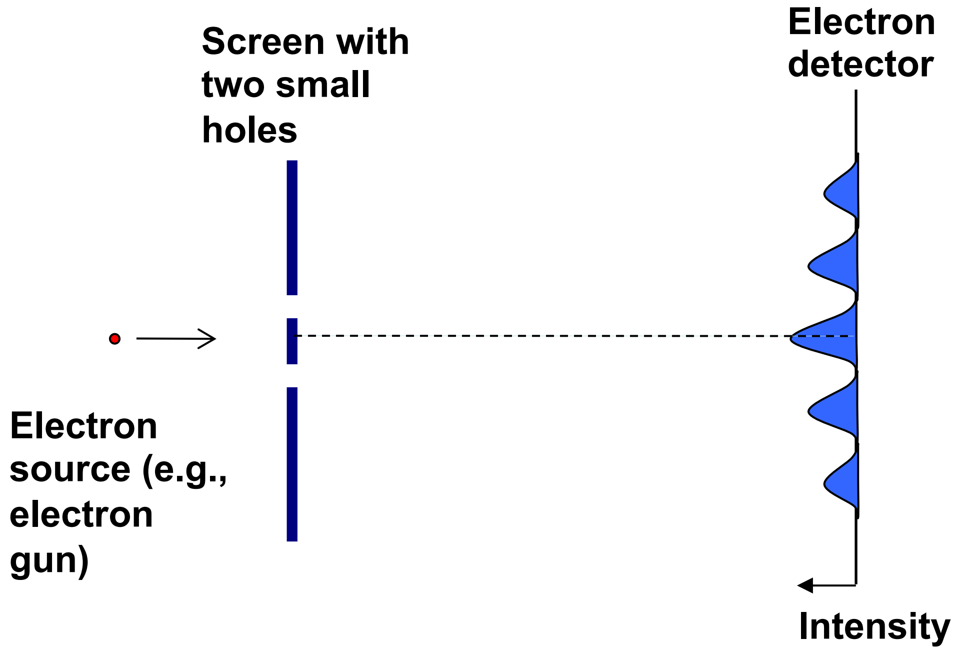
Case (ii)

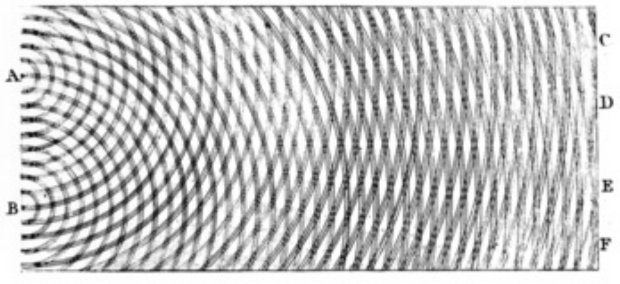


Electron diffraction

- In fact, electron diffraction experiment shows that electron behaves like a wave and shows interference patterns.
- Like a wave we can have constructive and destructive interferences for the wave coming from the holes.

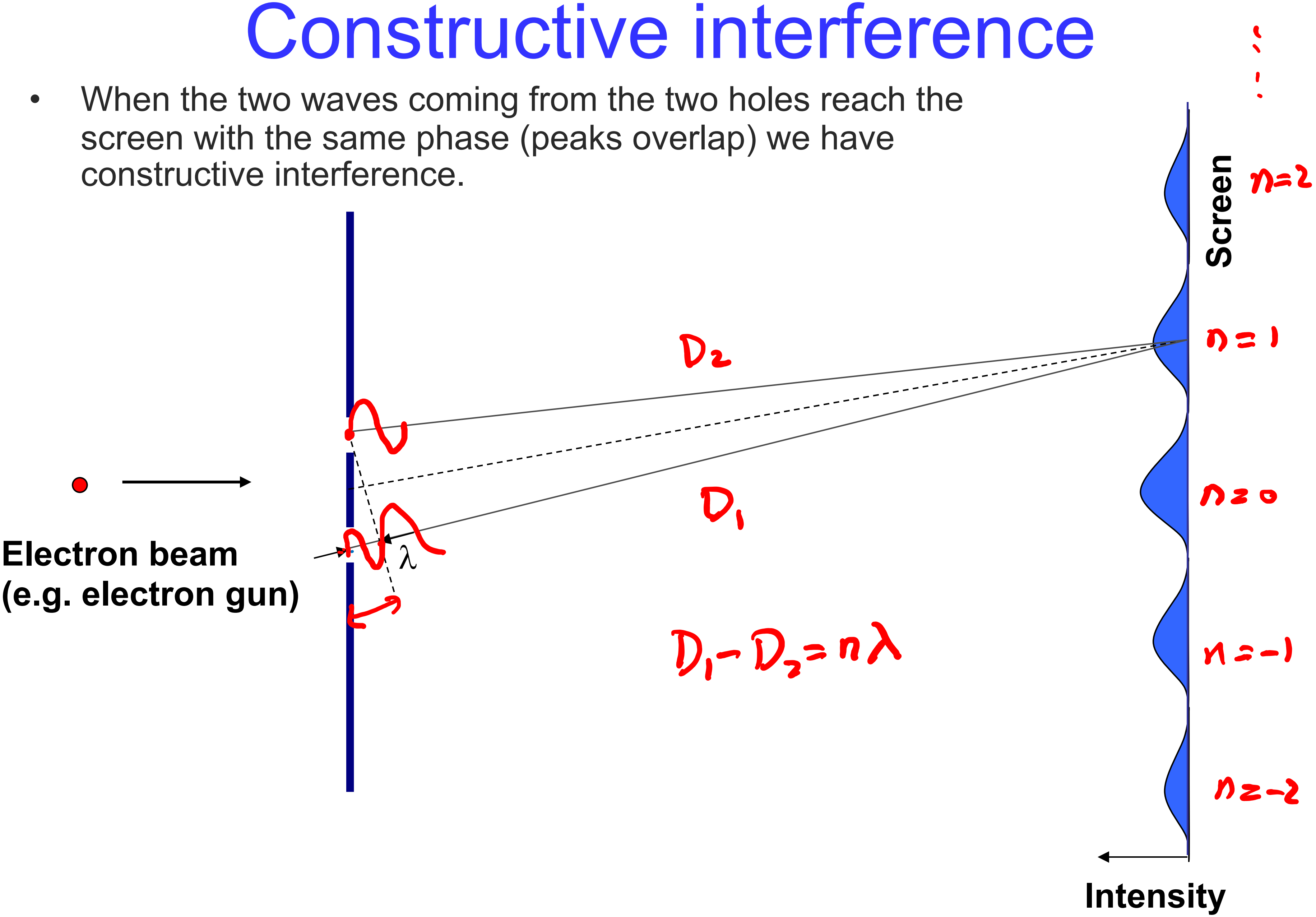
$|\psi|^2$





Constructive interference

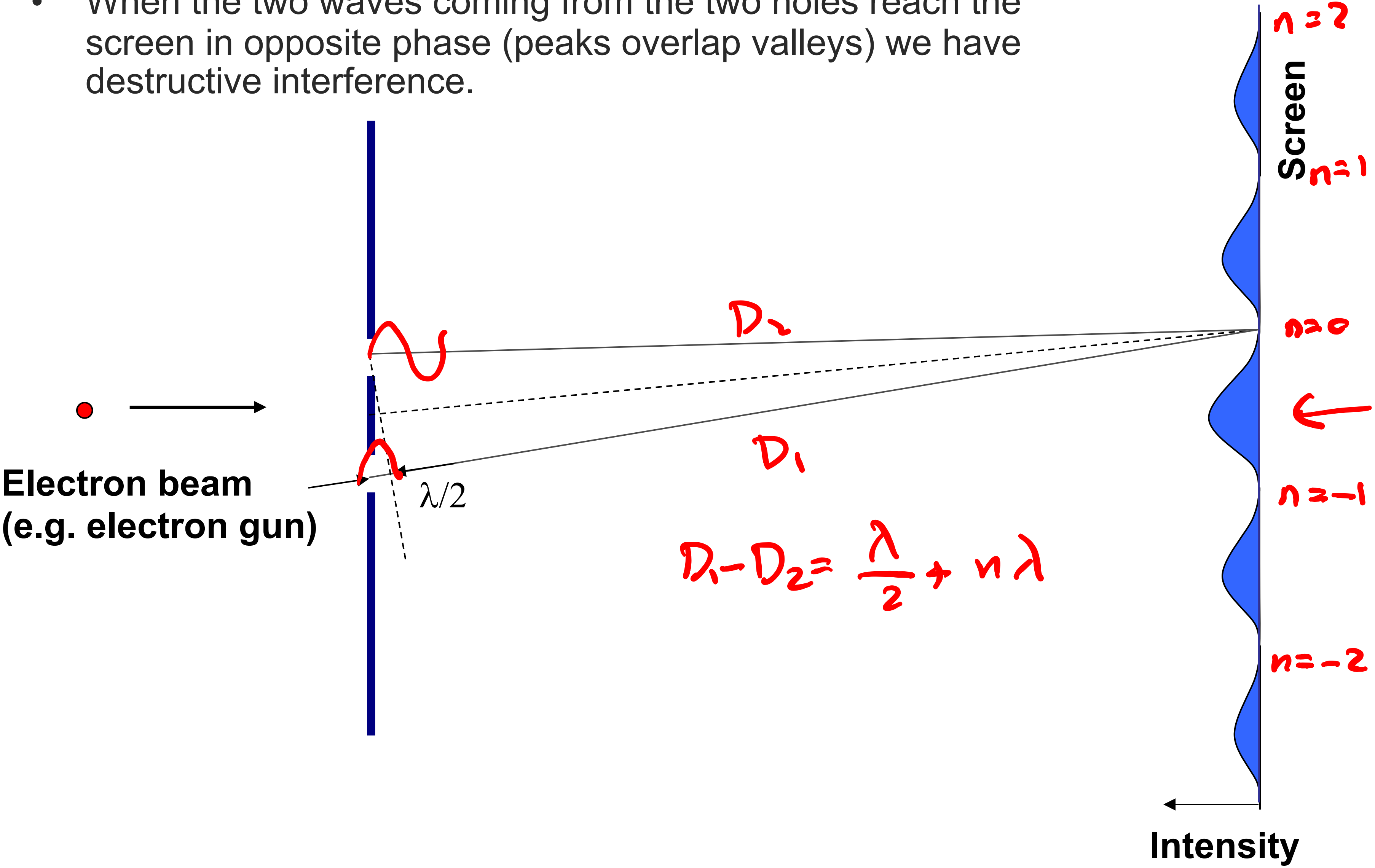
- When the two waves coming from the two holes reach the screen with the same phase (peaks overlap) we have constructive interference.



$D_1 - D_2 = n\lambda$

Destructive interference

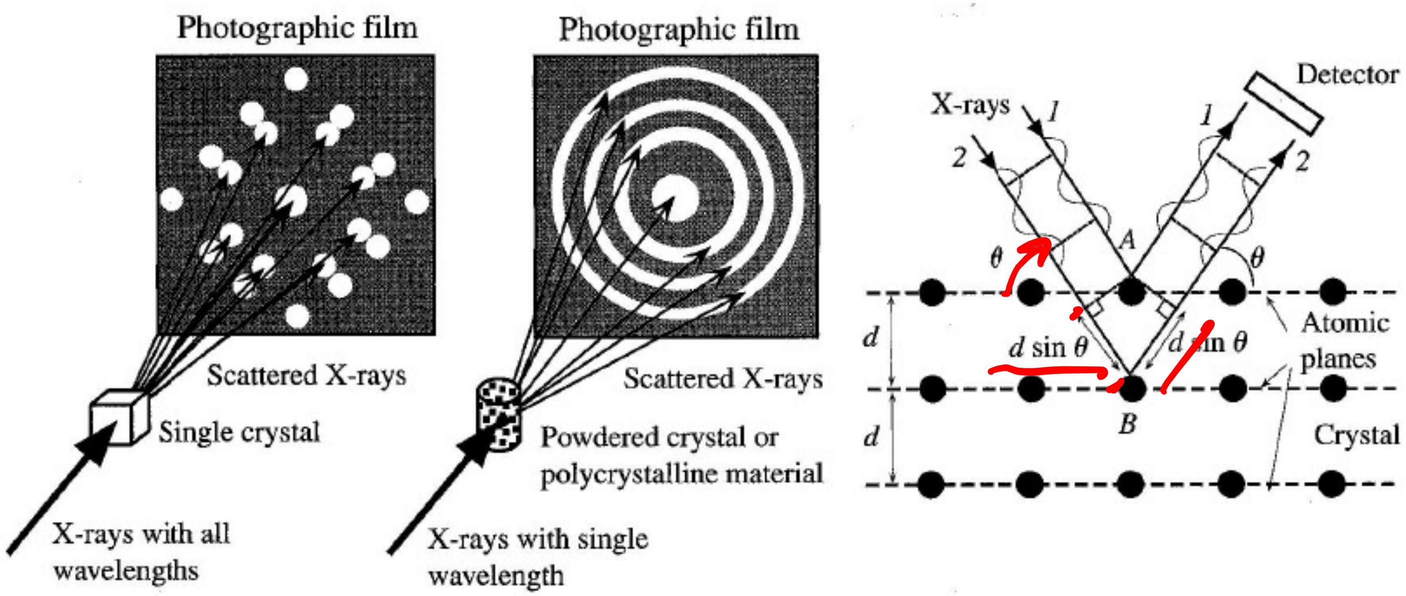
- When the two waves coming from the two holes reach the screen in opposite phase (peaks overlap valleys) we have destructive interference.

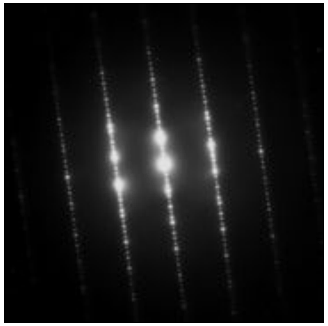


$$D_1 - D_2 = \frac{\lambda}{2} + n\lambda$$

Crystallography

- Scientists use X-ray and other wave sources to look at crystal planes in a material.
- The reflections are different for single crystal (we see sharp peaks from reflections of some plane sets) and amorphous (we do not see a sharp interference pattern).
- Bragg's law says that the maximum is when $2d\sin\theta = n\lambda, \qquad n = 1,2,3,\ldots$





wikipedia.com

See also:
http://www.mineralogie.uni-wuerzburg.de/crystal/teaching/teaching.html
http://en.wikipedia.org/wiki/Double_slit_experiment

Wave particle duality

- Electrons are waves and particles too.
- Have mass and charge
- Measure a discrete particle

  but
- ‘Interfere’ like waves

particle

$q, m_o = 9.1\times10^{-31}\,kg$

$\vec{p} = m\vec{v}$ → speed

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

$\frac{1}{2} m_o v^2 = KE = \frac{p^2}{2m}$

↑ speed

$E = h\nu$

potential energy

de Broglie Hypothesis

Relationship between
Momentum, *p* and wavelength λ

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

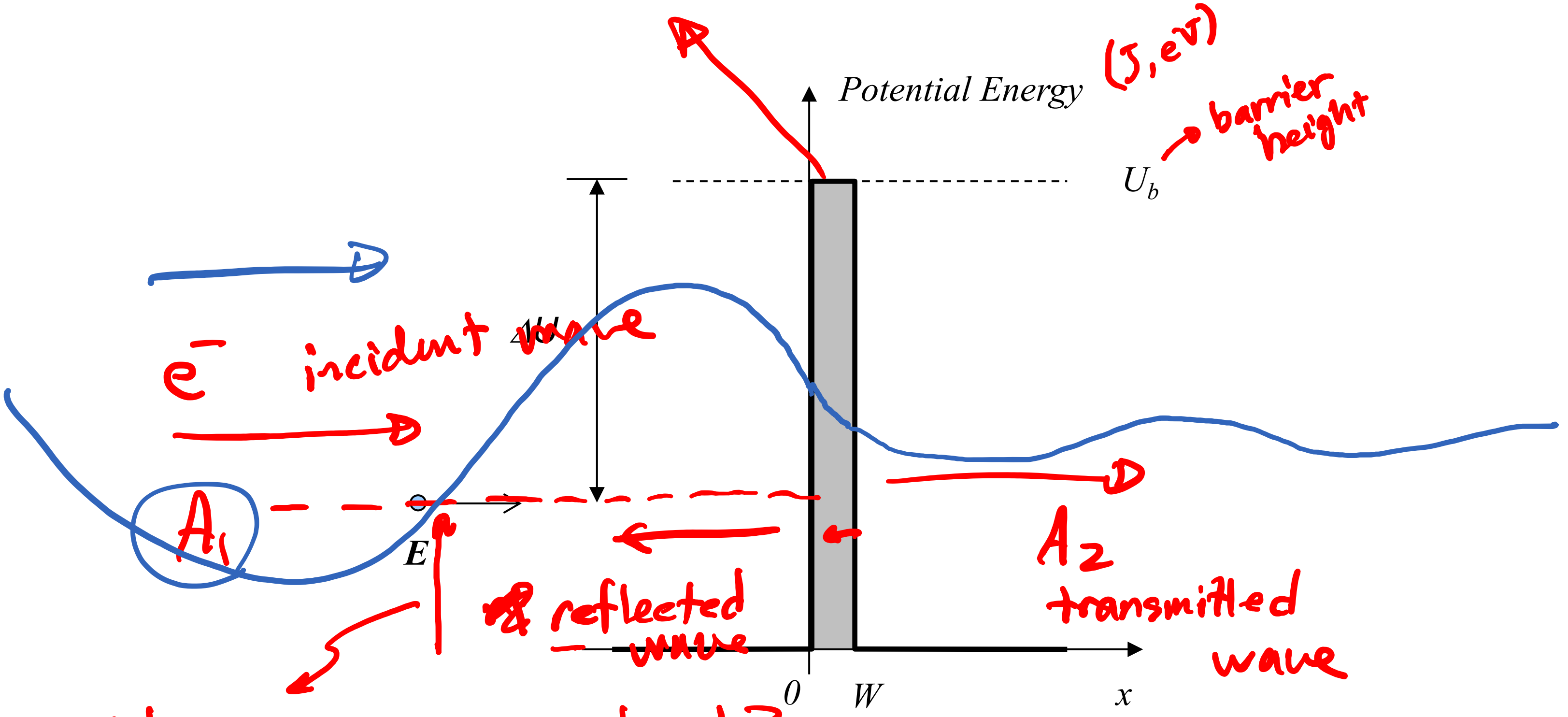
Quantum mechanics

- Equations and mathematics that are required to describe motion of particles and waves (e.g. electrons, photons) in matter.
- Schrödinger’s quantum mechanic description.

Potential Barrier and Quantum Tunneling

barrien energy is higher than total energy

$U_b > E$



total energy

$$E = \underset{\overset{\uparrow}{0}}{PE} + KE$$

$$T = \frac{|A_2|^2}{|A_1|^2}$$

width of barrier

The Schrödinger Wave Equation

- Electron behaves like a wave but also has a mass and a particle-like response.

$e^{j\theta} = \cos\theta + j\sin\theta$ $\underline{A\cos(kx - wt)}$

- Schrödinger tried to relate the particle and wave descriptions by inserting:

amplitude

wave number

frequency

$$\underline{\Psi(x,t)} = A\cdot e^{jkx - j\omega t} = A\cdot e^{j\frac{2\pi}{\lambda}x - j2\pi\nu t}$$

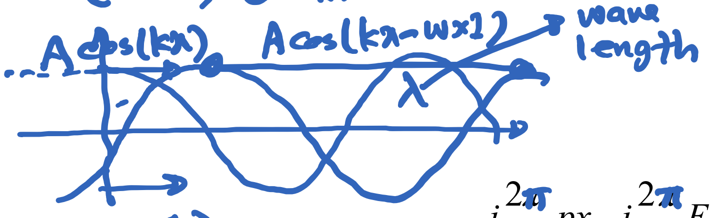
$k = \frac{2\pi}{\lambda}$ $\omega = 2\pi\nu$ $c = \frac{\omega}{k} = \lambda\nu$

$\Psi(x,t) = A e^{j(kx - wt)}$

$k > 0 \rightarrow$ moving in positive direction

$k < 0 \rightarrow$ " in negative direction

$e^{j\theta}$, $\theta = kx - wt$



$t = 1 \rightarrow (wx1)$

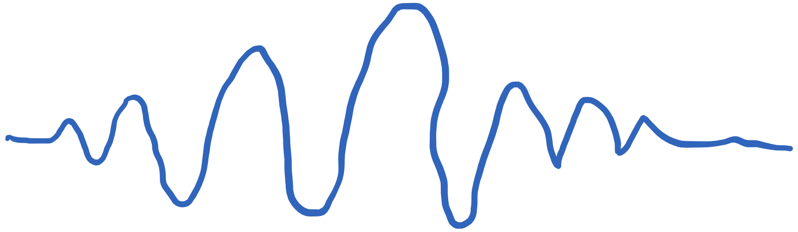
$$\Psi(x,t) = A\cdot e^{j\frac{2\pi}{h}px - j\frac{2\pi}{h}Et} = A\cdot e^{j\frac{p}{\hbar}x - j\frac{E}{\hbar}t}$$

Ψ

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

$E = h\nu \rightarrow \nu = \frac{E}{h}$

$\hbar = \frac{h}{2\pi}$



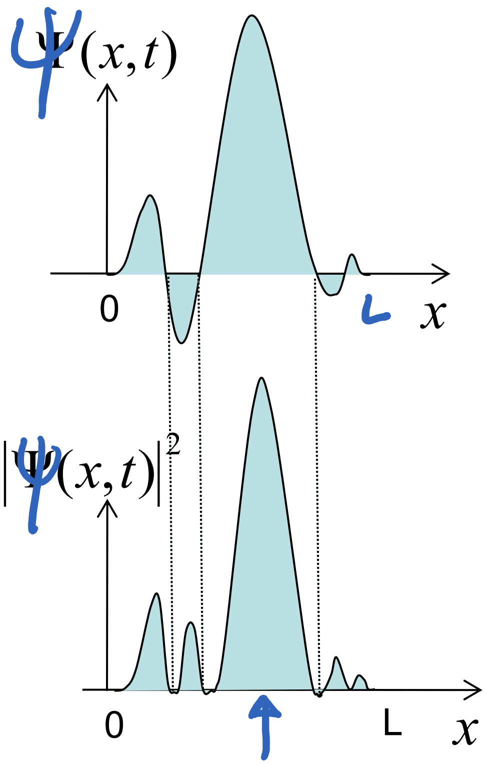
real electron wave function e^-

wave packet

What is Ψ?

∫ wave

- $\Psi(x,t)$ is the probability amplitude function.
- $|\Psi(x,t)|^2$ is the probability of finding the particle at x at time t.



- If we know that there is one electron between 0 and *L*

$$\int_0^L |\Psi(x,t)|^2 dx = 1$$

Normalization

Quantum operator

- In quantum mechanics, we find the value of parameters such as momentum and energy by applying their operators to the wave equation. In the next three slides we introduce operators for momentum, energy and kinetic energy.

$$\tilde{P}_x \Psi = P_x \cdot \Psi$$

$$\underline{\tilde{p}_x} \qquad \frac{\hbar}{j}\frac{\partial}{\partial x}$$

$$\Psi = A e^{jkx - j\omega t} = A e^{j\frac{p}{\hbar}x - j\frac{E}{\hbar}t}$$

$$\tilde{P}_x \Psi = \frac{\hbar}{j}\frac{\partial}{\partial x}\left[A e^{jP/\hbar\, x - jE/\hbar\, t}\right] = \frac{\cancel{\hbar}}{\cancel{j}} A \cdot \cancel{j}\frac{P}{\cancel{\hbar}} \cdot \cancel{A} e^{jP/\hbar\, x - jE/\hbar\, t}$$

$$= P \cdot \Psi(x,t)$$

$$\tilde{\vec{P}} \rightarrow \frac{\hbar}{j}\vec{\nabla}$$

$$\tilde{E} \qquad -\frac{\hbar}{j}\frac{\partial}{\partial t}$$

$$\tilde{E}\Psi = E \cdot \Psi$$

$$\tilde{E}\Psi = -\frac{\hbar}{j}\frac{\partial}{\partial t}\left[A e^{jP/\hbar\, x - jE/\hbar\, t}\right]$$

$$= \cancel{-}\frac{\cancel{\hbar}}{\cancel{j}}\left(\cancel{-}A\cancel{j}\frac{E}{\cancel{\hbar}}\right)\left[e^{jP/\hbar\, x - jE/\hbar\, t}\right] = E \cdot \Psi$$

Kinetic energy operator

$$\Psi = A e^{j\bar{k}\cdot\bar{r} - jE/\hbar\cdot t}$$

$$\Psi = A e^{(j\frac{p_x}{\hbar}x + j\frac{p_y}{\hbar}y + j\frac{p_z}{\hbar}z - j\frac{E}{\hbar}t}$$

$$KE = \frac{p_x^{\,2}}{2m} \qquad \widetilde{KE} \qquad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$\widetilde{KE}\,\Psi = KE\cdot\Psi \;, \qquad -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left[A e^{j\frac{p}{\hbar}x - jE/\hbar\, t}\right]$$

$$= -\frac{\cancel{\hbar^2}}{2m}\left(j\frac{p}{\cancel{\hbar}}\right)^2 A e^{j\frac{p}{\hbar}x - jE/\hbar\, t}$$

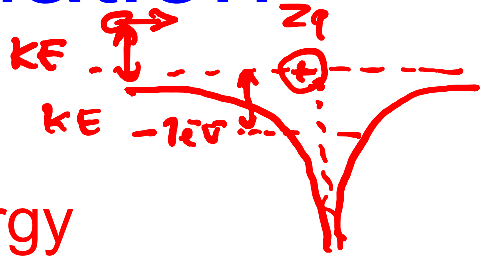
$$= \frac{p^2}{2m}\,\Psi(x,t) = ke\cdot\Psi$$

$$\widetilde{KE} \quad -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \boxed{-\frac{\hbar^2}{2m}\nabla^2}$$

"Anyone who can contemplate quantum mechanics without getting dizzy hasn't properly understood it"

- Niels Bohr (a founder of quantum mechanics)

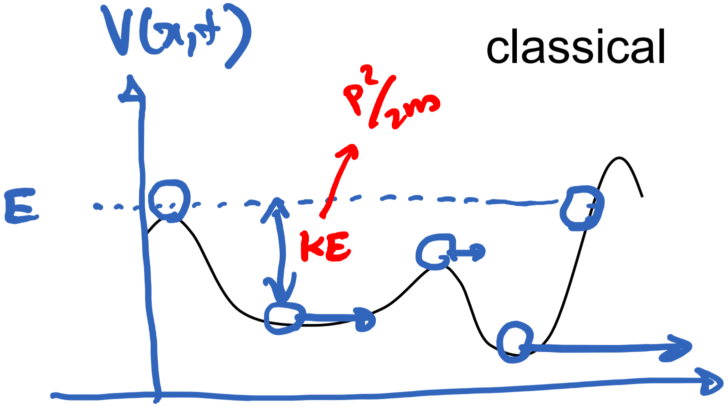
The Schrödinger Equation



Energy conservation:

Kinetic energy + potential energy = total energy

$$\frac{p^2}{2m} + V(x,t) = E$$



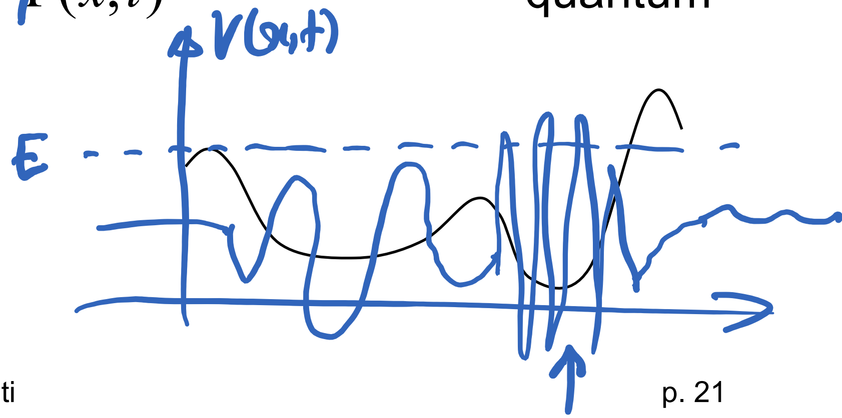
classical

unknown

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)+V(x,t)\Psi(x,t) = -\frac{\hbar}{j}\frac{\partial}{\partial t}\Psi(x,t)$$

quantum

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



Constant Potential Solution

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t)+V(x,t)\Psi(x,t)=-\frac{\hbar}{j}\frac{\partial}{\partial t}\Psi(x,t)$$

- Time independent potential $V(x,t)=V(x)$

$$\Psi(x,t)=\overset{X(x)}{\Psi_X(x)}\,\overset{T(t)}{\exp\left(-\frac{jEt}{\hbar}\right)}$$

$T(t)=e^{-j\frac{E}{\hbar}t}$

$X=\Psi_x$

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

Assume

$\Psi(x,t)=X(x)T(t)$

$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}XT+VXT=-\frac{\hbar}{j}\frac{\partial}{\partial t}XT$

$-\frac{\hbar^2}{2m}TX''+VXT=-\frac{\hbar}{j}XT' \xrightarrow{\times\frac{1}{XT}}$

$-\frac{\hbar^2}{2m}\frac{X''}{X}+V=-\frac{\hbar}{j}\frac{T'}{T}=\text{constant}=E$

total energy

$\rightarrow \begin{cases}-\frac{\hbar}{j}\frac{T'}{T}=E & \text{time}\\ -\frac{\hbar^2}{2m}\frac{X''}{X}+V=E & \text{space}\end{cases}$

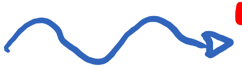
$-\frac{\hbar^2}{2m}X''+(V-E)X=0$

- Constant potential case $V(x)=U_0$
  - Case I: $E>U_0$

$\frac{d^2X}{dx^2}+\underbrace{\frac{2m}{\hbar^2}(E-U_0)}_{k^2}X=0 \rightarrow \frac{d^2X}{dx^2}+k^2X=0$

$$X(x)=\Psi_X(x)=Ae^{jkx}+Be^{-jkx} \qquad k=\sqrt{\frac{2m}{\hbar^2}(E-U_0)}=2\pi/\lambda$$

$\Psi(x,t)=X(x)T(t)=\left(Ae^{jkx}+Be^{-jkx}\right)e^{-jE/\hbar t} \rightarrow \Psi=Ae^{j(kx-E/\hbar t)}+Be^{j(-kx-E/\hbar t)}$

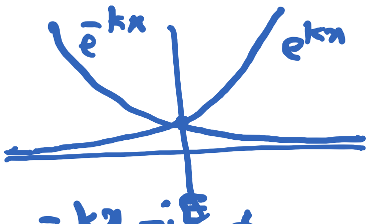


wave number

$\omega=E/\hbar$

  - Case II: $E<U_0$

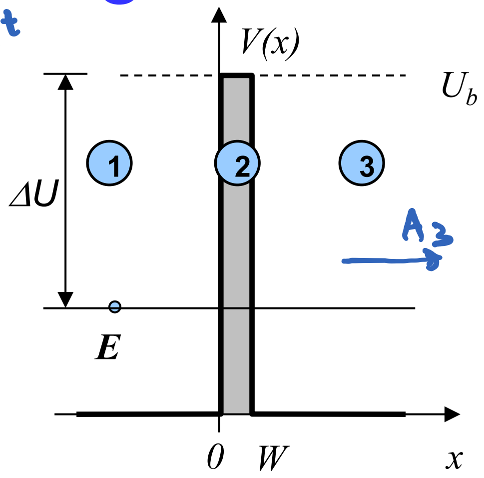
$\frac{d^2X}{dx^2}-\frac{2m}{\hbar^2}(U_0-E)X=0 \rightarrow \frac{d^2X}{dx^2}-k^2X=0$



$$\Psi_X(x)=Ae^{kx}+Be^{-kx} \qquad k=\sqrt{\frac{2m}{\hbar^2}(U_0-E)}$$

$\Psi(x,t)=X(x)T(t)=\left(Ae^{kx}+Be^{-kx}\right)e^{-jE/\hbar t}=Ae^{kx-jE/\hbar t}+Be^{-kx-j\frac{E}{\hbar}t}$

Potential Barrier and Tunneling



$V(x) = \begin{cases} 0 & ①, ③ \\ U_b & ② \end{cases}$

$T(t) = e^{-jE/\hbar t}$

① $V(x) = 0$ $\quad E > 0 \rightarrow$ sinusodial

$\Psi_1 = A_1 e^{jk_1x} + B_1 e^{-jk_1x}$ $\quad k_1 = \sqrt{\frac{2m}{\hbar^2}(E-0)}$

$\Psi_1(x,t) = A_1 e^{jk_1x - jE/\hbar t} + B_1 e^{-jk_1x - jE/\hbar t}$

incident wave

reflected wave

③ $V(x) = 0$, $\quad E > 0$

$\boxed{\Psi_3 = A_3 e^{jk_1x}} + B_3 e^{-jk_1x} \rightarrow B_3 = 0$

transmitted wave

$\Psi_3^* \Psi_3 = |\Psi_3|^2 = A_3^* \cancel{e^{-jk_1x}} A_3 \cancel{e^{jk_1x}} = A_3^* A_3 = |A_3|^2$

tunneling probability

$T = \frac{|A_3|^2}{|A_1|^2} = \left[1 + D \sinh^2(k_2 W)\right]^{-1}$

$\boxed{D = \frac{U_b^2}{4E(U_b - E)}}$

② $V(x) = U_b$, $\quad E < U_b \rightarrow$ expenential

$\Psi_2 = A_2 e^{k_2x} + B_2 e^{-k_2x}$ $\quad k_2 = \sqrt{\frac{2m}{\hbar^2}(U_b - E)}$

Boundary conditions

$x = 0 \rightarrow \Psi_1(0) = \Psi_2(0) \rightarrow A_1 + B_1 = A_2 + B_2$

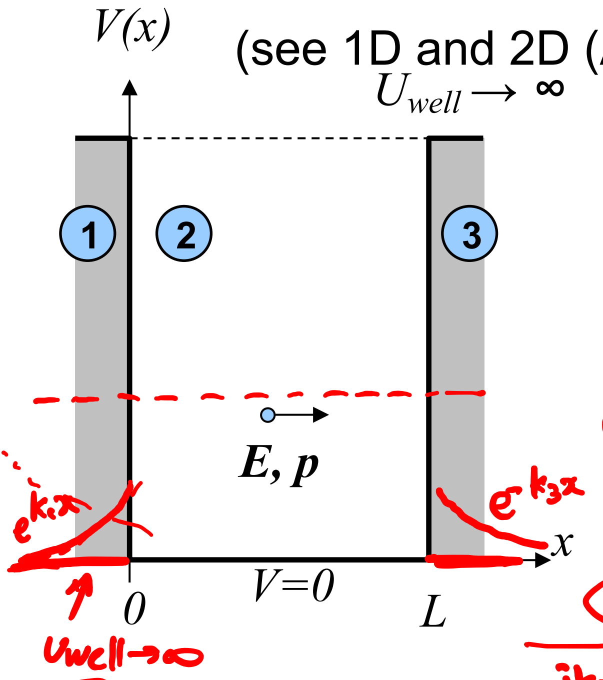
$x = 0 \rightarrow d\Psi_1/dx(0) = d\Psi_2/dx(0) \rightarrow A_1 jk_1 - B_1 jk_1 = A_2 k_2 - B_2 k_2$

$x = W \rightarrow \Psi_2(W) = \Psi_3(W) \rightarrow A_2 e^{k_2W} + B_2 e^{-k_2W} = A_3 e^{jk_1W}$

$x = W \rightarrow d\Psi_2/dx(W) = d\Psi_3/dx(W) = A_2 k_2 e^{k_2W} - B_2 k_2 e^{-k_2W} = jk_1 A_3 e^{jk_1W}$

Infinite Potential Well

(see 1D and 2D (Atkins) reading on course website under handouts)



A potential well can be used to represent electrons in an atom, quantum wells, and quantums.

$U(x) = V(x) = \begin{cases} 0 & 0 \le x \le L \\ V(x) = U_{well} \to \infty & \text{outside} \end{cases}$

infinite potential well

$0 < E < U_{well}$

① $V(x) = U_{well} \to \infty$ $E < U_{well}$ $U_{well} \to \infty$

$\psi_1(x) = A e^{k_1 x} + \cancel{B e^{-k_1 x}}$, $k_1 = \sqrt{\frac{2m}{\hbar^2}(U_{well} - E)} \to k_1 \to \infty$

$U_{well} \to \infty \Rightarrow k_1 \to \infty \Rightarrow A_1 = B_1 = 0$, $\psi_1 = 0$

③ $V(x) = U_{well} \to \infty$ $\psi_3 = 0$

$\boxed{k_2 = \sqrt{\frac{2mE}{\hbar^2}}}$

② $E > 0 \to \psi_2 = A_2 e^{jk_2 x} + B_2 e^{-jk_2 x}$ $\Big\} \to \psi_2 = A_2 (e^{jk_2 x} - e^{-jk_2 x}) = A \sin(k_2 x)$

$x = 0 \to \psi_2(0) = \psi_1(0) = 0 \to A_2 + B_2 = 0$

$x = L \to \psi_2(L) = \psi_3 = 0 \to A \sin(k_2 L) = 0 \to k_2 L = n\pi$ quantization

$\psi_2 = A \sin\left(\frac{n\pi}{L} x\right)$, $k_2 = \sqrt{\frac{2mE}{\hbar^2}} = \frac{n\pi}{L} \to$

$k_2 = \frac{n\pi}{L}$, $n = 1,2,3,\ldots$ $E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$

$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$

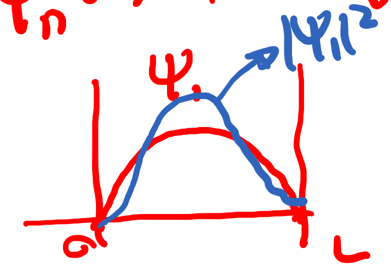
$\int_0^L \psi^2 dx = 1 \to \int_0^L A^2 \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$

$\int_0^L A^2 \left[\frac{1}{2} - \underbrace{\cancel{\frac{\cos\left(\frac{2n\pi x}{L}\right)}{2}}}_{0}\right] dx = 1 \to A^2 \frac{L}{2} = 1 \to A = \sqrt{\frac{2}{L}}$

$$\boxed{\psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) e^{-j\frac{E}{\hbar}t}}$$

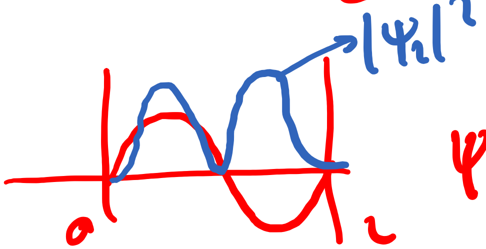
$\psi_n(x) = A\sin\left(\frac{n\pi}{L}x\right)$, $E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$

n=1



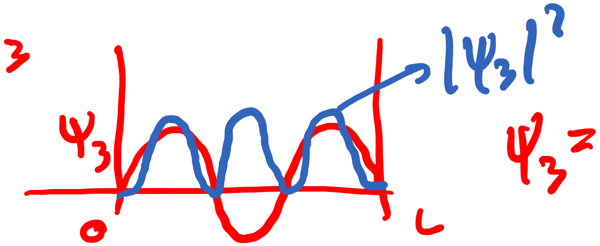
$\psi_1 = A\sin\left(\frac{\pi}{L}x\right)$ $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$

n=2

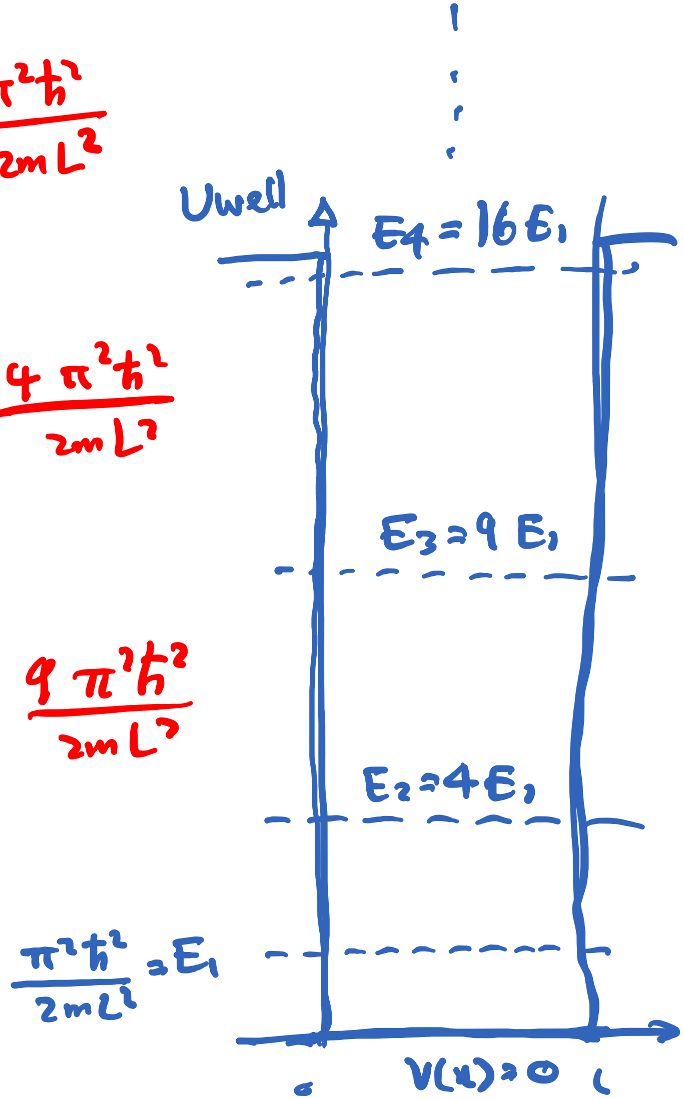


$\psi_2 = A\sin\left(\frac{2\pi}{L}x\right)$ $E_2 = \frac{4\pi^2\hbar^2}{2mL^2}$

n=3



$\psi_3 = A\sin\left(\frac{3\pi}{L}x\right)$ $E_3 = \frac{9\pi^2\hbar^2}{2mL^2}$

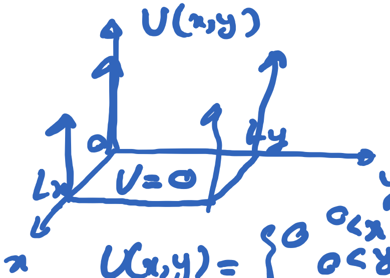


2D Infinite Well Solution

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\Psi_{n_x,n_y}(x,y) = \overset{A}{\sqrt{\frac{4}{L_x L_y}}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \quad e^{-jE/\hbar\, t}$$

$$E(n_x,n_y) = \frac{\hbar^2}{2m}\left(\overbrace{\frac{n_x^2\pi^2}{L_x^2}}^{E_x} + \overbrace{\frac{n_y^2\pi^2}{L_y^2}}^{E_y}\right)$$



$$U(x,y) = \begin{cases} 0 & 0<x<L_x,\ 0<y<L_y \\ \infty & \text{outside} \end{cases}$$

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + \overset{=0}{U(x,y)}\Psi = E\Psi \rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\Psi = E\Psi$$

$$\text{Assume: } \Psi = XY \rightarrow -\frac{\hbar^2}{2m}\left[X''Y + XY''\right] = EXY \rightarrow -\frac{\hbar^2}{2m}\left(\frac{X''}{X} + \frac{Y''}{Y}\right) = E \rightarrow$$

$$\begin{cases} -\frac{\hbar^2}{2m}\frac{X''}{X} = E_x \rightarrow \\ -\frac{\hbar^2}{2m}\frac{Y''}{Y} = E_y \\ \underbrace{E = E_x + E_y} \end{cases}$$

$$-\frac{\hbar^2}{2m}X'' - E_x X = 0$$

$$X = A_2 e^{+jk_x x} + B_2 e^{-jk_x x}$$

$$k_x = \sqrt{\frac{2mE_x}{\hbar^2}}$$

$$X(x) = A\sin\left(\frac{n_x\pi}{L_x}x\right)$$

$$n_x = 1, 2, 3, \ldots$$

$$Y = A_2' e^{jk_y y} + B_2' e^{-jk_y y}$$

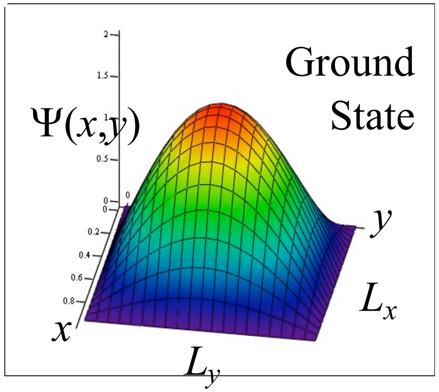
$$k_y = \sqrt{\frac{2mE_y}{\hbar^2}}$$

$$Y(y) = A\sin\left(\frac{n_y\pi}{L_y}y\right)$$

$$n_y = 1, 2, 3, \ldots$$

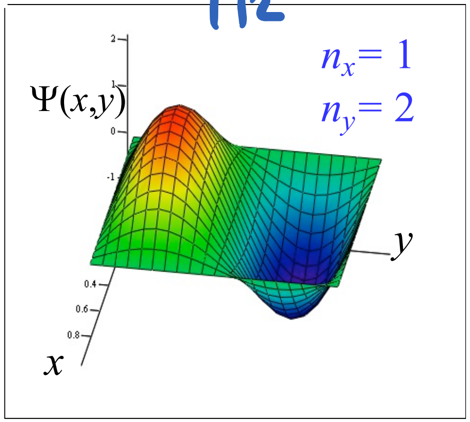
$$\Psi(x,y) = XY = A\sin\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)$$

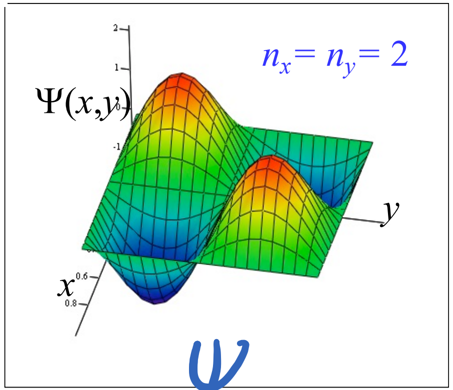
$n_x = n_y = 1$



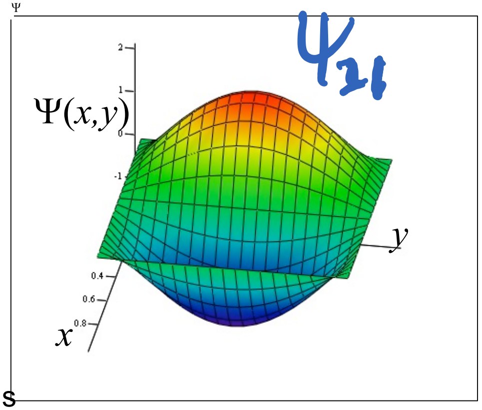
Ψ_{11}

Ψ_{12}





Ψ_{22}



Ψ_{21}

square potential well

$L_x = L_y = a$

$$E = \frac{\hbar^2}{2m}\left(\frac{n_x^2\pi^2}{a^2} + \frac{n_y^2\pi^2}{a^2}\right) = \frac{\hbar^2\pi^2}{2ma^2}\left(n_x^2 + n_y^2\right)$$

$$E_{11} = \frac{2}{2}\,\frac{\hbar^2\pi^2}{ma^2} = \frac{\hbar^2\pi^2}{ma^2}$$ ground state

$E_{12} = \frac{5}{2} E_{11}$

$E_{21} = 5/2\, E_{11}$

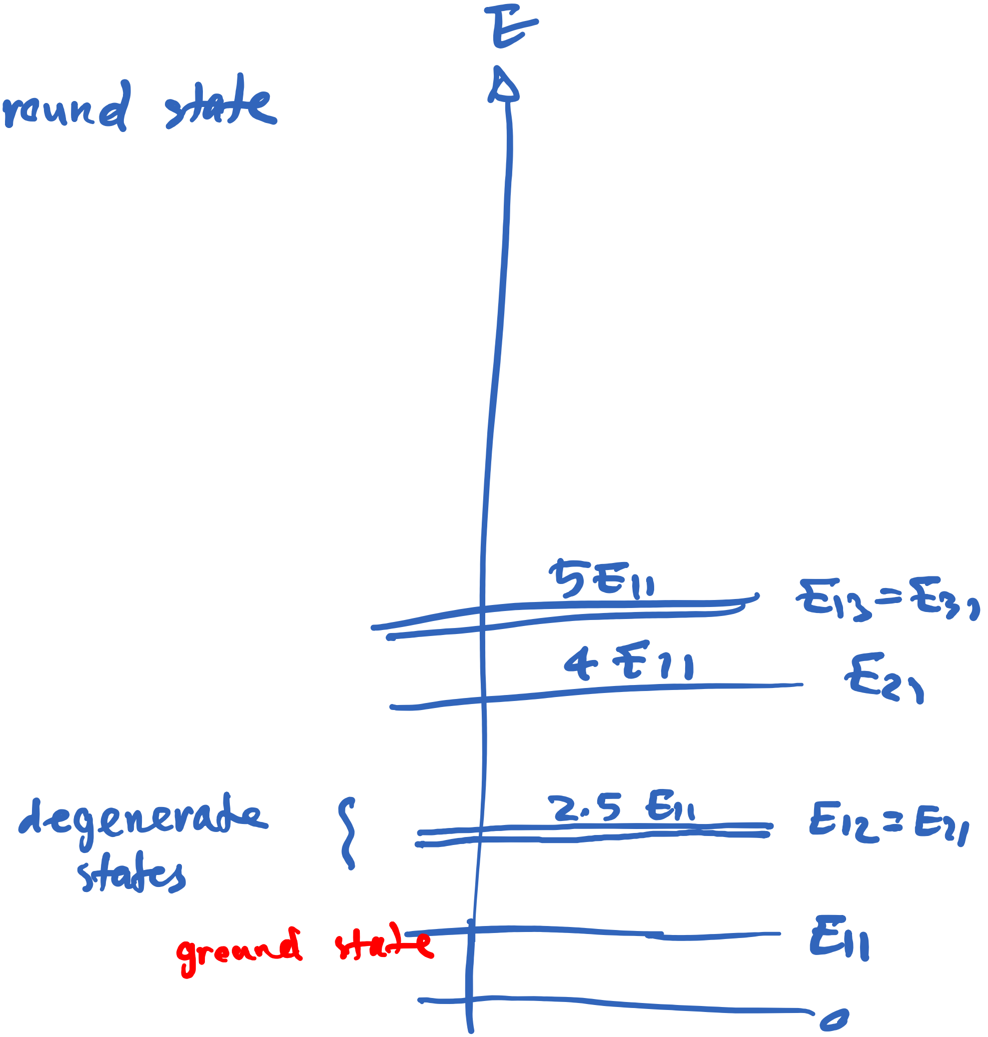
$E_{22} = 4 E_{11}$

$E_{13} = 5 E_{11}$

$E_{31} = 5 E_{11}$

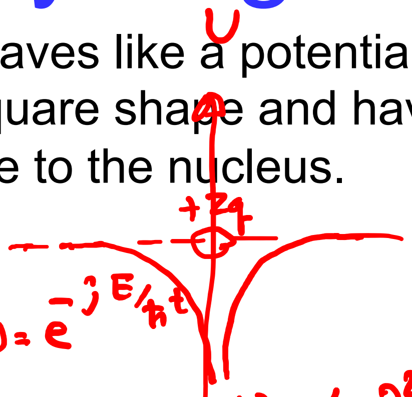
$E_{23} = E_{32} = \frac{13}{2} E_{11}$

$E_{33} = 9 E_{11}$



Hydrogen Atom

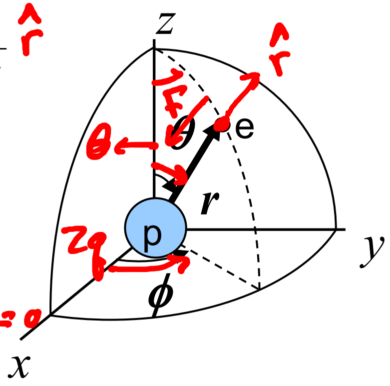
- A hydrogen atom behaves like a potential well for electron. This potential well will not have a square shape and have a Coulomb 1/r dependence, where r is the distance to the nucleus.



$$U(r,\theta,\varphi) = -\frac{Zq}{4\pi\varepsilon_0 r}$$

Time-independent potential : $T(t) = e^{-jE/\hbar t}$

$$F_s = -\frac{Zq^2}{4\pi\varepsilon_0 r^2}\hat{r}$$



$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r}) + (U(\vec{r}) - E)\Psi(\vec{r}) = 0$$

$-\hbar^2/2m\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi$

$\left(-\frac{q}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}} - E\right)\psi = 0$

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

$\Psi_{nlm_l}(r,\theta,\phi) = R_n(r)\Theta_l(\theta)\Phi_{m_l}(\varphi)$ s (spin quantum number)

orbital → magnetic quantum number

shell number $n \geq 1, 2, 3, \ldots$ $0 \leq l \leq n-1$, $-l \leq m_l \leq l$

$$\boxed{\Psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}}$$

→ Bohr's radius

$n=1 \rightarrow l=0 \rightarrow m_l=0 \rightarrow \Psi_{100}, E_{100}$

(s orbital)

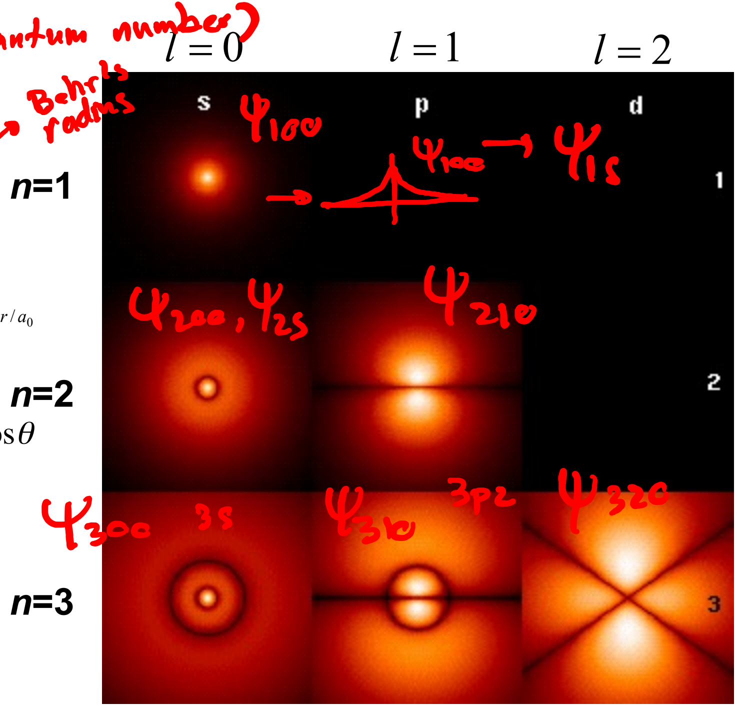
$n=2 \rightarrow$ $l=0\ (s) \rightarrow m_l=0 \rightarrow \Psi_{200}, E_{200}$

$$\Psi_{200} = \frac{1}{\sqrt{32\pi a_0^3}}\left(2-\frac{r}{a_0}\right)e^{-r/a_0}$$

$l=1 \rightarrow m_l = \begin{cases} -1 & \Psi_{21-1}\ 2p_x \\ 0 & \Psi_{210}\ 2p_z \\ 1 & \Psi_{211}\ 2p_y \end{cases}$

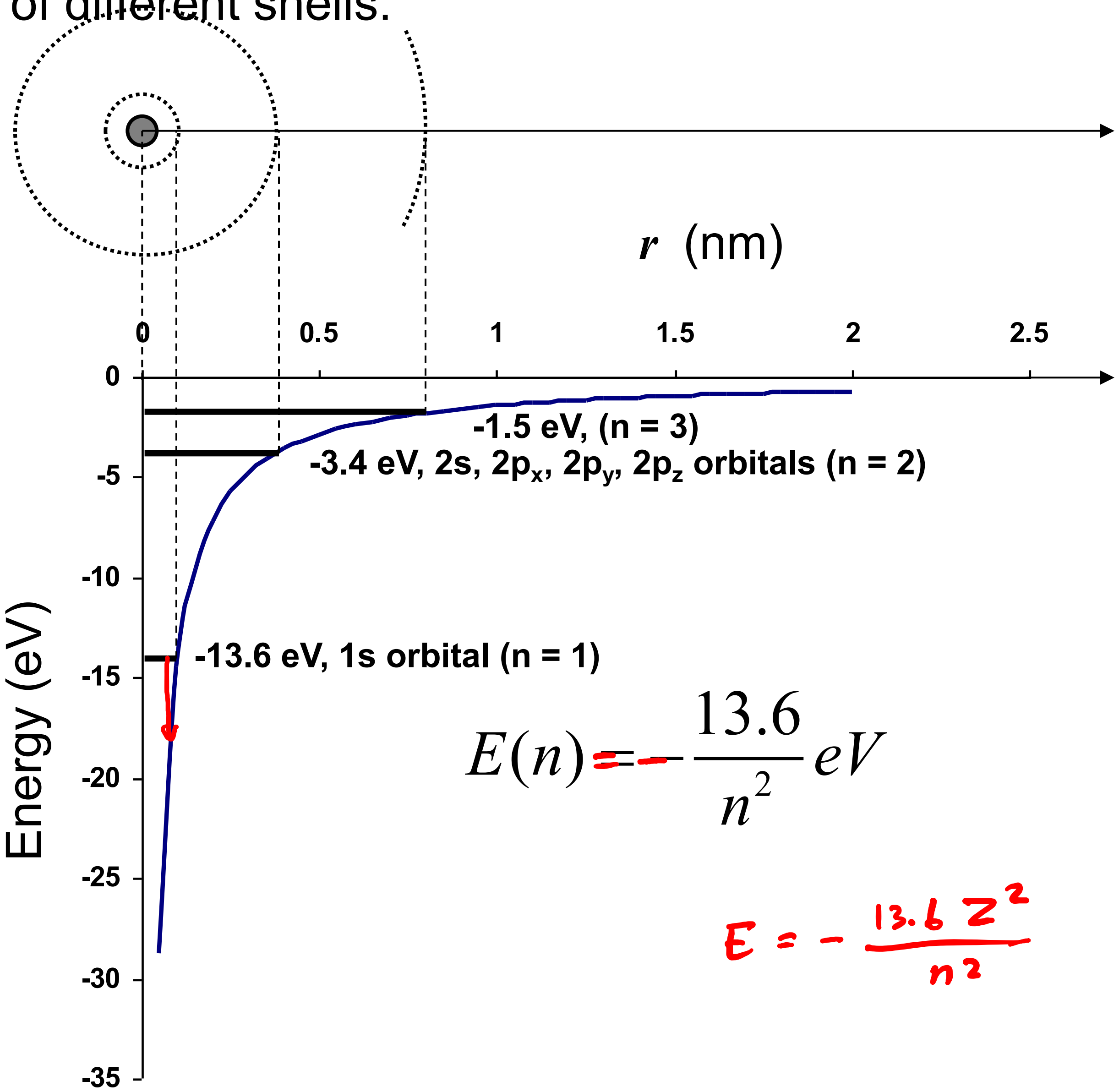
$$\Psi_{210} = \frac{1}{\sqrt{32\pi a_0^3}} r e^{-r/2a_0}\cos\theta$$

$n=3 \rightarrow \begin{cases} l=0\ (s) \rightarrow m_l=0 \rightarrow \Psi_{300}, \Psi_{3s} \\ l=1\ (p) \Rightarrow m_l=-1,0,1 \rightarrow \Psi_{31-1}, \Psi_{310}, \Psi_{311} \\ l=2\ (d) \rightarrow m_l=-2,-1,0,1,2 \rightarrow 5\ d \text{ orbitals} \end{cases}$



Energy and Electron Shells

Energy of different shells:

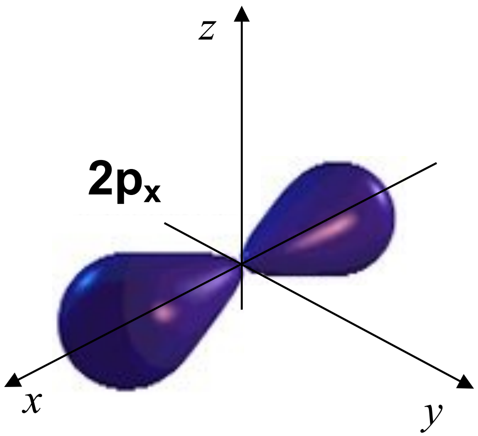


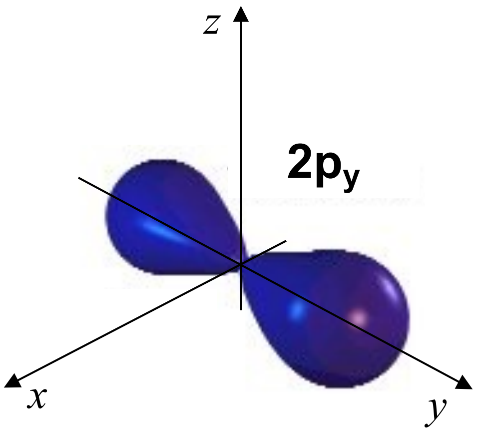
$$E(n) = -\frac{13.6}{n^2} eV$$

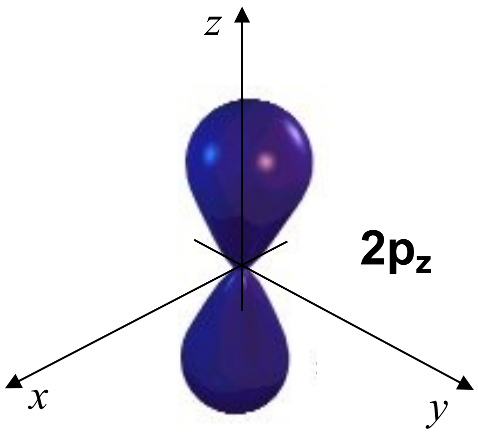
$$E = -\frac{13.6 Z^2}{n^2}$$

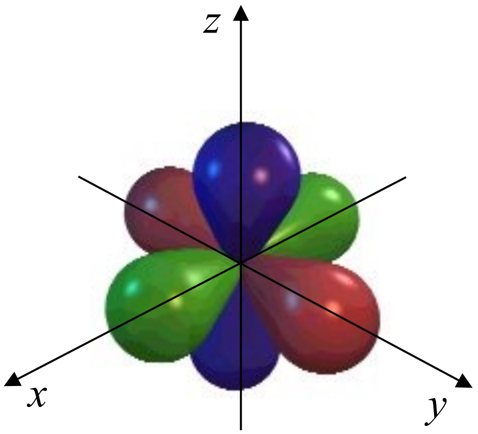
p Orbitals

- For p orbitals, $l = 1$ and $m_l = -1,0,1$ leading to three orbitals in different directions.







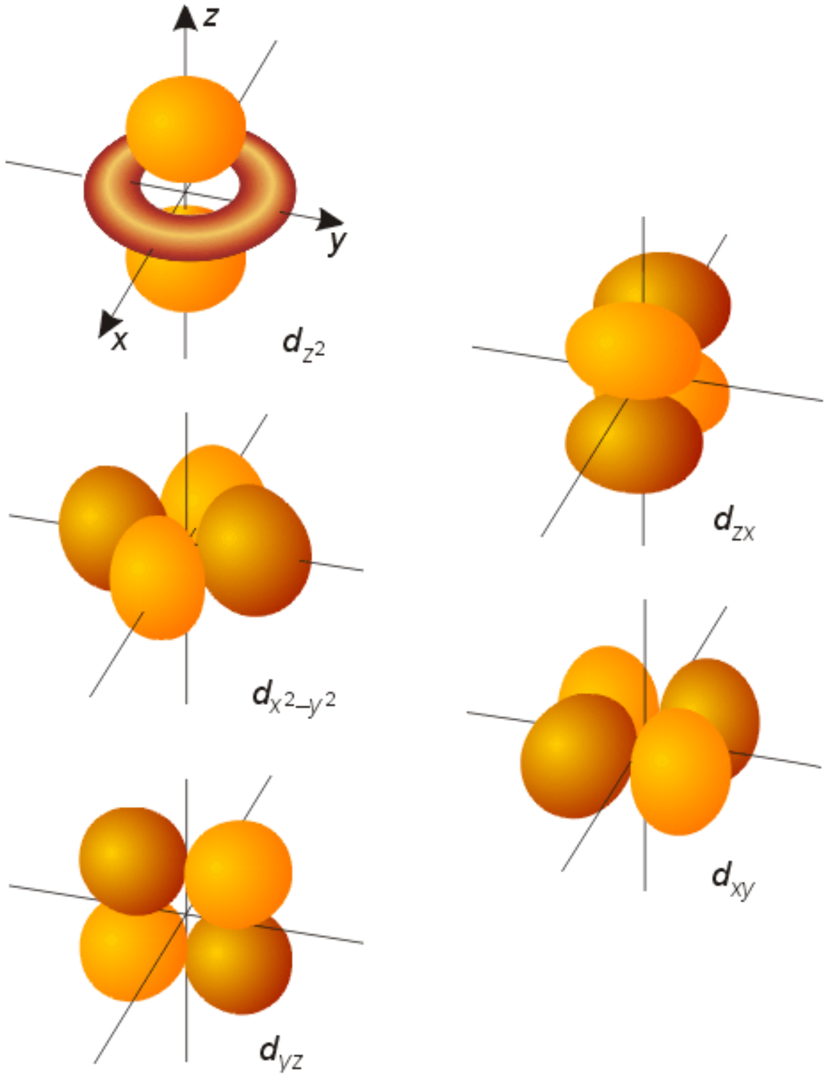


http://library.thinkquest.org/15567/lessons/4.html

http://www.chemistry.uvic.ca/chem222/Notes/lect3v1.htm

d Orbitals

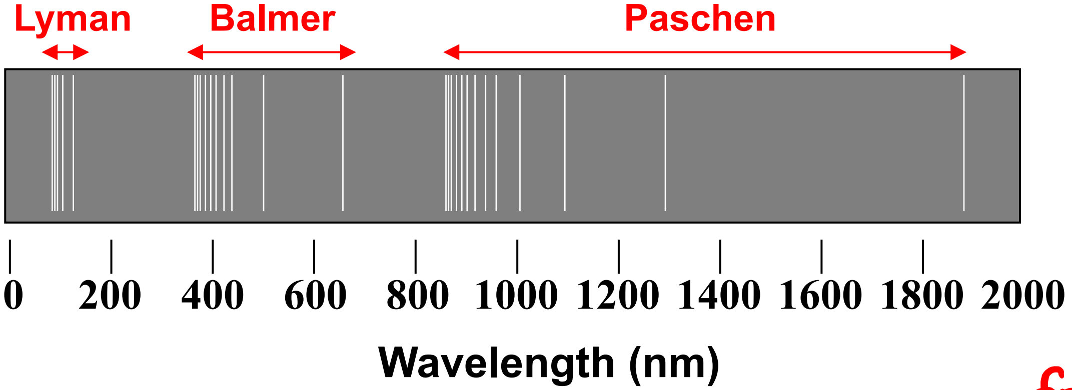
- For d orbitals, $l = 2$ and $m_l = -2,-1,0,1,2$ leading to five orbitals with different shapes.

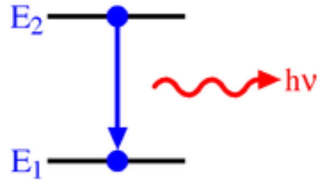


http://www.chemistry.uvic.ca/chem222/Notes/lect3v1.htm

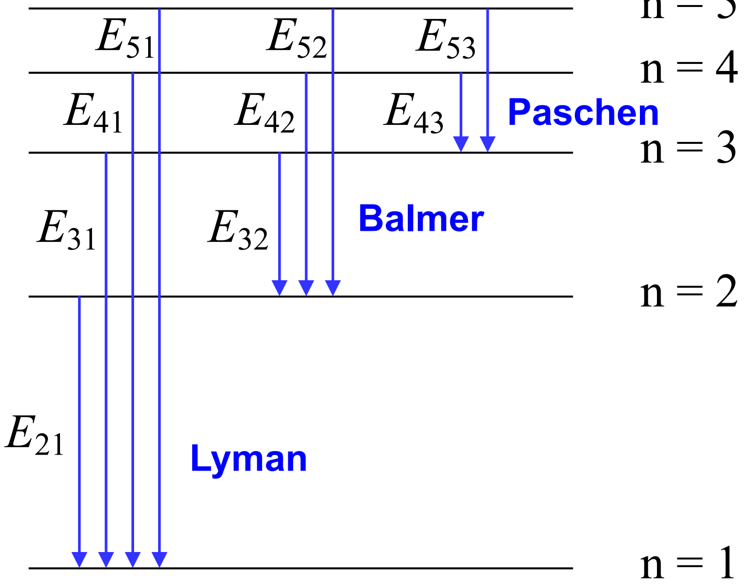
Emission (Absorption) Spectrum

- Movement of electron from a shell (state) at higher energy to a shell (state) at lower energy can emit an energy packet (photon or light). The emission wavelength is specific to each atom and acts like the signature of that atom.





$E_{ph} = h\nu = E_2 - E_1$



frequency ↓ → 1st shell → shell n

Lyman $\nu = cR\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$, $n = 2,3,4,\ldots$ UV photons

Balmer $\nu = cR\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$, $n = 3,4,5,\ldots$ visible

2nd shell

Paschen $\nu = cR\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$, $n = 4,5,6,\ldots$ IR

$$R = 109{,}678 \text{ cm}^{-1} = \frac{mq^4}{8\epsilon_0^2 h^3 c}$$

Atkins, Physical Chemistry, 3rd ed.

http://csep10.phys.utk.edu/astr162/lect/light/absorption.html

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch6/bohr.html