Applied Statistical Mechanics
Lecture Note - 2

Classical Mechanics and / Qunatum Mechanics

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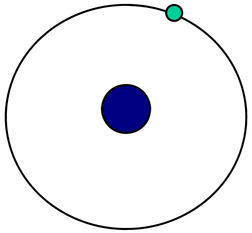
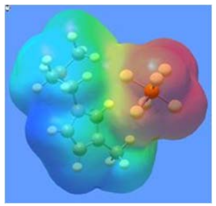
Mechanics /Thermodynamics

- Mechanics
  - Dealing with objects and motions
  - Dealing with mechanical variables
    - Velocity, acceleration, force, ….
- Thermodynamics
  - Dealing with heat, work and energy
  - Dealing with thermodynamic functions
    - Internal energy, Enthalpy, Entropy, Gibbs energy,…

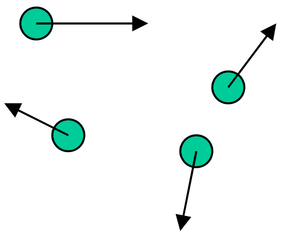
Mechanics and Thermodynamics

Quantum Mechanics





Classical Mechanics



Statistical Thermodynamics

Thermodynamic Properties

T, P, V

U, H, A, H, S

Classical Mechanics

- Newtonian Mechanics

$$\mathbf{F} = m\mathbf{a} = m\ddot{\mathbf{r}}$$

$$\mathbf{r} = \mathbf{r}(x, y, z)$$

$$\ddot{\mathbf{r}} = \frac{d^2\mathbf{r}}{dt^2}$$

$$\mathbf{F} = -\nabla U$$

$$= -(\mathbf{i}\frac{\partial U}{\partial x} + \mathbf{j}\frac{\partial U}{\partial x} + \mathbf{k}\frac{\partial U}{\partial x})$$

Lagrangian Mechanics

- Invariant equation under coordinate transformation

$$L = K - U$$

$$K = \frac{m\dot{q}^2}{2}$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) = \frac{\partial L}{\partial q_j} \qquad j = 1,2,3,\ldots$$

Hamiltonian Mechanics

- More convenient for quantum mechanics and statistical mechanics

$$H = K + U$$

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_i \frac{\mathbf{p}_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

$$\downarrow$$

Legendre transformation

$$\left[\frac{\partial H}{\partial \mathbf{r}_i}\right] = -\dot{\mathbf{p}}_i$$

$$\left[\frac{\partial H}{\partial \mathbf{p}_i}\right] = \dot{\mathbf{r}}_i$$

Quantum Mechanics

- Quantum Mechanics
  - Relation between structure and (Particle / Atom / Molecule) and its energy (or energy distribution)

Introduction and Principles → Simple applications : Particles → Atomic Structure → Molecular Structure

Classical Physics

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- Described by Newton's Law of Motion (17th century)
  - Successful for explaining the motions of objects and planets

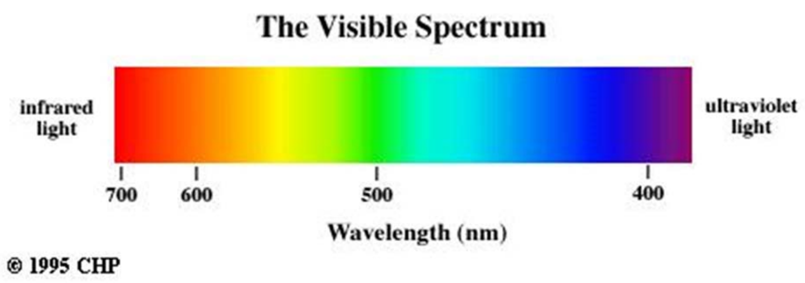
$$H = \sum_i \frac{p_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

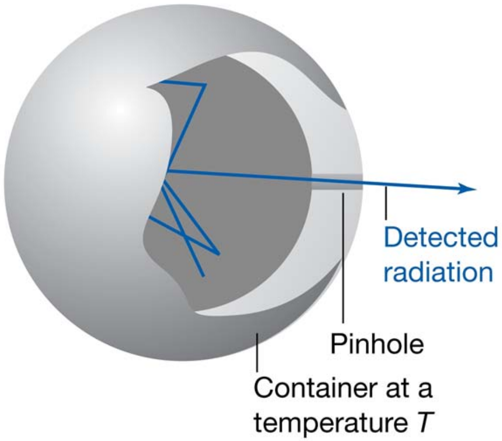
  - In the end of 19th century, experimental evidences accumulated showing that classical mechanics failed when applied to very small particles.

Sir Isaac Newton

The failures of Classical Physics

- Black-body radiation
  - A hot object emits light (consider hot metals)
  - At higher temperature, the radiation becomes shorter wavelength (red → white → blue)
  - Black body : an object capable of emitting and absorbing all frequencies uniformly





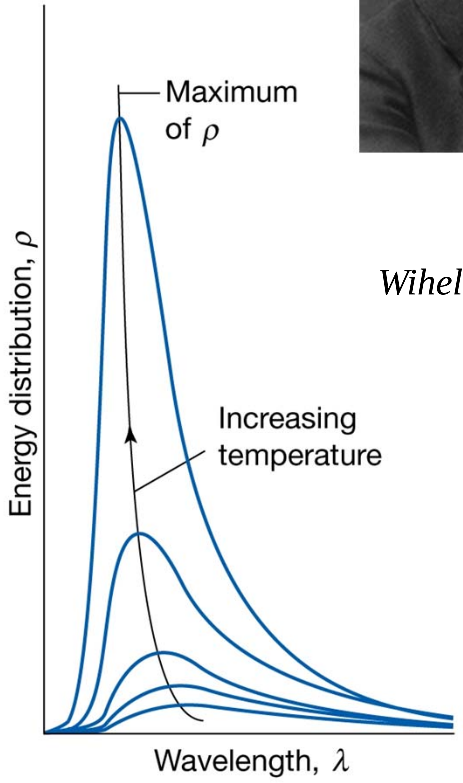
The failures of classical physics

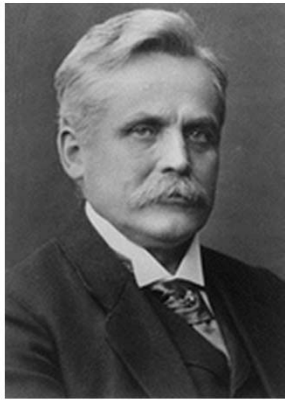
- Experimental observation
  - As the temperature raised, the peak in the energy output shifts to shorter wavelengths.
  - Wien displacement law

$$T\lambda_{\max} = \frac{1}{5}c_2 \qquad c_2 = 1.44\,\text{cm K}$$

  - Stefan-Boltzmann law

$$\mathrm{E} = E/V = aT^4 \qquad M = \sigma T^4$$

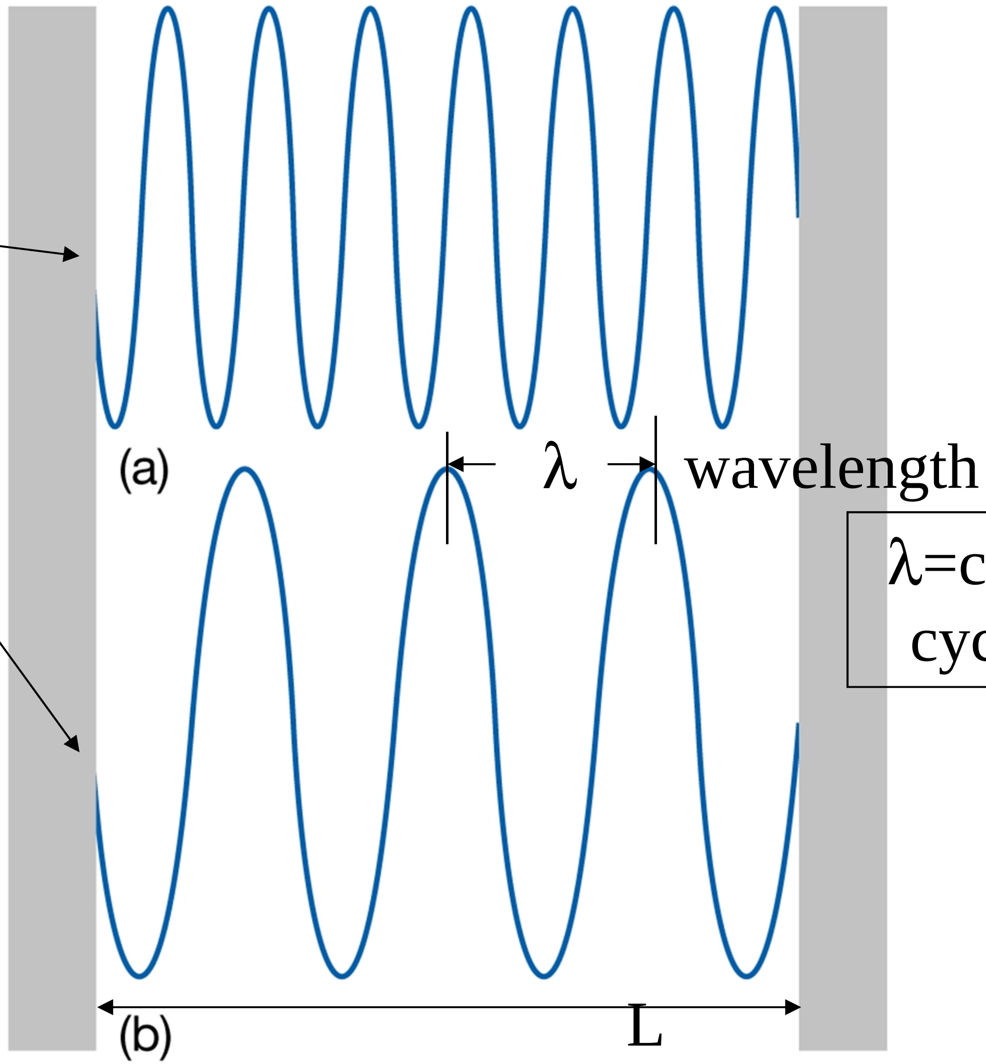




Wihelm Wien

Standing Wave

Zero amplitude at boundary



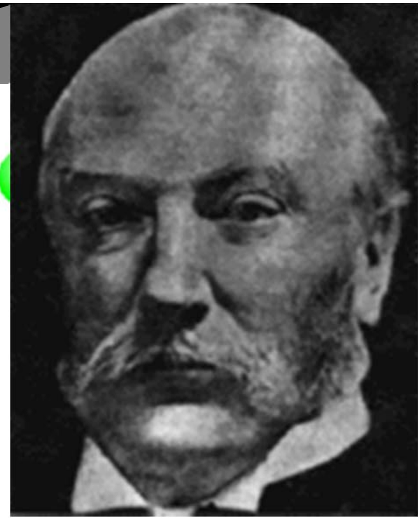
λ=c/ν , ν = # of cycles per sec

Rayleigh – Jeans law

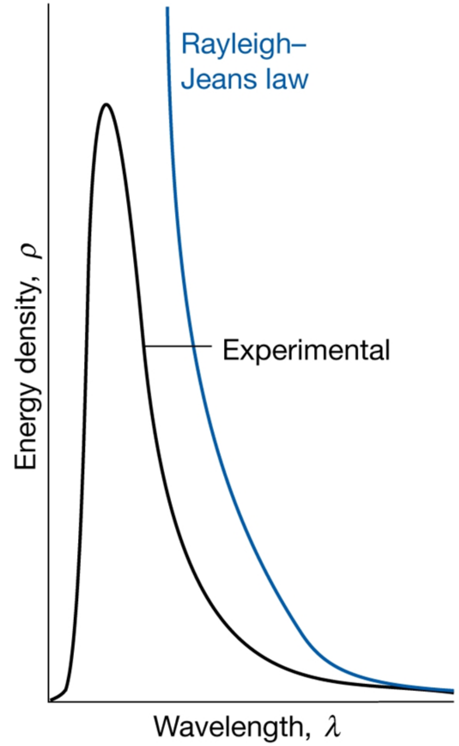
- First attempted to describe energy distribution
- Used classical mechanics and equi-partition principle

$$dE = \rho d\lambda \qquad \rho = \frac{8\pi kT}{\lambda^4}$$

- Although successful at high wavelength, it fails badly at low wavelength.
- Ultraviolet Catastrophe
  - Even cool object emits visible and UV region
  - We all should have been fried !



Lord Rayleigh



Planck's Distribution

- Energies are limited to discrete value
  - Quantization of energy

$$E = nh\nu \qquad , \; n = 0,1,2,...$$

- Planck's distribution

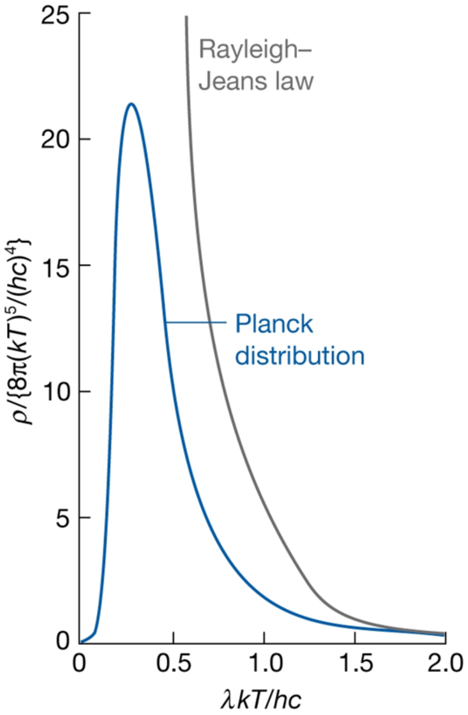
$$dE = \rho d\lambda \qquad \rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

- At high frequencies approaches the Rayleigh-Jeans law

$$(e^{hc/\lambda kT} - 1) = (1 + \frac{hc}{\lambda kT} + ...) - 1 \approx \frac{hc}{\lambda kT}$$

- The Planck's distribution also follows Stefan-Boltzmann's Las

Max Planck



Heat Capacities

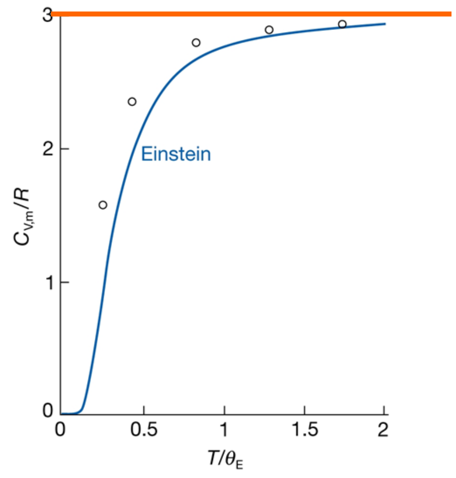
- Dulong Petit's Law
  - The molar heat capacities of monoatomic solids are the same , close to 25 J/mol. K
  - Can be justified using classical mechanics
  - Mean energy of an atom oscillates about its mean position of solid is kT

$$U_m = 3N_A kT = 3RT$$

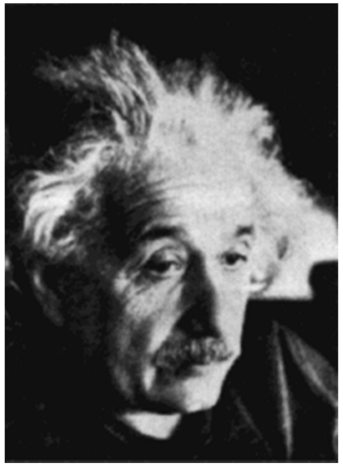
$$C_v = \left(\frac{\partial U_m}{\partial T}\right)_V = 3R = 24.9 \text{ J/mol K}$$

- Unfortunately, at low T the value

approaches to zero

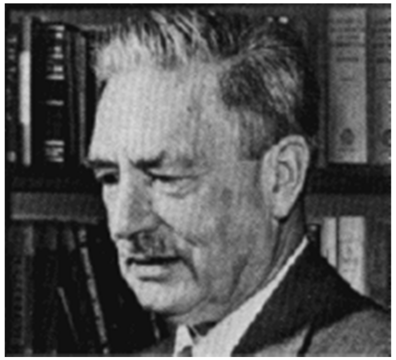


Einstein and Debye Formula



- Einstein used the hypothesis that energy of oscillation is confined to discrete value

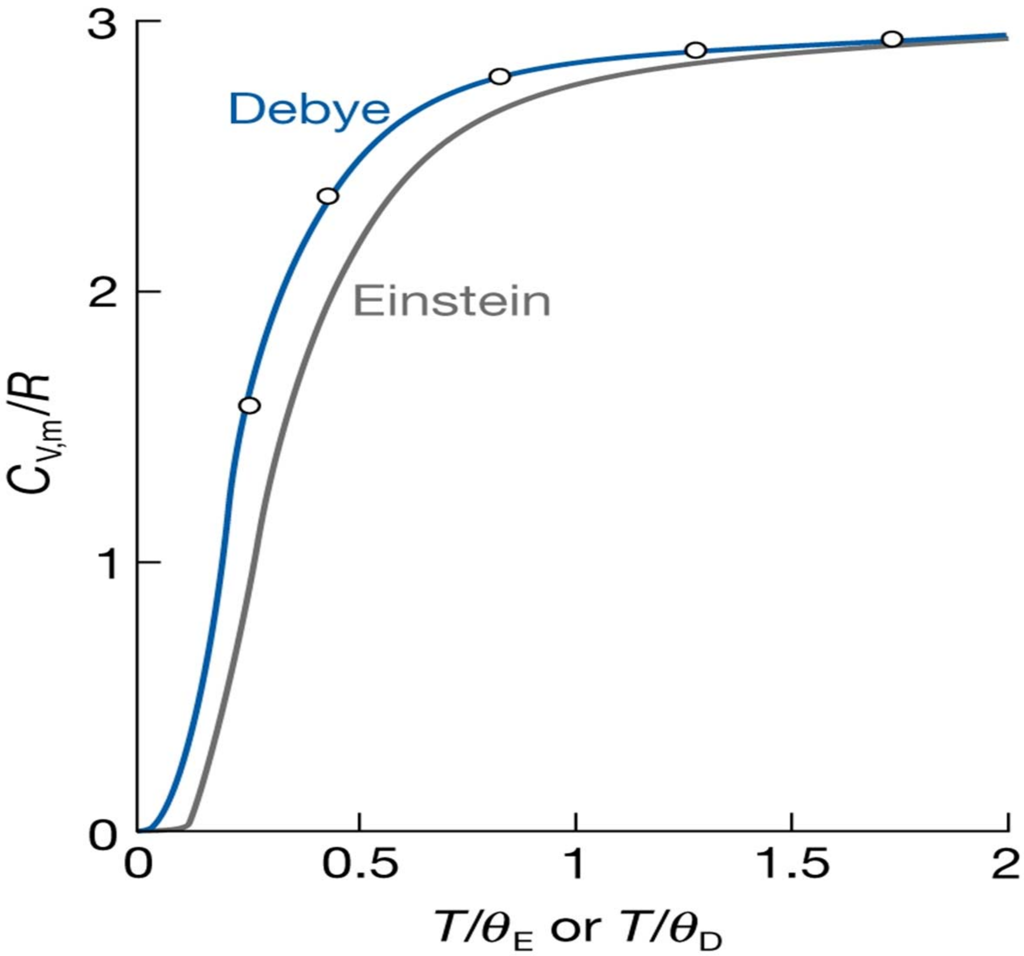
$$C_v = 3Rf^2 \qquad f = \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/2T}-1}\right)$$



- Debye later refined Einstein formula taking into account that atoms are not oscillating at the same frequency.

$$C_v = 3Rf \qquad f = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T}\left[\frac{x^4 e^x}{(1-e^x)^2}\right]dx$$

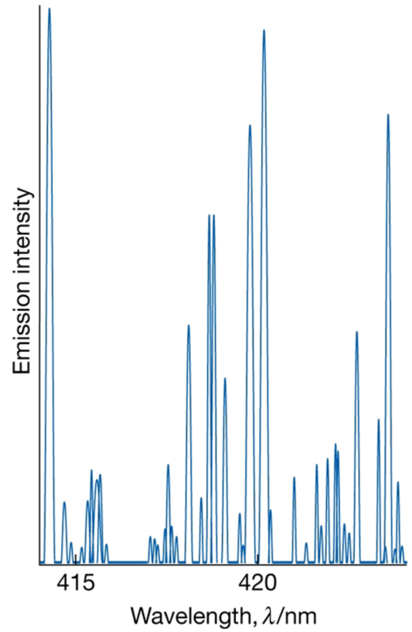
Einstein and Debye's Theory



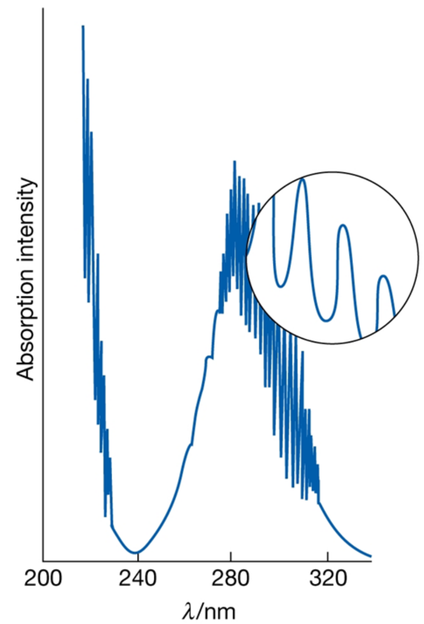
Atomic and Molecular Spectra

- Light comes from exited atomic lamps shows sharp, specific lines, rather than a broad continua.

- This observation can be understood if we assume that the energy of atoms and molecules is confined to discrete values.



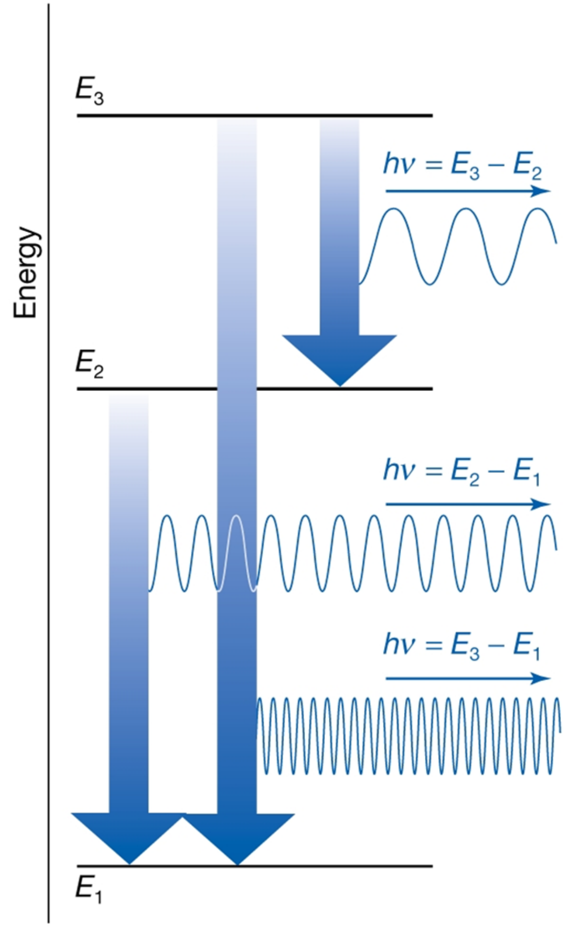
An atomic spectrum



A molecular spectrum

Atomic and Molecular Spectra

- Spectral lines can be accounted for if we assume that a molecule emits a photon as it changes between discrete energy levels.



Wave-Particle Duality -The particle character of wave

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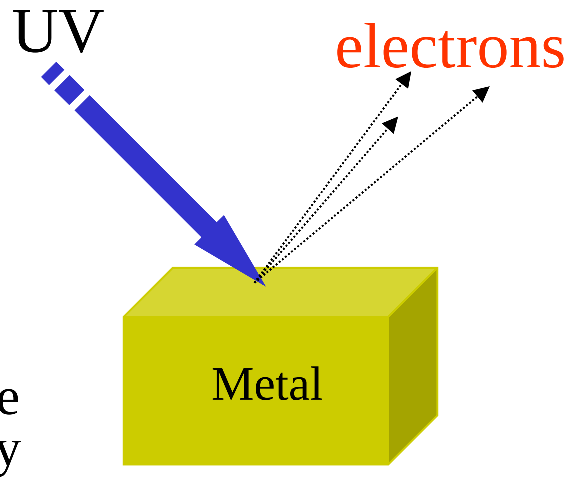
- Particle character of electromagnetic radiation
  - Observation :
    - Energies of electromagnetic radiation of frequency ν can only have $E = 0, h\nu, 2h\nu, \ldots$ (corresponds to particles $n = 0, 1, 2, \ldots$ with energy $= h\nu$)
  - Particles of electromagnetic radiation : Photon
  - Discrete spectra from atoms and molecules can be explained as generating a photon of energy hν .

    $\Delta E = h\nu$

Wave-Particle Duality
-The particle character of wave

- Photoelectric effect
  - Ejection of electrons from metals when they are exposed to UV radiation
  - Experimental characteristic
    - No electrons are ejected, regardless of the intensity of radiation, unless its frequency exceeds a threshold value characteristic of the metal.
    - The kinetic energy of ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation .
    - Even at low light intensities, electrons are ejected immediately if the frequency is above threshold.



Wave-Particle Duality
-The particle character of wave

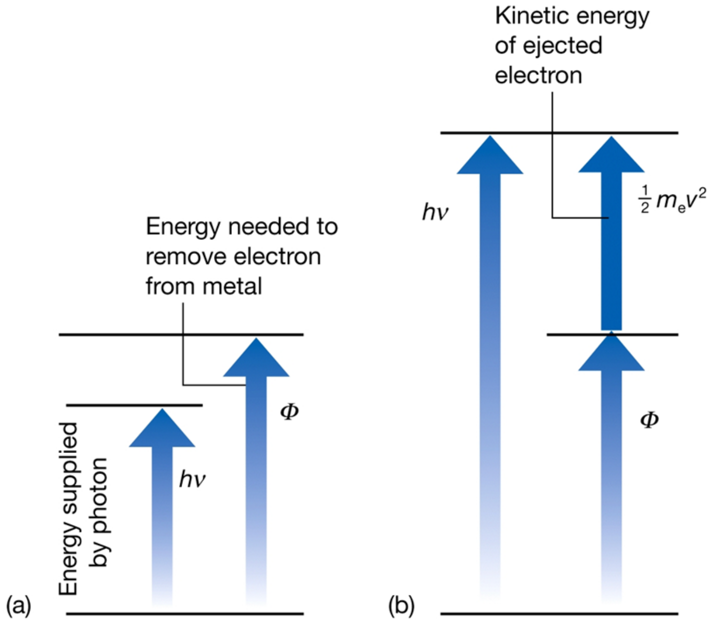
- Photoelectric effect
  - Observations suggests ;
    - Collision of particle – like projectile that carries energy
    - Kinetic energy of electron = hν –Φ

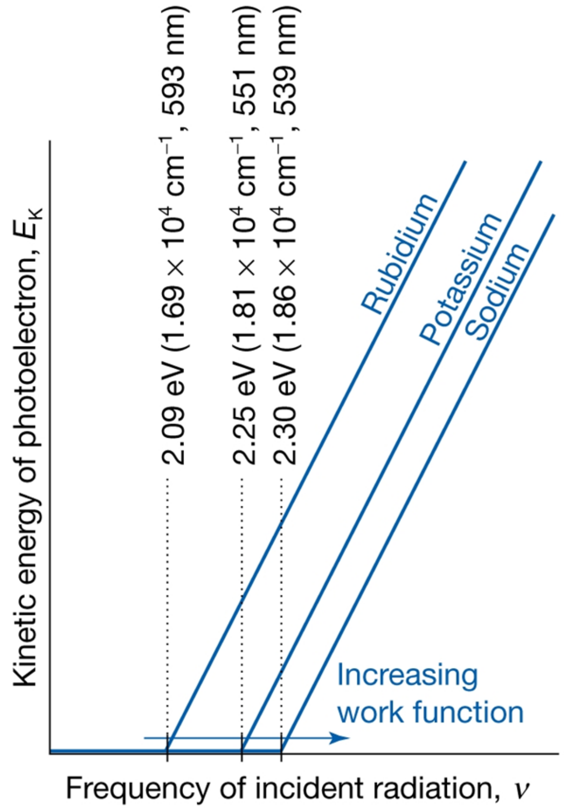
      Φ : work function (characteristic of the meltal)

      energy required to remove a electron from the metal to infinity
    - For the electron ejection , hν > Φ required.
    - In case hν < Φ , no ejection of electrons

Wave-Particle Duality
-The particle character of wave

- Photoelectric effect



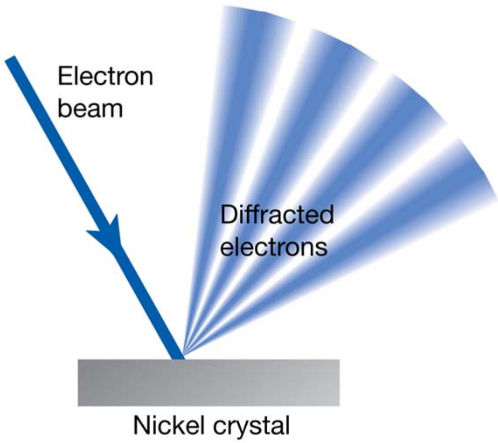


Wave-Particle Duality
-The wave character of particles

- Diffraction of electron beam from metal surface
  - Davison and Germer (1925)
  - Diffraction is characteristic property of wave
  - Particles (electrons) have wave like properties !

  - From interference pattern, we can get structural information of a surface

    LEED (Low Energy Electron Diffraction)



Wave Particle Duality

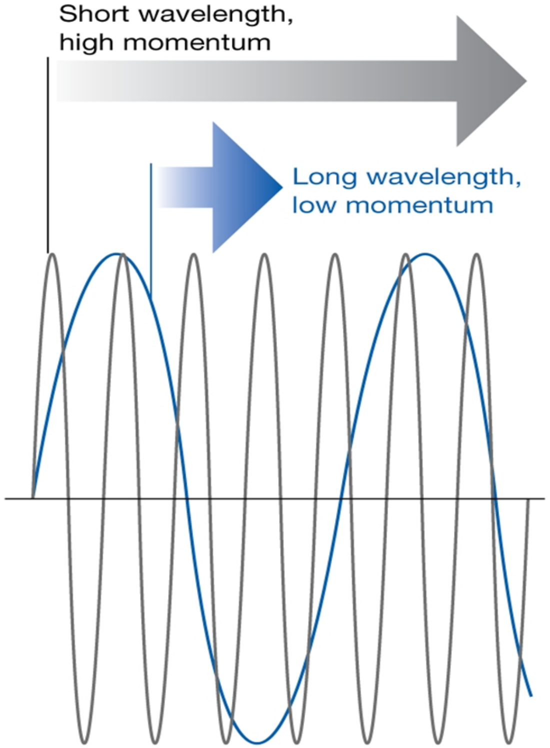
- De Brogile Relation (1924)
  - Any particle traveling with a linear momentum p has wave length λ

Matter wave: $p = mv = h/\lambda$

  - Macroscopic bodies have high momenta (large p)

→small wave length

→wave like properties are not observed



Schrödinger equation

- 1926, Erwin Schrödinger (Austria)
  - Describe a particle with wave function
  - Wave function has full information about the particle

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

→ **Time independent Schrödinger equation for a particle in one dimension**

2^{nd} order differential equation : Can be easily solved when V(x) and B.C are known !

An example

- Constant potential energy V(x) = V

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

A solution of this equation is

$$\psi = e^{ikx} = \cos kx + i \sin kx \qquad k = \left\{\frac{2m(E - V)}{\hbar^2}\right\}^{1/2}$$

Schrodinger Equation
: General form

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Table 11.1 The Schrödinger equation

For one-dimensional systems:

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

where $V(x)$ is the potential energy of the particle and E is its total energy. For three-dimensional system

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

where V may depend on position and ∇^2 ('del squared') is

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

In systems with spherical symmetry:

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

In the general case the Schrödinger equation is written

$$H\psi = E\psi$$

Where H is the hamiltonian operator for the system:

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

For the evolution of a system with time, it is necessary to solve the time-dependent Schrödinger equation

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

$H\Psi = E\,\Psi$

$H = T + V$

: Hamiltonian operator

The Born interpretation of the Wave Function

- The Wave function
  - Contains all the dynamic information about the system
  - Born made analogy with the wave theory of light (square of the amplitude is interpreted as intensity – finding probability of photons)
  - Probability to find a particle is proportional to $|\psi|^2 = \psi^* \psi$ **Probability Density**
  - It is OK to have negative values for wave function

Max Born

Born interpretation of the Wave Function

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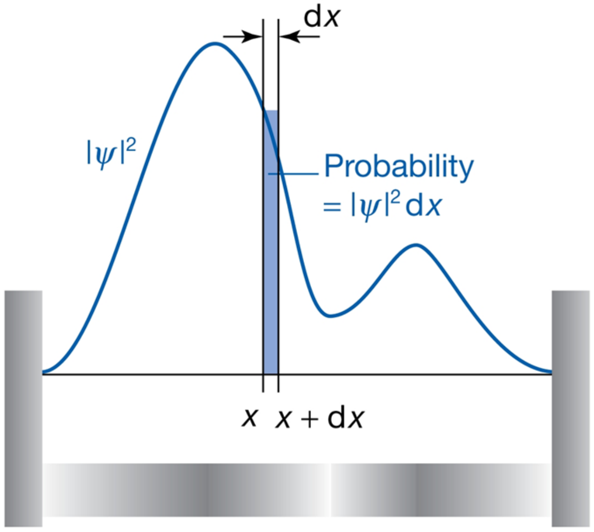
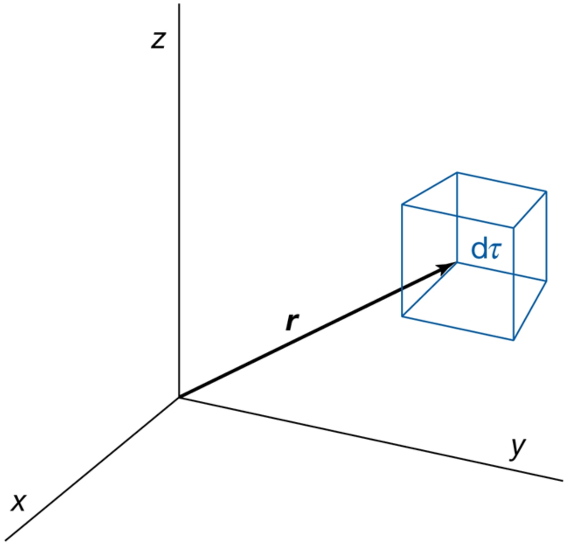
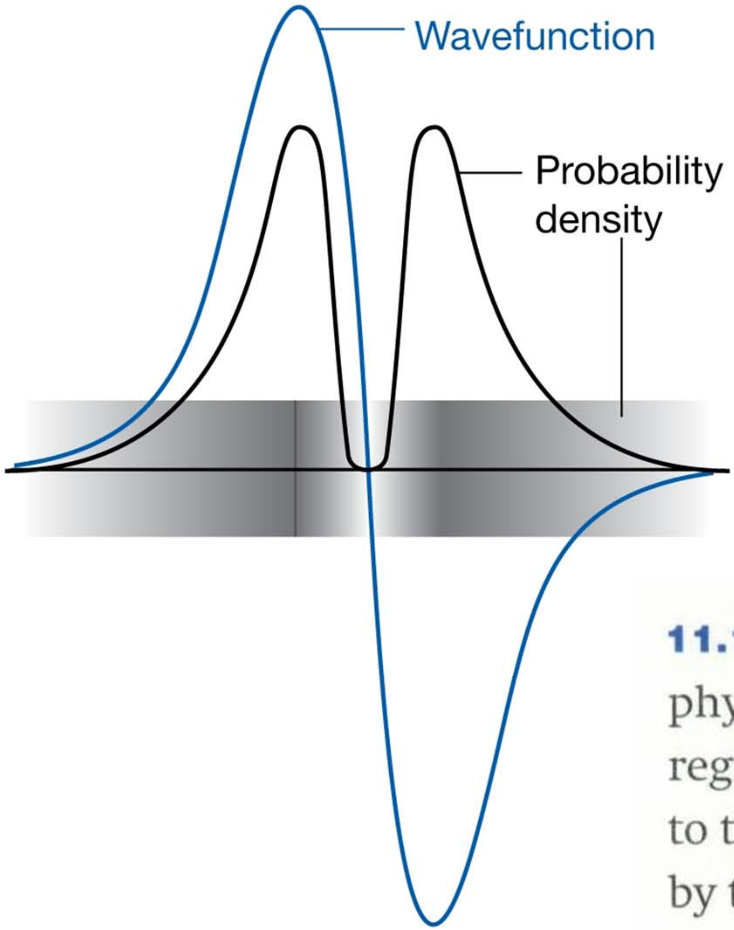
If the wavefunction of a particle has the value ψ at some point x, then the probability of finding the particle between x and $x + dx$ is proportional to $|\psi|^2 dx$.





If the wavefunction of a particle has the value ψ at some point r, then the probability of finding the particle in an infinitesimal volume $d\tau = dx\,dy\,dz$ at that point is proportional to $|\psi|^2 d\tau$.

Born interpretation of the Wave Function



11.17 The sign of a wavefunction has no direct physical significance: the positive and negative regions of this wavefunction both correspond to the same probability distribution (as given by the square modulus of ψ and depicted by the density of shading).

Normalization

- When ψ is a solution, so is $N\psi$
- We can always find a ***normalization const.*** such that the proportionality of Born becomes equality

$$N^2 \int \psi^* \psi dx = 1$$

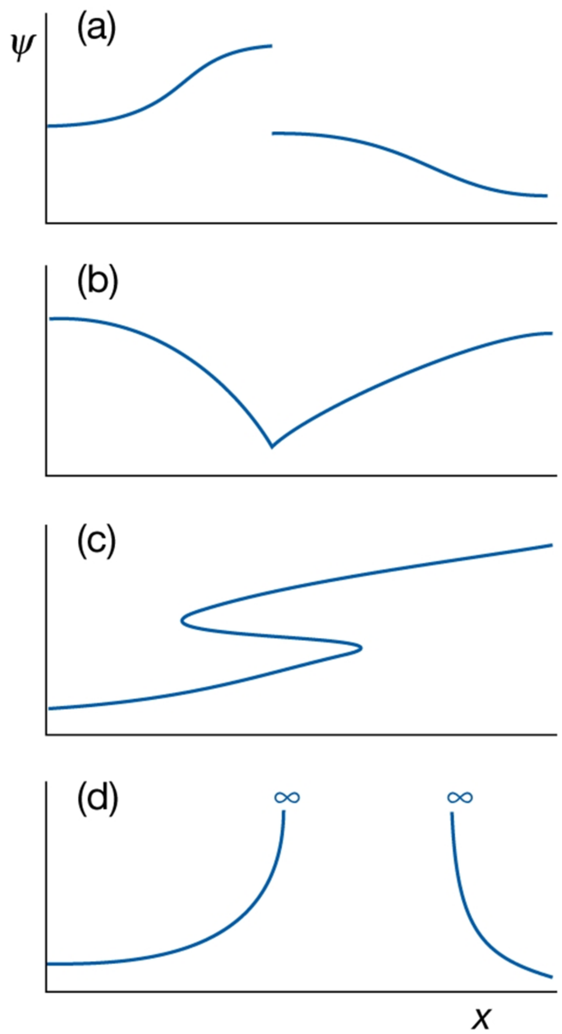
$$\int \psi^* \psi dx = 1$$

$$\int \psi^* \psi dxdydz = \int \psi^* \psi d\tau = 1$$

Normalization const. are already contained in wave function

Quantization

- Energy of a particle is quantized
  - → Acceptable energy can be found by solving Schrödinger equation
  - → There are certain limitation in energies of particles



The information in a wavefunction

- Simple case
  - One dimensional motion, *V=0*

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

Solution

$$\psi = Ae^{ikx} + Be^{-ikx} \qquad E = \frac{k^2\hbar^2}{2m}$$

Probability Density

B = 0

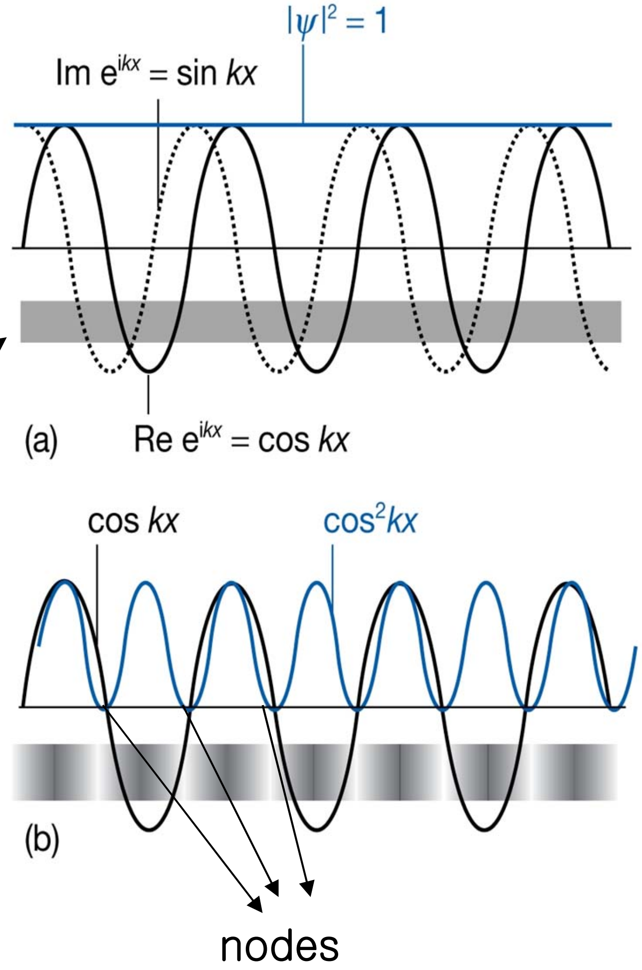
$$\psi = Ae^{ikx} \qquad |\psi|^2 = |A|^2$$

A = 0

$$\psi = Be^{-ikx} \qquad |\psi|^2 = |B|^2$$

A = B

$$\psi = 2A\cos kx \qquad |\psi|^2 = 4|A|\cos^2 kx$$



Eigenvalues and eigenfucntions

- Momentum

$$E = \frac{k^2\hbar^2}{2m} = \frac{p^2}{2m} \longrightarrow \quad p = k\hbar$$

- Succinct form of Schrödinger eqn.

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

Hamiltonian operator

Kinetic energy operator

Potential energy operator

Eigenvalues and eigenfucntions

- Eigenvalue equation

(Operator)(function) = (constant factor)*(same function)

$$\hat{\Omega}\psi = \omega\psi$$

Operator

Eigenfunction → Solution : Wave function

Eigenvalue → Allowed energy (quantization)

$$(\text{operator corresponding to observable})\psi = (\text{value of observable})\times\psi$$

Operators

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$$\hat{\Omega}\psi = \omega\psi$$

• Position	x	$\hat{x} = x\times$
• Momentum	p_x	$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$
• Potential energy	$V = \frac{1}{2}kx^2$	$\hat{V} = \frac{1}{2}kx^2\times$
• Kinetic energy	$E_K = \frac{p_x^2}{2m}$	$\hat{E}_K = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$
• Total energy		$\hat{H} = \hat{E}_K + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}$

Example

$$\psi = Ae^{ikx}$$

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

$$\frac{\hbar}{i}\frac{d}{dx}\psi = p_x\psi$$

$$\frac{\hbar}{i}\frac{d}{dx}Ae^{ikx} = -khAe^{ikx} = kh\psi$$

$$p_x = +kh$$

$$\psi = Be^{-ikx}$$

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$$

$$\frac{\hbar}{i}\frac{d}{dx}\psi = p_x\psi$$

$$\frac{\hbar}{i}\frac{d}{dx}Be^{-ikx} = khBe^{ikx} = -kh\psi$$

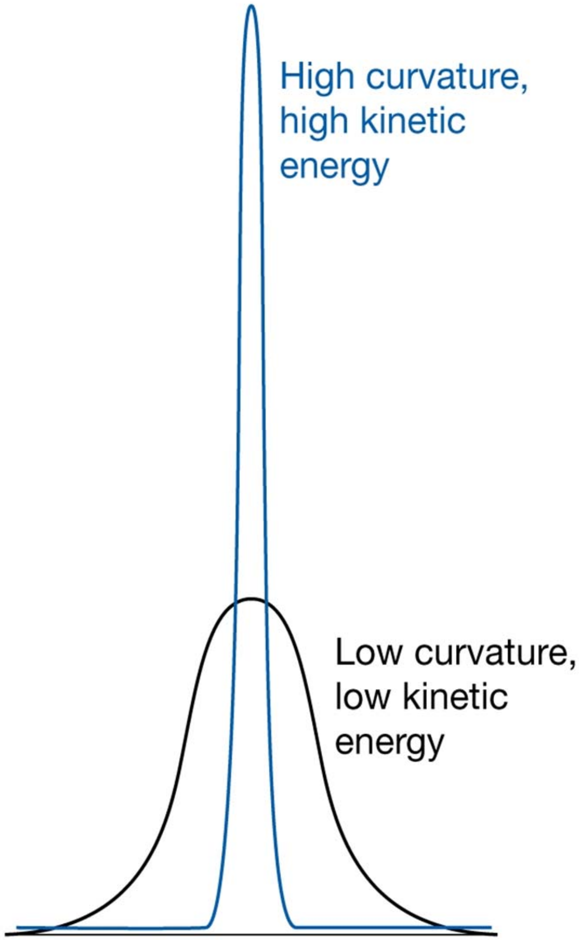
$$p_x = -kh$$

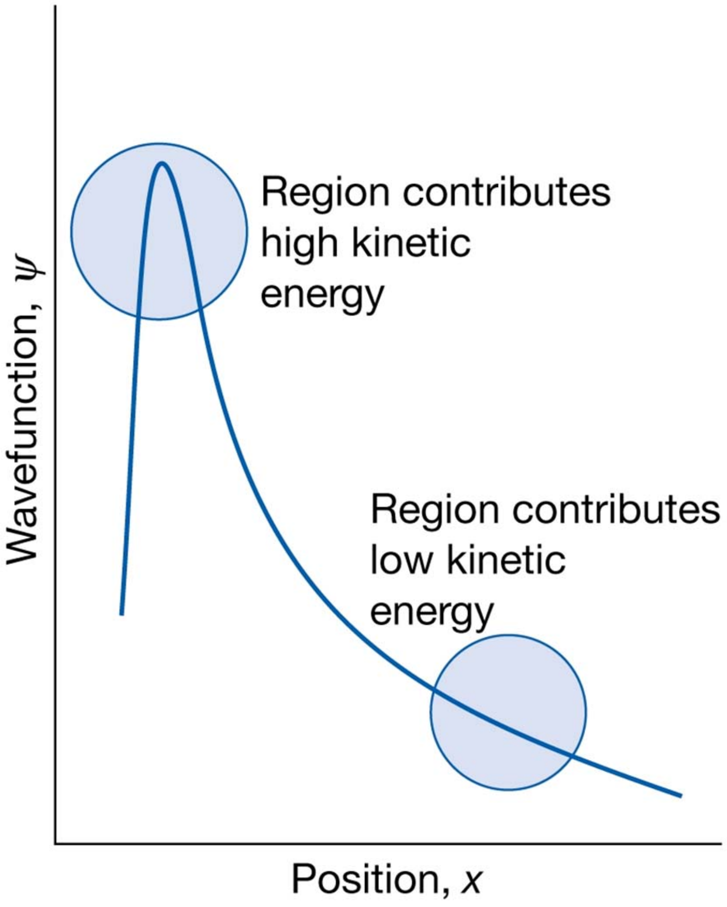
→ Corresponds to de Brogile relation
but with two direciton

$$p_x = k\hbar = h/\lambda$$

$$\lambda = 2\pi/k$$

Properties of Wavefuncitons





Superposition and expectation value

A = B

$$\psi = 2A\cos kx \qquad |\psi|^2 = 4|A|\cos^2 kx$$

$$\hat{p}_x\psi = \frac{2\hbar}{i}\frac{d\cos kx}{dx} = \frac{2k\hbar}{i}A\sin kx$$

This expression is not eigenvalue equation

→ **Can be interpreted as a liner combination of** e^{ikx} and e^{-ikx}

$$\psi = \psi_{+k\hbar} + \psi_{-k\hbar}$$

$$\psi = c_1\psi_1 + c_2\psi_2 + \ldots = \sum_k c_k\psi_k$$

Superposition and expected value

- **When the momentum is measure, in a single observation one of the eigenvalues corresponding to the wave function k,that contributes to the superposition will be found**
- **The proportionality of measuring a particular eigenvalue in a series of observation is proportional to square modulus of coeff. In the linear combination** $|c_k|^2$
- **The average value of a large number of observation is given by expected value :**

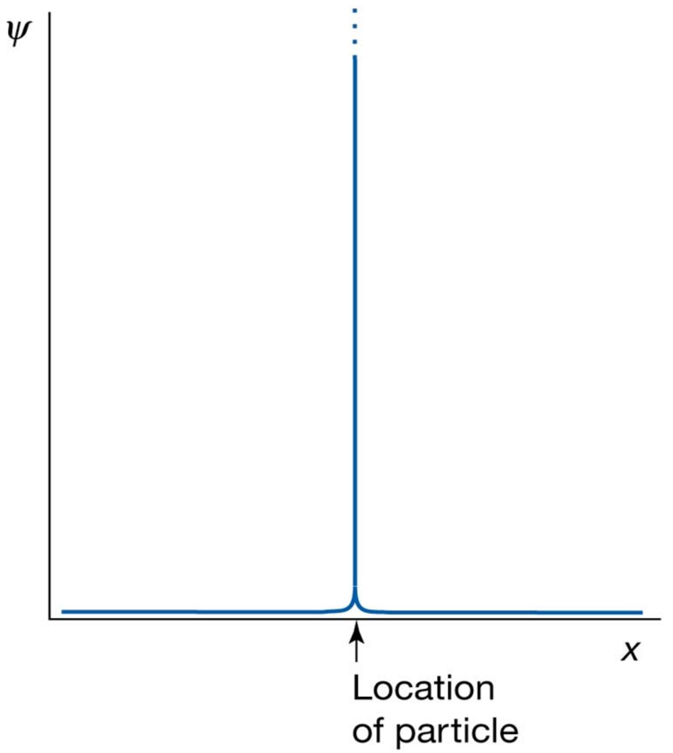
$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi d\tau$$

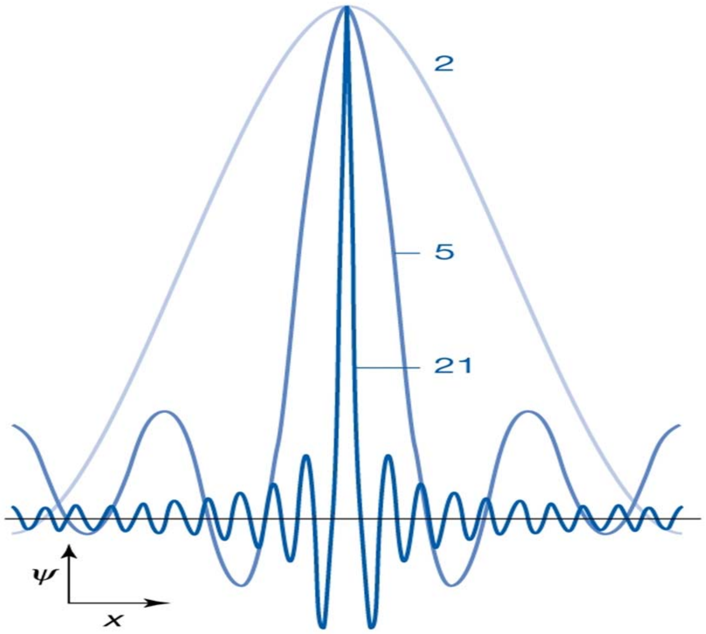
The uncertainty principle

- When momentum is known precisely, the position cannot be predicted precisely
  - Shown by examples
  - Only probability can be predicted

The uncertainty principle

- When the position is known precisely,





→ Location becomes precise at the expense of uncertainty in the momentum