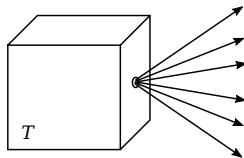
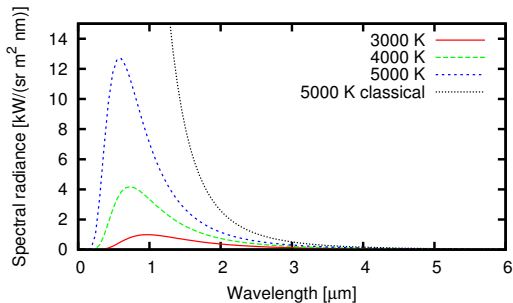


Review of basic quantum mechanics

Reading:

- ▶ Kasap: 3.1 - 3.6, 4.6
- ▶ Griffiths QM: 1 - 2

Blackbody radiation



- ▶ Spectrum of light (EM waves) emitted by a perfect absorber (black body)
- ▶ Experimental realization of blackbody: pinhole in a closed box
- ▶ Spectrum peaks at a wavelength inversely proportional to T
- ▶ Solar spectrum \approx black body radiation at 5800 K
- ▶ (All this was known before 1900!)

1D wave in a box

- ▶ Find non-trivial solutions of the wave equation

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial^2 f}{v^2 \partial t^2}$$

trapped inside a 1D box i.e. boundary conditions $f(0) = f(L) = 0$

- ▶ General solution $f(x, t) = Ae^{i(kx - \omega t)} + Be^{i(-kx - \omega t)}$ with $\omega = vk$
- ▶ Apply boundary conditions:
 - $f(0) = 0 \Rightarrow A + B = 0$
 - $f(L) = 0 \Rightarrow Ae^{ikL} + Be^{-ikL} = 0$
- ▶ Solve to get $B = -A$ and $\sin(kL) = 0$
- ▶ Not all wavevectors allowed, $k = n\pi/L$ for $n = 1, 2, \dots$
- ▶ Net solution are standing waves $f(x, t) = C \sin \frac{n\pi x}{L} e^{-i(n\pi v/L)t}$

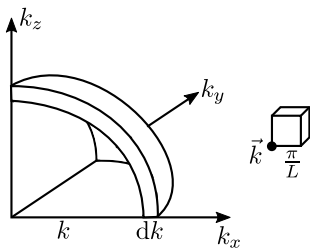
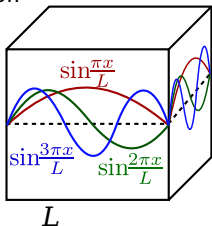
EM modes in a box

- ▶ Standing EM waves in a box: $\sin \frac{n\pi x}{L}$ in each direction
- ▶ Overall modes: $\sin \frac{n_x \pi x}{L} \sin \frac{n_y \pi y}{L} \sin \frac{n_z \pi z}{L}$
- ▶ Wavevector $\vec{k} = (k_x, k_y, k_z) = \left(\frac{n_x \pi}{L}, \frac{n_y \pi}{L}, \frac{n_z \pi}{L} \right)$
- ▶ Between wavevector magnitude k and $k + dk$:
- ▶ Volume in \vec{k} -space: $\frac{4\pi k^2 dk}{8}$
- ▶ Volume per \vec{k} : $\left(\frac{\pi}{L}\right)^3$
- ▶ Number of modes per \vec{k} : 2 polarizations
- ▶ Number of modes per unit volume:

$$2 \cdot \frac{4\pi k^2 dk}{8} \cdot \left(\frac{L}{\pi}\right)^3 \cdot \frac{1}{L^3} = \frac{k^2 dk}{\pi^2}$$

- ▶ In terms of wavelength $\lambda = 2\pi/k$:

$$\frac{1}{\pi^2} \left(\frac{2\pi}{\lambda}\right)^2 \left|d\frac{2\pi}{\lambda}\right| = \frac{1}{\pi^2} \left(\frac{2\pi}{\lambda}\right)^2 \frac{2\pi d\lambda}{\lambda^2} = \frac{8\pi}{\lambda^4} d\lambda$$



Classical theory: equipartition theorem

- ▶ Each mode: classical wave with any amplitude A with energy $E = c_0 A^2$
- ▶ At temperature T , probability of energy E is $\propto e^{-E/(k_B T)}$
- ▶ Average energy at temperature T is

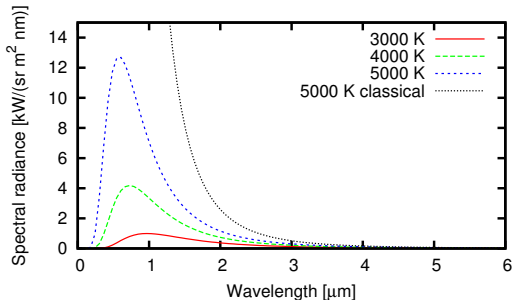
$$\begin{aligned}
 \langle E \rangle &\equiv \frac{\int_0^\infty dA e^{-E/(k_B T)} E}{\int_0^\infty dA e^{-E/(k_B T)}} \\
 &= \frac{\int_0^\infty d\sqrt{E/c_0} e^{-E/(k_B T)} E}{\int_0^\infty d\sqrt{E/c_0} e^{-E/(k_B T)}} \\
 &= \frac{\int_0^\infty dE e^{-E/(k_B T)} E^{1/2}}{\int_0^\infty dE e^{-E/(k_B T)} E^{-1/2}} \\
 &= \frac{(k_B T)^{3/2} \Gamma(3/2)}{(k_B T)^{1/2} \Gamma(1/2)} \\
 &= \frac{k_B T}{2}
 \end{aligned}$$

- ▶ Oscillators: kinetic and potential energies $\Rightarrow \langle E \rangle = k_B T$
- ▶ EM waves: electric and magnetic fields $\Rightarrow \langle E \rangle = k_B T$

Rayleigh-Jean's law

- ▶ Number of modes per wavelength: $\frac{8\pi}{\lambda^4}$
- ▶ Energy per mode: $k_B T$
- ▶ Power radiated per surface area: $\times \frac{c}{4}$
- ▶ Spectral power per surface area:

$$I_\lambda = \frac{8\pi}{\lambda^4} \cdot k_B T \cdot \frac{c}{4} = \frac{2\pi c k_B T}{\lambda^4}$$



Planck hypothesis

- ▶ Energies for a mode with frequency ν only allowed in increments of $h\nu$
- ▶ In terms of angular frequency $\omega = 2\pi\nu$, in increments of $\hbar\omega$
- ▶ With an as yet-undetermined constant h (or $\hbar = h/(2\pi)$)
- ▶ At temperature T , n units of energy $h\nu$ with probability $\propto e^{-nh\nu/(k_B T)}$
- ▶ Average number of energy units

$$\begin{aligned}
 \langle n \rangle &\equiv \frac{\sum_n e^{-nh\nu/(k_B T)} n}{\sum_n e^{-nh\nu/(k_B T)}} = \frac{\sum_n e^{-n\alpha} n}{\sum_n e^{-n\alpha}} && (\alpha \equiv h\nu/(k_B T)) \\
 &= \frac{-\frac{d}{d\alpha} \sum_n e^{-n\alpha}}{\sum_n e^{-n\alpha}} = -\frac{d}{d\alpha} \ln \sum_n e^{-n\alpha} \\
 &= -\frac{d}{d\alpha} \ln \frac{1}{1 - e^{-\alpha}} = \frac{e^{-\alpha}}{1 - e^{-\alpha}} \\
 &= \frac{1}{e^{h\nu/(k_B T)} - 1} \\
 \langle E \rangle &= \langle n \rangle h\nu = \frac{h\nu}{e^{h\nu/(k_B T)} - 1}
 \end{aligned}$$

Modification of equipartition theorem

- ▶ Average energy per mode changes to

$$\langle E \rangle = \frac{h\nu}{e^{h\nu/(k_B T)} - 1}$$

- ▶ For $h\nu \ll k_B T$

$$\langle E \rangle \approx \frac{h\nu}{h\nu/(k_B T)} = k_B T$$

classical regime with $\langle n \rangle \gg 1$

- ▶ For $h\nu \gg k_B T$

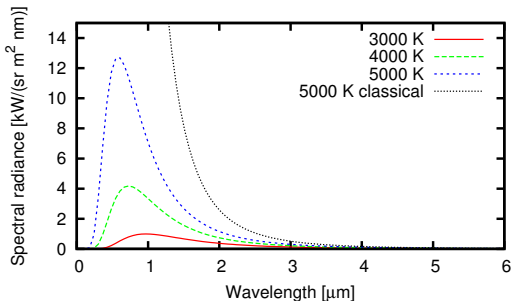
$$\langle E \rangle \approx \frac{h\nu}{e^{h\nu/(k_B T)}} = h\nu e^{-h\nu/(k_B T)}$$

new regime with $\langle n \rangle \ll 1$

Planck's law

- ▶ Number of modes per wavelength: $\frac{8\pi}{\lambda^4}$ (as before)
- ▶ Energy per mode: $\frac{hc/\lambda}{e^{hc/(\lambda k_B T)} - 1}$ (new, using $\nu = c/\lambda$)
- ▶ Power radiated per surface area: $\times \frac{c}{4}$ (as before)
- ▶ Spectral power per surface area:

$$I_\lambda = \frac{8\pi}{\lambda^4} \cdot \frac{hc/\lambda}{e^{hc/(\lambda k_B T)} - 1} \cdot \frac{c}{4} = \frac{2\pi hc^2}{\lambda^5 (e^{hc/(\lambda k_B T)} - 1)}$$



Planck's law features

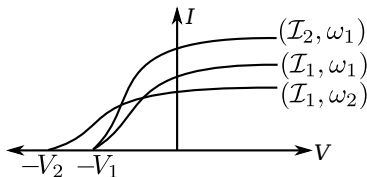
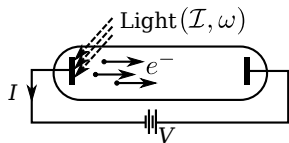
- ▶ Has a maximum at $\lambda \approx \frac{hc}{5k_B T}$ (Wein's displacement law)
- ▶ Determine $h = 6.626 \times 10^{-34}$ Js, $\hbar = h/(2\pi) = 1.055 \times 10^{-34}$ Js
- ▶ Total energy per surface area radiated by black body (Stefan's law)

$$\begin{aligned}
 P_S &\equiv \int_0^\infty d\lambda I_\lambda = \int_0^\infty d\lambda \frac{2\pi hc^2}{\lambda^5 (e^{hc/(\lambda k_B T)} - 1)} \\
 &= \int_0^\infty d\left(\frac{hc}{xk_B T}\right) \frac{2\pi hc^2}{(hc/(xk_B T))^5 (e^x - 1)} && (x \equiv hc/(\lambda k_B T)) \\
 &= 2\pi hc^2 \left(\frac{hc}{k_B T}\right)^{-4} \int_0^\infty x^{-2} dx \frac{x^5}{(e^x - 1)} \\
 &= T^4 \cdot \underbrace{\frac{2\pi k_B^4 \pi^4}{h^3 c^2}}_{\sigma} \\
 \sigma &= \frac{2\pi^5 k_B^4}{15h^3 c^2} = 5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \text{K}^4)
 \end{aligned}$$

- ▶ Agrees very well with radiated heat measurements.
(What is the classical result for σ ?)

Photoelectric effect

- ▶ Light ejects electrons from cathode $\Rightarrow I$ at $V = 0$
- ▶ $V \uparrow \Rightarrow I \uparrow$ till saturation (all ejected electrons collected)
- ▶ $V \downarrow \Rightarrow I \downarrow$ till $I = 0$:
all electrons stopped at $V = -V_0$
- ▶ Increase intensity \mathcal{I} :
higher saturation I but same stopping V
- ▶ Increase frequency ω :
higher stopping V
- ▶ Stopping action: $eV_0 = KE_{\max}$
- ▶ Experiment finds $eV_0 \propto (\omega - \omega_0)$
- ▶ In fact $eV_0 = \hbar(\omega - \omega_0)$
- ▶ Different cathodes \Rightarrow different ω_0
but same slope \hbar identical to that
from Planck's law!
- ▶ Light waves with angular frequency ω behave like
particles (photons) with energy $\hbar\omega$ (Einstein, 1905)
- ▶ Why does the saturation $I \downarrow$ when $\omega \uparrow$ at constant \mathcal{I} ?



Compton scattering

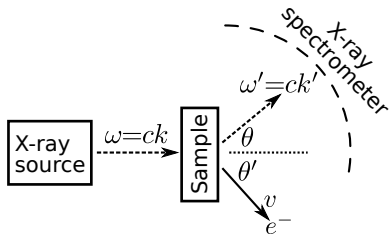
- ▶ X-ray ejects electron with part of its energy and remainder comes out as secondary X-ray
- ▶ Energy conservation $\hbar\omega = \hbar\omega' + \frac{1}{2}mv^2$ (assuming $\omega_0 \ll \omega$)
- ▶ Output X-ray at angle θ has specific frequency ω' . Why?
- ▶ Photon also has momentum $\vec{p} = \hbar\vec{k}$ (magnitude $\hbar\omega/c$)
- ▶ Momentum conservation

$$\frac{\hbar\omega}{c} = \frac{\hbar\omega'}{c} \cos \theta + mv \cos \theta'$$

$$0 = \frac{\hbar\omega'}{c} \sin \theta - mv \sin \theta'$$

- ▶ Eliminate electron unknowns (v, θ')

$$\cos \theta = \frac{\omega^2 + \omega'^2 - \frac{2mc^2}{\hbar}(\omega - \omega')}{2\omega\omega'}$$



Wave-particle duality

- ▶ Light is a wave: electric and magnetic fields oscillating $\sim e^{-i\omega t}$
 - ▶ All of classical wave-optics: diffraction etc.
- ▶ Light is particulate: photons with energy $\hbar\omega$ and momentum $\hbar\omega/c$
 - ▶ Black-body radiation
 - ▶ Photoelectric effect
 - ▶ Compton scattering

Electrons

- ▶ Discovered as 'cathode rays' in vacuum tube experiments (1869)
- ▶ Deflection by magnetic fields to measure charge/mass (1896)
- ▶ Charge measured in Millikan's oil drop experiment (1909)
- ▶ Particle with mass $m \approx 9 \times 10^{-31}$ kg and charge $-e \approx -1.6 \times 10^{-19}$ C known by early days of atomic theory and quantum theory
- ▶ Is it also a wave?

De Broglie wavelength

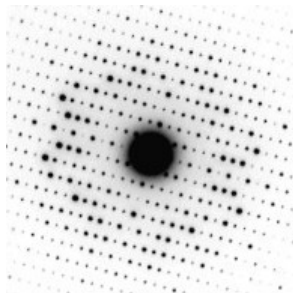
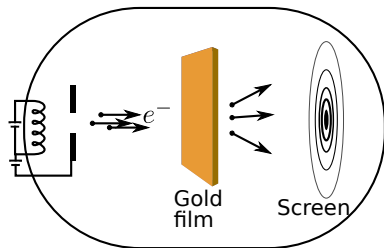
- ▶ Yes! With wavelength $\lambda = h/p$ where p is the momentum
- ▶ For wavevector \vec{k} (of magnitude $2\pi/\lambda$), this $\Rightarrow \vec{p} = \hbar\vec{k}$ (same as photon)
- ▶ In terms of kinetic energy:

KE [eV]	$\lambda = \frac{h}{\sqrt{2mKE}}$ [Å]	electrons $\lambda = \frac{h}{\sqrt{2mKE+(KE/c)^2}}$ [Å]	photons $\lambda = \frac{hc}{KE}$ [Å]
1	12.3	12.3	1.24×10^4
10	3.88	3.88	1.24×10^3
100	1.23	1.23	124
10^3	0.388	0.388	12.4
10^4	0.123	0.122	1.24
10^5	0.0388	0.0370	0.124
10^6	0.0123	0.00872	0.0124

- ▶ This rule applies to all particles / matter, not just electrons and photons
- ▶ What is your typical wavelength when walking? (Why don't you diffract?)

Electron diffraction

- ▶ Use gold film as grating (GP Thomson, 1927)
- ▶ Polycrystalline \Rightarrow rings (like powder X-ray diffraction)
- ▶ Modern version: transmission electron microscopy (TEM)
- ▶ ~ 100 keV energies $\Rightarrow \lambda \sim 0.05$ Å \Rightarrow atomic resolution



Schrodinger equation

- ▶ The wave equation for non-relativistic particles with mass m

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

- ▶ Wave function $\psi(\vec{r}, t)$: analogous to $\vec{E}(\vec{r}, t)$ or $\vec{B}(\vec{r}, t)$ for EM waves
- ▶ For EM wave, intensity is proportional to $|E|^2$
- ▶ Interpret intensity as the probability of finding light
- ▶ Quantum mechanically, $|\psi(\vec{r})|^2$ is the probability density of finding particle at \vec{r} (normalized as $\int d\vec{r} |\psi(\vec{r})|^2 = 1$)
- ▶ Note $\vec{E}(\vec{r})$ actually is the wavefunction of a photon in the quantum theory of EM waves

Free particle

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

- ▶ Let potential be constant in space and time i.e. $V(\vec{r}, t) = V_0$
- ▶ Solution of the form $\psi(\vec{r}, t) = e^{i(\vec{k} \cdot \vec{r} - \omega t)}$

$$\frac{\hbar^2 k^2}{2m} + V_0 = \hbar \omega$$

$$\underbrace{\frac{p^2}{2m}}_{\text{Kinetic}} + \underbrace{V_0}_{\text{Potential}} = \underbrace{E}_{\text{Total}}$$

- ▶ Note how De Broglie and Planck hypothesis connect classical and quantum relations.)
- ▶ Where is the particle?
Everywhere with a well-defined momentum $\vec{p} = \hbar \vec{k}$

Time-independent Schrodinger equation

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

- ▶ Let potential be constant in space i.e. $V(\vec{r}, t) = V(\vec{r})$
- ▶ LHS independent of t : separation of variables $\psi(\vec{r}, t) = \psi(\vec{r})T(t)$

$$\frac{-\frac{\hbar^2 \nabla^2 \psi(\vec{r})}{2m} + V(\vec{r})\psi(\vec{r})}{\psi(\vec{r})} = \frac{i\hbar \frac{\partial T(t)}{\partial t}}{T(t)} = \text{const.} = E \quad (\text{say})$$

- ▶ Then $T(t) = e^{-iEt/\hbar}$ and $\psi(\vec{r})$ is an eigenfunction of

$$-\frac{\hbar^2 \nabla^2 \psi}{2m} + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \quad (\text{Time-independent Schrodinger equation})$$

- ▶ Note for time dependence $e^{-i(E/\hbar)t}$, angular frequency is E/\hbar , energy is the eigenvalue E

Particle in a box

- ▶ Need to solve time-independent Schrodinger equation

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

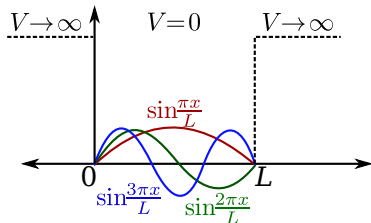
- ▶ When $V(x) \rightarrow \infty$, $\psi(x) \rightarrow 0$ for finite E
- ▶ Effectively, with $\psi(0) = \psi(L) = 0$, solve

$$\partial_x^2 \psi = - \underbrace{\frac{2mE}{\hbar^2}}_{k^2} \psi(x)$$

- ▶ Solutions $\cos kx$ and $\sin kx$ (or $e^{\pm ikx}$)
- ▶ Boundary conditions only allow $\sin \frac{n\pi x}{L}$

$$k = n \frac{\pi}{L} \quad \text{and} \quad E = n^2 \frac{\hbar^2 \pi^2}{2mL^2}$$

- ▶ Energy is 'quantized': only discrete values allowed



Particle in a box: ground state

- States with discrete energies and (normalized) wavefunctions:

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

labeled by 'quantum number' n

- Lowest energy ($n = 1$ here) is ground state:

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2}, \quad \psi_1(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

- What should it have been classically?

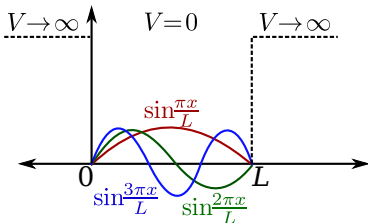
Zero. E_1 is confinement energy $\approx \frac{0.38 \text{ eV}}{(L \text{ in nm})^2}$

- Where is the particle?

Distributed between 0 and L with probability $\frac{2}{L} \sin^2 \frac{\pi x}{L}$ (**Range: L**)

- What is its momentum?

Since $\sin k_1 x = (e^{ik_1 x} - e^{-ik_1 x})/2i$, one of $\pm \hbar k_1$ i.e. $\pm \frac{\hbar \pi}{L}$ (**Range: $\frac{2\pi \hbar}{L}$**)



Heisenberg's uncertainty principle

- ▶ In previous example: range in x was L and range in p was $\frac{2\pi\hbar}{L}$
- ▶ More precisely, standard deviation in x is $\Delta x = \sqrt{\frac{1}{12} - \frac{1}{2\pi^2}}L \approx 0.18L$ and standard deviation in p is $\Delta p = \frac{\pi\hbar}{L}$
- ▶ Narrower well \Rightarrow reduce Δx , but increase Δp
- ▶ In this case, $\Delta x \cdot \Delta p \approx 0.57\hbar$
- ▶ Heisenberg's uncertainty principle

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

- ▶ What is the corresponding relation for photons?
- ▶ Exactly the same: in fact this is purely a wave-mechanics property

$$\Delta x \cdot \Delta k \geq \frac{1}{2}$$

applicable to all classical waves as well

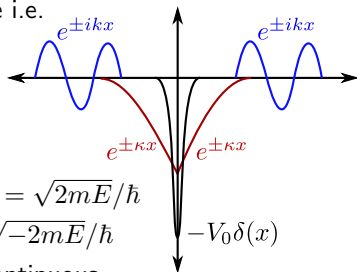
Another example: 1D ' δ -atom'

- ▶ Consider the potential $V(x) = -V_0\delta(x)$ (an infinitely-deep, infinitenely-narrow well)
- ▶ Except at $x = 0$, potential is zero everywhere i.e.

$$\partial_x^2\psi = -\frac{2mE}{\hbar^2}\psi(x)$$

with solutions $e^{\pm ix\sqrt{2mE}/\hbar}$

- ▶ For $E > 0$, oscillatory solutions $e^{\pm ikx}$ with $k = \sqrt{2mE}/\hbar$
- ▶ For $E < 0$, bound solutions $e^{\pm \kappa x}$ with $\kappa = \sqrt{-2mE}/\hbar$
- ▶ In general $\psi(x)$ and $\psi'(x) \equiv \partial_x\psi$ must be continuous
- ▶ But where $V \rightarrow \infty$, $\psi'(x)$ will be discontinuous



Derivative discontinuity of wavefunction

- ▶ Schrodinger equation in a δ -potential:

$$-\frac{\hbar^2}{2m}\partial_x\psi'(x) - V_0\delta(x)\psi(x) = E\psi(x)$$

- ▶ Integrate in a small neighbourhood around $x = 0$

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{+\epsilon} dx\partial_x\psi'(x) - V_0\int_{-\epsilon}^{+\epsilon} dx\delta(x)\psi(x) = E\int_{-\epsilon}^{+\epsilon} dx\psi(x)$$

$$-\frac{\hbar^2}{2m}[\psi'(+\epsilon) - \psi'(-\epsilon)] - V_0\psi(0) = E\int_{-\epsilon}^{+\epsilon} dx\psi(x)$$

- ▶ Take limit $\epsilon \rightarrow 0$:

$$-\frac{\hbar^2}{2m}[\psi'(0^+) - \psi'(0^-)] - V_0\psi(0) = 0$$

$$\psi'(0^+) - \psi'(0^-) = -\frac{2mV_0}{\hbar^2}\psi(0)$$

δ -atom: bound state

- ▶ Consider the $E < 0$ case, where solutions are $e^{\pm\kappa x}$ for $x < 0$ and $x > 0$
- ▶ For $x < 0$, only $e^{\kappa x}$ because $e^{-\kappa x} \rightarrow \infty$ as $x \rightarrow -\infty$
- ▶ For $x > 0$, only $e^{-\kappa x}$ because $e^{\kappa x} \rightarrow \infty$ as $x \rightarrow +\infty$
- ▶ With continuity, $\psi(x) = Ae^{-\kappa|x|}$
- ▶ Derivative condition:

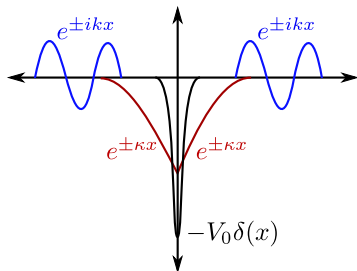
$$A(-\kappa) - A(\kappa) = -\frac{2mV_0}{\hbar^2}A$$

gives $\kappa = \frac{mV_0}{\hbar^2}$

- ▶ Single bound state ($E < 0$)

$$\psi(x) = \sqrt{\kappa}e^{-\kappa|x|}$$

which is the ground state in this potential

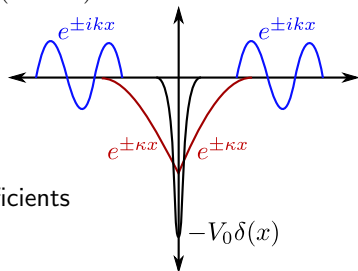


δ -atom: free states

- ▶ Consider the $E > 0$ case, where solutions are $e^{\pm ikx}$ for $x < 0$ and $x > 0$
- ▶ For $x < 0$, $Ae^{ikx} + Be^{-ikx}$ (no restrictions)
- ▶ For $x > 0$, $Ce^{ikx} + De^{-ikx}$ (no restrictions)
- ▶ Continuity $\Rightarrow A + B = C + D$
- ▶ Derivative condition:

$$(ikC - ikD) - (ikA - ikB) = -\frac{2mV_0}{\hbar^2}(A + B)$$

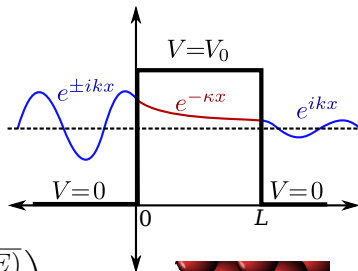
- ▶ Two free variables and two dependent among A, B, C, D
- ▶ If $D = 0$, A incoming wave from $-\infty$, reflects to B and transmits to C
- ▶ Solve to get reflection and transmission coefficients



Tunneling

- ▶ Consider particle with energy $0 < E < V_0$
- ▶ Classically, particle cannot cross barrier V_0 higher than its energy
- ▶ $\psi \propto e^{\pm ikx}$ with $k = \sqrt{2mE}/\hbar$ in $V = 0$ regions
- ▶ $\psi \propto e^{\pm \kappa x}$ with $\kappa = \sqrt{2m(V_0 - E)}/\hbar$ in $V = V_0$ regions
- ▶ Match wavefunctions at $x = 0$ and $x = L$ for wave incoming from left
- ▶ Probability of 'tunneling' to the right

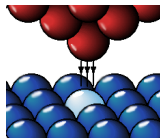
$$P \sim e^{-\kappa L} = \exp\left(-\frac{L\sqrt{2m(V_0 - E)}}{\hbar}\right)$$



- ▶ For more general barrier shape

$$P \sim \exp\left(-\frac{\int_{V(x) > E} dx \sqrt{2m(V(x) - E)}}{\hbar}\right)$$

- ▶ Responsible for atomic resolution in STM



How do waves show particulate behaviour?

- ▶ So far, only option in free space are particles distributed *everywhere*.
- ▶ Above true for energy and momentum eigenstates
- ▶ No longer the case for states which combine many energies and momenta
- ▶ Example: combine k around k_0 with Gaussian distribution of width σ_k

$$c(k) = \frac{1}{\sqrt{\sigma_k} \sqrt{2\pi}} e^{-(k-k_0)^2 / (2\sigma_k^2)}$$

- ▶ This Gaussian 'wave-packet' has

$$\begin{aligned} \psi(x, t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dk c(k) e^{i(kx - \omega(k)t)} \quad \left(\hbar\omega(k) = \frac{\hbar^2 k^2}{2m} \right) \\ &= \frac{1}{\sqrt{2\pi\sigma_k} \sqrt{2\pi}} \int_{-\infty}^{\infty} dk \exp \left[-\frac{(k - k_0)^2}{2\sigma_k^2} + i(kx - \omega(k)t) \right] \end{aligned}$$

Gaussian wavepacket

$$\begin{aligned}
 \psi(x, t) &= \frac{1}{\sqrt{2\pi\sigma_k}\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \exp \left[-\frac{(k - k_0)^2}{2\sigma_k^2} + i(kx - \omega(k)t) \right] \\
 &= \frac{1}{\sqrt{2\pi\sigma_k}\sqrt{2\pi}} \int_{-\infty}^{\infty} dk \exp \left[\begin{array}{c} -\frac{(k - k_0)^2}{2\sigma_k^2} + ikx \\ -i(\omega(k_0)t + \omega'(k_0)(k - k_0)t + \dots) \end{array} \right] \\
 &= \frac{e^{i(k_0x - \omega(k_0)t)}}{\sqrt{2\pi\sigma_k}\sqrt{2\pi}} \int_{-\infty}^{\infty} d\Delta k \exp \left[-\frac{\Delta k^2}{2\sigma_k^2} + i\Delta k(x - \omega'(k_0)t) \right] \\
 &= \frac{e^{i(k_0x - \omega(k_0)t) - \sigma_k^2(x - \omega'(k_0)t)^2/2}}{\sqrt{2\pi\sigma_k}\sqrt{2\pi}} \underbrace{\int_{-\infty}^{\infty} d\Delta k e^{-\frac{\{\Delta k - i\sigma_k^2(x - \omega'(k_0)t)\}^2}{2\sigma_k^2}}}_{\sqrt{2\pi}\sigma_k} \\
 &= \exp [i(k_0x - \omega(k_0)t)] \cdot \frac{\exp \left[-\frac{(x - \omega'(k_0)t)^2}{2(\sigma_k^{-1})^2} \right]}{\sqrt{\sigma_k^{-1}}\sqrt{2\pi}}
 \end{aligned}$$

Group and phase velocities

- ▶ Gaussian wavepacket

$$\psi(x, t) = \exp [i(k_0 x - \omega(k_0)t)] \cdot \frac{\exp \left[-\frac{(x - \omega'(k_0)t)^2}{2(\sigma_k^{-1})^2} \right]}{\sqrt{\sigma_k^{-1}} \sqrt{2\pi}}$$

- ▶ Localized by Gaussian with width $\sigma_x = \sigma_k^{-1}$ centered at $x_0 = \omega'(k_0)t$
- ▶ Spread $\Delta k = \sigma_k / \sqrt{2}$ and $\Delta x = \sigma_x / \sqrt{2}$ (Why?)
- ▶ Minimum uncertainty product: $\Delta k \cdot \Delta x = 1/2$
- ▶ Packet centered at x_0 moves with group velocity

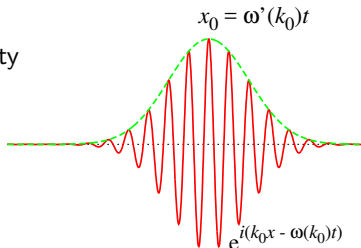
$$v_g = \frac{\partial \omega}{\partial k}$$

- ▶ Underlying waves propagate with phase velocity

$$v_p = \frac{\omega}{k}$$

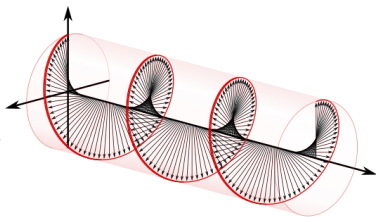
- ▶ For free particle with $\omega = \hbar k^2 / (2m)$

$$v_g = \frac{p}{m} \quad \text{and} \quad v_p = \frac{p}{2m} \quad (p = \hbar k)$$



Spin

- ▶ EM wave propagating along x : $E_0 \hat{y} e^{i(kx - \omega t)}$ or $E_0 \hat{z} e^{i(kx - \omega t)}$
(two independent polarizations)
- ▶ Linearly combine to $E_0 \frac{\hat{y} + i\hat{z}}{\sqrt{2}} e^{i(kx - \omega t)}$ or $E_0 \frac{\hat{y} - i\hat{z}}{\sqrt{2}} e^{i(kx - \omega t)}$: circular polarizations
- ▶ Quantize to a photon: circular polarizations will have (internal) angular momentum $\pm \hbar$
- ▶ Angular momentum quantized in units of \hbar
- ▶ Since maximum magnitude is 1, photon is a spin $s = 1$ particle
- ▶ Electrons have internal angular momentum $\pm \hbar/2$
- ▶ Electrons have spin $s = 1/2$
- ▶ Integer spins: **bosons**, any number per state
eg. photons, phonons, He^4 etc.
- ▶ Half-integer spins: **fermions**, maximum one per state
eg. electrons, protons, neutrons, He^3 etc.



Particles in a 3D box

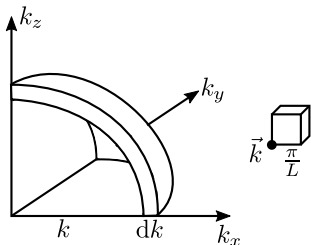
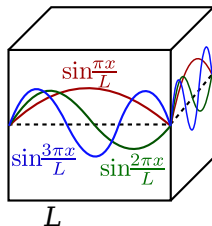
- ▶ Standing EM waves in a box:

$$\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \text{ in each direction}$$

- ▶ Electronic wavefunctions: exactly the same!
- ▶ Overall modes: $\left(\frac{2}{L}\right)^{3/2} \sin \frac{n_x\pi x}{L} \sin \frac{n_y\pi y}{L} \sin \frac{n_z\pi z}{L}$
- ▶ Wavevector $\vec{k} = (k_x, k_y, k_z) = \left(\frac{n_x\pi}{L}, \frac{n_y\pi}{L}, \frac{n_z\pi}{L}\right)$
- ▶ Number of EM modes per \vec{k} : 2 polarizations
- ▶ Number of e^- states per \vec{k} : 2 spins
- ▶ Number of modes per unit volume between k and $k + dk$:

$$2 \cdot \frac{4\pi k^2 dk}{8} \cdot \left(\frac{L}{\pi}\right)^3 \cdot \frac{1}{L^3} = \frac{k^2 dk}{\pi^2}$$

- ▶ Energy per photon $\varepsilon = \hbar\omega = \hbar c|\vec{k}|$
- ▶ Energy per electron $\varepsilon = \hbar\omega = \frac{\hbar^2|\vec{k}|^2}{2m}$



Average number of particles per mode of energy ε

Probability of n particles $\propto e^{-n\alpha}$, where $\alpha = \frac{\varepsilon - \mu}{k_B T}$ and chemical potential μ controls number (zero for massless particles like photons)

Bosons: (eg. photons)

$$\begin{aligned}\langle n \rangle &\equiv \frac{\sum_{n=0}^{\infty} e^{-n\alpha} n}{\sum_{n=0}^{\infty} e^{-n\alpha}} \\ &= -\frac{d}{d\alpha} \ln \sum_n e^{-n\alpha} \\ &= -\frac{d}{d\alpha} \ln \frac{1}{1 - e^{-\alpha}} \\ &= \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) - 1}\end{aligned}$$

(Bose-Einstein distribution)

$$\langle E \rangle = \langle n \rangle \varepsilon = \frac{\varepsilon}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) - 1}$$

Fermions: (eg. electrons)

$$\begin{aligned}\langle n \rangle &\equiv \frac{\sum_{n=0}^1 e^{-n\alpha} n}{\sum_{n=0}^1 e^{-n\alpha}} \\ &= \frac{e^0 \cdot 0 + e^{-\alpha} \cdot 1}{e^0 + e^{-\alpha}} \\ &= \frac{1}{e^{\alpha} + 1} \\ &= \frac{1}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1}\end{aligned}$$

(Fermi-Dirac distribution)

$$\langle E \rangle = \langle n \rangle \varepsilon = \frac{\varepsilon}{\exp\left(\frac{\varepsilon - \mu}{k_B T}\right) + 1}$$

Classical equipartition result: $\langle E \rangle = k_B T$