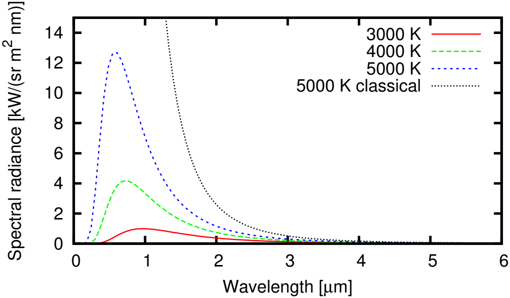
MTLE-6120: Advanced Electronic Properties of Materials

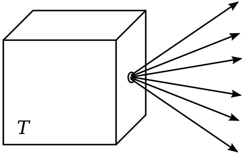
Review of basic quantum mechanics

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

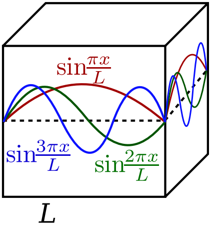
$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial^2 f}{v^2 \partial t^2}$$

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

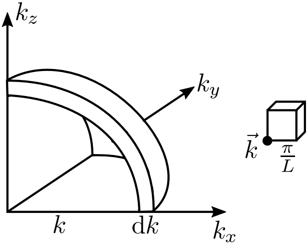
- General solution $f(x,t) = Ae^{i(kx-\omega t)} + Be^{i(-kx-\omega t)}$ with $\omega = vk$
- Apply boundary conditions:
$f(0) = 0 \Rightarrow A + B = 0$
$f(L) = 0 \Rightarrow Ae^{ikL} + Be^{-ikL} = 0$
- Solve to get $B = -A$ and $\sin(kL) = 0$
- Not all wavevectors allowed, $k = n\pi/L$ for $n = 1, 2, \ldots$
- 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 $k + \mathrm{d}k$:
- Volume in $\vec{k}$-space: $\frac{4\pi k^2 \mathrm{d}k}{8}$
- Volume per $\vec{k}$: $\left(\frac{\pi}{L}\right)^3$
- Number of modes per $\vec{k}$: 2 polarizations
- Number of modes per unit volume:



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



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

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

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

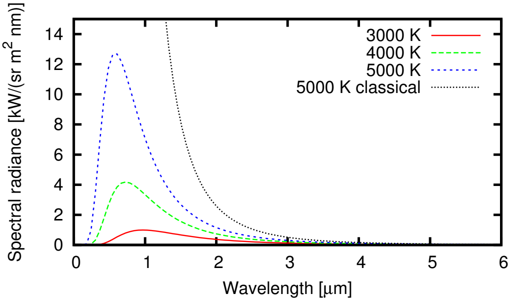
$$
\begin{aligned}
\langle E \rangle &\equiv \frac{\int_0^\infty \mathrm{d}A e^{-E/(k_B T)} E}{\int_0^\infty \mathrm{d}A e^{-E/(k_B T)}} \\
&= \frac{\int_0^\infty \mathrm{d}\sqrt{E/c_0} e^{-E/(k_B T)} E}{\int_0^\infty \mathrm{d}\sqrt{E/c_0} e^{-E/(k_B T)}} \\
&= \frac{\int_0^\infty \mathrm{d}E e^{-E/(k_B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

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

Rayliegh-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

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

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 $h\nu \gg k_B T$

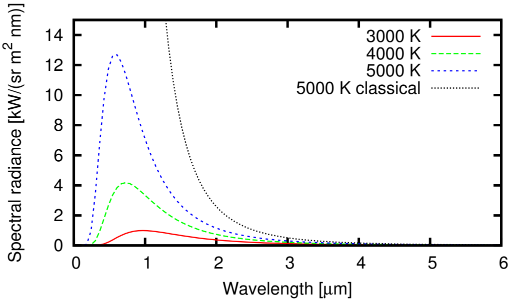
$$\langle E \rangle \approx \frac{h\nu}{e^{h\nu/(k_B T)}} = h\nu e^{-h\nu/(k_B T)}$$

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:

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



Planck's law features

- Has a maximum at $\lambda \approx \frac{hc}{5k_BT}$ (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)

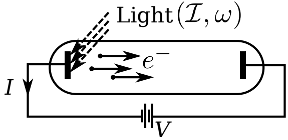
$$
\begin{aligned}
P_S &\equiv \int_0^\infty \mathrm{d}\lambda I_\lambda = \int_0^\infty \mathrm{d}\lambda \frac{2\pi hc^2}{\lambda^5 \left(e^{hc/(\lambda k_B T)} - 1\right)} \\
&= \int_0^\infty \mathrm{d}\left(\frac{hc}{xk_BT}\right) \frac{2\pi hc^2}{(hc/(xk_BT))^5 \left(e^x - 1\right)} \qquad (x \equiv hc/(\lambda k_B T)) \\
&= 2\pi hc^2 \left(\frac{hc}{k_BT}\right)^{-4} \int_0^\infty x^{-2} \mathrm{d}x \frac{x^5}{(e^x - 1)} \\
&= T^4 \cdot \underbrace{\frac{2\pi k_B^4}{h^3c^2} \frac{\pi^4}{15}}_{\sigma}
\end{aligned}
$$

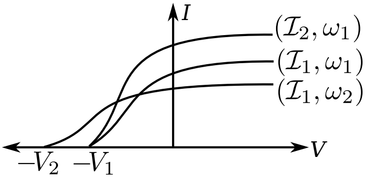
$$
\sigma = \frac{2\pi^5 k_B^4}{15h^3c^2} = 5.67 \times 10^{-8}\ \mathrm{W/(m^2K^4)}
$$

- 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: $eV_0 = \mathrm{KE}_{\max}$
- 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 $\mathcal{I}$?

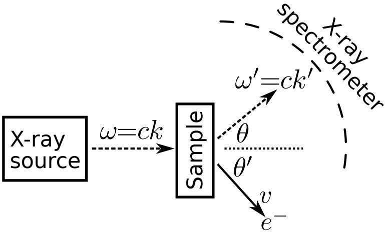
Compton scattering

- 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 $\omega_0 << \omega$)
- 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

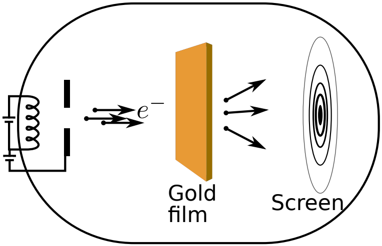
- Yes! With wavelength $\lambda = h/p$ where p is the momentum
- For wavevector $\vec{k}$ (of magnitude $2\pi/\lambda$), this $\Rightarrow \vec{p} = \hbar\vec{k}$ (same as photon)
- In terms of kinetic energy:

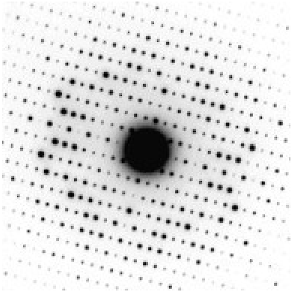
KE [eV]	electrons $\lambda = \frac{h}{\sqrt{2m\mathrm{KE}}}$ [Å]	electrons $\lambda = \frac{h}{\sqrt{2m\mathrm{KE}+(\mathrm{KE}/c)^2}}$ [Å]	photons $\lambda = \frac{hc}{\mathrm{KE}}$ [Å]
1	12.3	12.3	1.24×10^4
10	3.88	3.88	1.24×10^3
100	1.23	1.23	124
10^3	0.388	0.388	12.4
10^4	0.123	0.122	1.24
10^5	0.0388	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 $|E|^2$
- Intepret 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 $\psi(\vec{r},t) = \psi(\vec{r})T(t)$

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

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

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

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

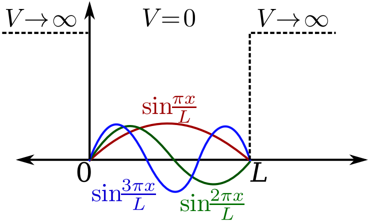
Particle in a box

- Need to solve time-independent Schrodinger equation

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

- When $V(x) \to \infty$, $\psi(x) \to 0$ 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 $\sin \frac{n\pi x}{L}$

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

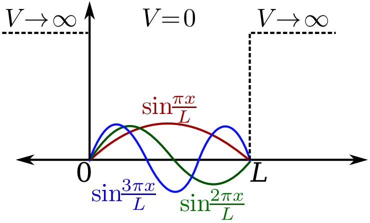
- Energy is 'quantized': only discrete values allowed

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

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

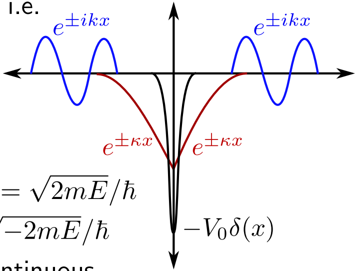
applicable to all classical waves as well

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 $V \to \infty$, $\psi'(x)$ 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 $x = 0$

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

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

- Take limit $\epsilon \to 0$:

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

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

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 $e^{-\kappa x} \to \infty$ as $x \to -\infty$
- For $x > 0$, only $e^{-\kappa x}$ because $e^{\kappa x} \to \infty$ as $x \to +\infty$
- With continuity, $\psi(x) = Ae^{-\kappa|x|}$
- Derivative condition:

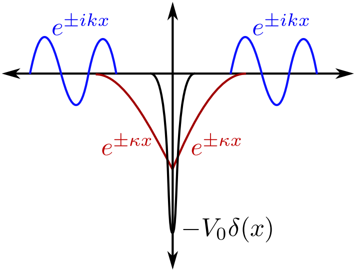
$$A(-\kappa) - A(\kappa) = -\frac{2mV_0}{\hbar^2}A$$

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

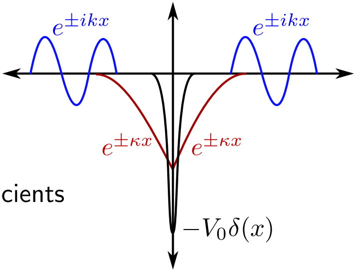


δ-atom: free states

- 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:

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

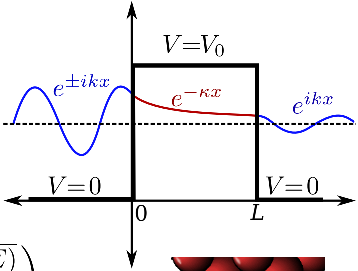
- Two free variables and two dependent among A, B, C, D
- If $D = 0$, A incoming wave from $-\infty$, reflects to B and transmits to C
- Solve to get reflection and transmission coefficients



Tunneling

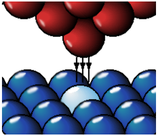
- Consider particle with energy $0 < E < V_0$
- Classically, particle cannot cross barrier V_0 higher than its energy
- $\psi \propto e^{\pm ikx}$ with $k = \sqrt{2mE}/\hbar$ in $V = 0$ regions
- $\psi \propto e^{\pm \kappa x}$ with $\kappa = \sqrt{2m(V_0 - E)}/\hbar$ in $V = V_0$ regions
- Match wavefunctions 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

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



- 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

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

Gaussian wavepacket

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

Group and phase velocities

- Gaussian wavepacket

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

- 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

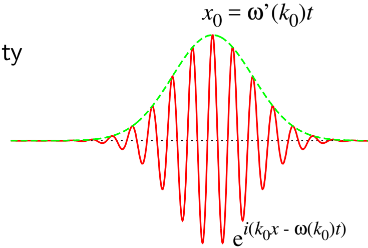
$$v_g = \frac{\partial \omega}{\partial k}$$

- Underlying waves propagate with phase velocity

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

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

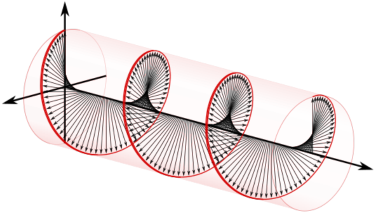
$$v_g = \frac{p}{m} \text{ and } v_p = \frac{p}{2m} \quad (p = \hbar k)$$



Rensselaer

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 $\pm\hbar$



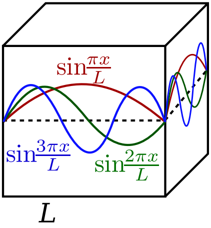
- Angular momentum quantized in units of $\hbar$
- Since maximum magnitude is 1, photon is a spin $s = 1$ particle
- Electrons have internal angular momentum $\pm\hbar/2$
- Electrons have spin $s = 1/2$
- Integer spins: **bosons**, any number per state eg. photons, phonons, He^4 etc.
- Half-integer spins: **fermions**, maximum one per state eg. electrons, protons, neutrons, He^3 etc.

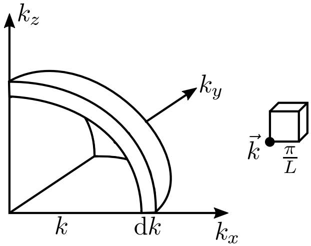
Particles in a 3D box

- Standing EM waves in a box:
  $\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$ 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 $k+\mathrm{d}k$:

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

- 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)

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

(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: $\langle E\rangle = k_B T$