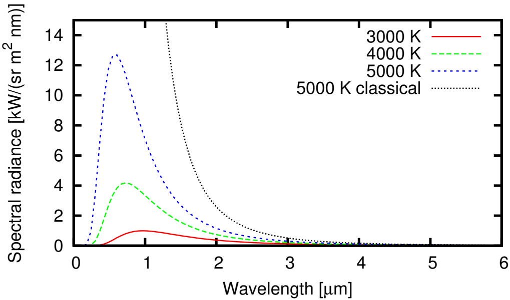
# MTLE-6120: Advanced Electronic Properties of Materials

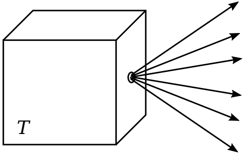
## Review of basic quantum mechanics

Reading:

- Kasap: 3.1 - 3.8, 4.6
- Griffiths QM: 1 - 2, 9.1 - 9.2

# 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!)

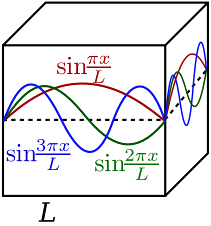
# EM modes in a box

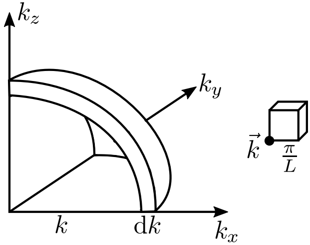
- Standing EM waves in a box: $\sin\frac{n\pi x}{L}$ in each direction
- Overall modes: $\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}$
- Wavevector $\vec{k} = (k_x, k_y, k_z) = \left(\frac{n_x\pi}{L}, \frac{n_y\pi}{L}, \frac{n_z\pi}{L}\right)$
- Between wavevector magnitude $k$ 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

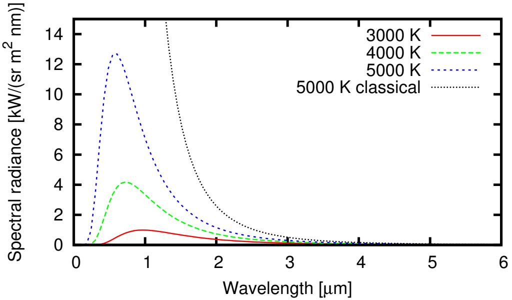
$$\begin{aligned}\langle E \rangle &\equiv \frac{\int_0^\infty \mathrm{d}A e^{-E/(k_B T)} E}{\int_0^\infty \mathrm{d}A e^{-E/(k_B T)}} \\ &= \frac{\int_0^\infty \mathrm{d}\sqrt{E/c_0} e^{-E/(k_B T)} E}{\int_0^\infty \mathrm{d}\sqrt{E/c_0} e^{-E/(k_B T)}} \\ &= \frac{\int_0^\infty \mathrm{d}E e^{-E/(k_B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

- 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 $\nu$ 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

$$\langle n \rangle \equiv \frac{\sum_n e^{-nh\nu/(k_B T)} n}{\sum_n e^{-nh\nu/(k_B T)}} = \frac{\sum_n e^{-n\alpha} n}{\sum_n e^{-n\alpha}} \qquad (\alpha \equiv h\nu/(k_B T))$$

$$= \frac{-\frac{\mathrm{d}}{\mathrm{d}\alpha} \sum_n e^{-n\alpha}}{\sum_n e^{-n\alpha}} = -\frac{\mathrm{d}}{\mathrm{d}\alpha} \ln \sum_n e^{-n\alpha}$$

$$= -\frac{\mathrm{d}}{\mathrm{d}\alpha} \ln \frac{1}{1 - e^{-\alpha}} = \frac{e^{-\alpha}}{1 - e^{-\alpha}}$$

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

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

# 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 $h\nu \gg k_B T$

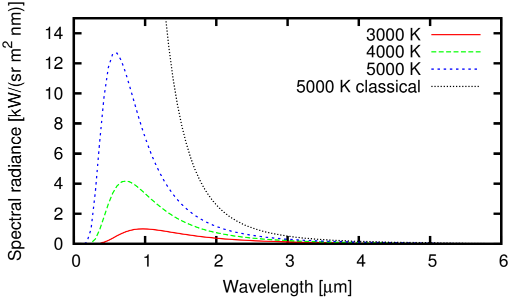
$$\langle E \rangle \approx \frac{h\nu}{e^{h\nu/(k_B T)}} = h\nu e^{-h\nu/(k_B T)}$$

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)

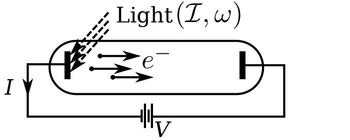
$$\begin{aligned}
P_S &\equiv \int_0^\infty \mathrm{d}\lambda I_\lambda = \int_0^\infty \mathrm{d}\lambda \frac{2\pi hc^2}{\lambda^5\left(e^{hc/(\lambda k_B T)} - 1\right)} \\
&= \int_0^\infty \mathrm{d}\left(\frac{hc}{xk_BT}\right) \frac{2\pi hc^2}{(hc/(xk_BT))^5\,(e^x - 1)} \qquad (x \equiv hc/(\lambda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

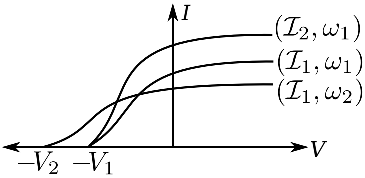
$$\sigma = \frac{2\pi^5 k_B^4}{15h^3c^2} = 5.67 \times 10^{-8}\ \mathrm{W/(m^2K^4)}$$

- Agrees very well with radiated heat measurements.
  (What is the classical result for $\sigma$?)

# 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 $\omega$:
  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 $\omega_0$
  but same slope $\hbar$ identical to that
  from Planck's law!




- Light waves with angular frequency $\omega$ behave like particles (photons) with energy $\hbar\omega$ (Einstein, 1905)
- Why does the saturation $I \uparrow$ when $\omega \uparrow$ at constant $\mathcal{I}$?

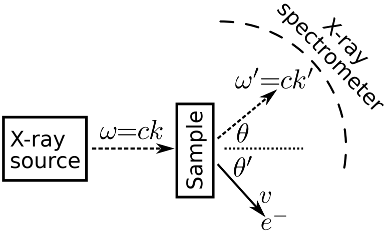
# Compton scattering

- 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 $\theta$ has specific frequency $\omega'$. 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 $(v, \theta')$

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



# 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

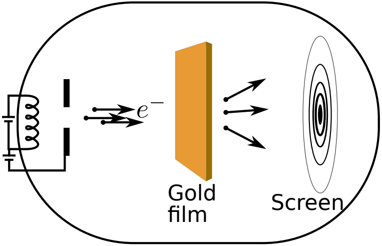
- Yes! With wavelength $\lambda = h/p$ where p is the momentum
- For wavevector $\vec{k}$ (of magnitude $2\pi/\lambda$), this $\Rightarrow \vec{p} = \hbar\vec{k}$ (same as photon)
- In terms of kinetic energy:

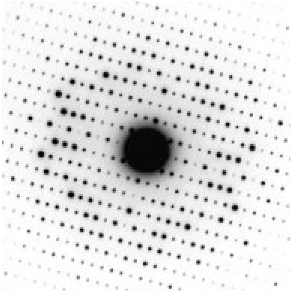
| KE [eV] | electrons | | photons |
|---|---|---|---|
| | $\lambda = \frac{h}{\sqrt{2m\mathrm{KE}}}$ [Å] | $\lambda = \frac{h}{\sqrt{2m\mathrm{KE}+(\mathrm{KE}/c)^2}}$ [Å] | $\lambda = \frac{hc}{\mathrm{KE}}$ [Å] |
| 1 | 12.3 | 12.3 | $1.24 \times 10^4$ |
| 10 | 3.88 | 3.88 | $1.24 \times 10^3$ |
| 100 | 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)
- $\sim 100$ 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 $E$

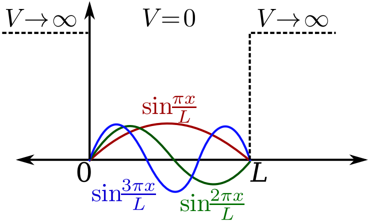
# Particle in a box

- 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 $\sin \frac{n\pi x}{L}$

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

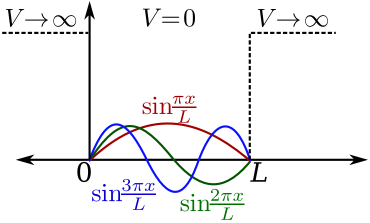
- Energy is ‘quantized’: only discrete values allowed

# 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 $\Delta x$, but increase $\Delta p$
- 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

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

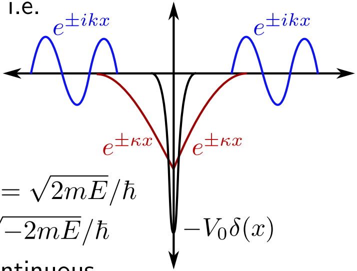
applicable to all classical waves as well

# Another example: 1D '$\delta$-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 $\delta$-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 $\epsilon \to 0$:

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

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

# $\delta$-atom: bound state

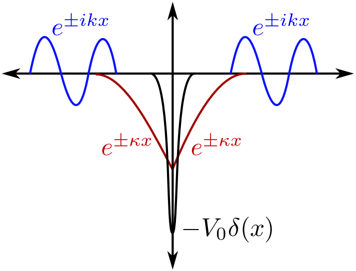
- Consider the $E < 0$ case, where solutions are $e^{\pm\kappa x}$ for $x < 0$ and $x > 0$
- For $x < 0$, only $e^{\kappa x}$ because $e^{-\kappa x} \to \infty$ as $x \to -\infty$
- For $x > 0$, only $e^{-\kappa x}$ because $e^{\kappa x} \to \infty$ as $x \to +\infty$
- With continuity, $\psi(x) = Ae^{-\kappa|x|}$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

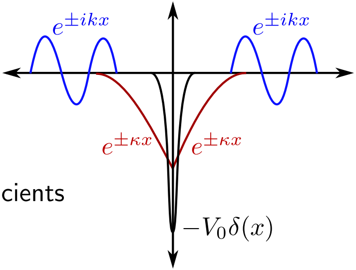


# $\delta$-atom: free states

- 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:

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

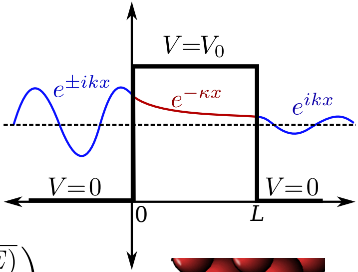
- Two free variables and two dependent among $A, B, C, D$
- If $D = 0$, $A$ incoming wave from $-\infty$, reflects to $B$ and transmits to $C$
- Solve to get reflection and transmission coefficients



# 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

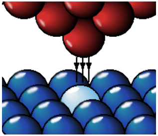
$$P \sim e^{-\kappa L} = \exp\left(-\frac{L\sqrt{2m(V_0 - E)}}{\hbar}\right)$$




- 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 $\sigma_k$

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

- This Gaussian 'wave-packet' has

$$\psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}k c(k) e^{i(kx-\omega(k)t)} \qquad \left(\hbar\omega(k) = \frac{\hbar^2 k^2}{2m}\right)$$

$$= \frac{1}{\sqrt{2\pi\sigma_k\sqrt{2\pi}}} \int_{-\infty}^{\infty} \mathrm{d}k \exp\left[-\frac{(k-k_0)^2}{2\sigma_k^2} + i(kx - \omega(k)t)\right]$$

# Gaussian wavepacket

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\sigma_k\sqrt{2\pi}}}\int_{-\infty}^{\infty} \mathrm{d}k \exp\left[-\frac{(k-k_0)^2}{2\sigma_k^2} + i(kx - \omega(k)t)\right]$$

$$= \frac{1}{\sqrt{2\pi\sigma_k\sqrt{2\pi}}}\int_{-\infty}^{\infty} \mathrm{d}k \exp\left[\begin{array}{c} -\frac{(k-k_0)^2}{2\sigma_k^2} + ikx \\ -i(\omega(k_0)t + \omega'(k_0)(k-k_0)t + \cdots) \end{array}\right]$$

$$= \frac{e^{i(k_0x - \omega(k_0)t)}}{\sqrt{2\pi\sigma_k\sqrt{2\pi}}}\int_{-\infty}^{\infty} \mathrm{d}\Delta k \exp\left[-\frac{\Delta k^2}{2\sigma_k^2} + i\Delta k(x - \omega'(k_0)t)\right]$$

$$= \frac{e^{i(k_0x - \omega(k_0)t) - \sigma_k^2(x-\omega'(k_0)t)^2/2}}{\sqrt{2\pi\sigma_k\sqrt{2\pi}}} \underbrace{\int_{-\infty}^{\infty} \mathrm{d}\Delta k e^{\frac{-\{\Delta k - i\sigma_k^2(x-\omega'(k_0)t)\}^2}{2\sigma_k^2}}}_{\sqrt{2\pi}\sigma_k}$$

$$= \exp\left[i(k_0x - \omega(k_0)t)\right] \cdot \frac{\exp\left[-\frac{(x-\omega'(k_0)t)^2}{2(\sigma_k^{-1})^2}\right]}{\sqrt{\sigma_k^{-1}\sqrt{2\pi}}}$$

# 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

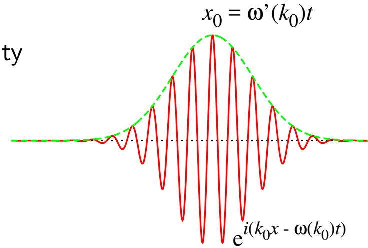
$$v_g = \frac{\partial \omega}{\partial k}$$

- Underlying waves propagate with phase velocity

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

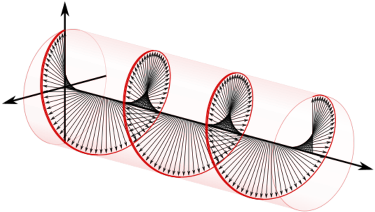
- For free particle with $\omega = \hbar k^2/(2m)$

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



# 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



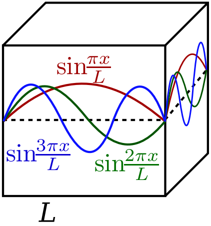
- Quantize to a photon: circular polarizations will have (internal) angular momentum $\pm\hbar$
- Angular momentum quantized in units of $\hbar$
- Since maximum magnitude is 1, photon is a spin $s = 1$ particle
- Electrons have internal angular momentum $\pm\hbar/2$
- Electrons have spin $s = 1/2$
- 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.

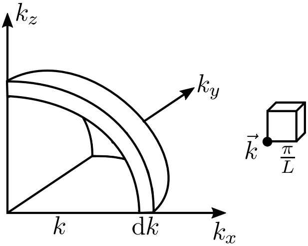
# Particles in a 3D box

- 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 $\varepsilon$

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

**Bosons:** (eg. photons)

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

(Bose-Einstein distribution)

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

**Fermions:** (eg. electrons)

$$\langle n\rangle \equiv \frac{\sum_{n=0}^{1} e^{-n\alpha} n}{\sum_{n=0}^{1} e^{-n\alpha}} = \frac{e^0\cdot 0 + e^{-\alpha}\cdot 1}{e^0 + e^{-\alpha}} = \frac{1}{e^{\alpha}+1} = \frac{1}{\exp\left(\frac{\varepsilon-\mu}{k_BT}\right)+1}$$

(Fermi-Dirac distribution)

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

Classical equipartition result: $\langle E\rangle = k_BT$

# Hydrogenic atom

- Single electron with a nucleus of charge $+Ze$, where $Z$ is the atomic number
- $Z = 1$ is hydrogen, $Z = 2$ is a $He^+$ ion, $Z = 3$ is $Li^{2+}$ etc.
- Schrodinger equation

$$-\frac{\hbar^2 \nabla^2 \psi(\vec{r})}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r}\psi(\vec{r}) = E\psi(\vec{r})$$

separable in spherical coordinates resulting in eigenfunctions

$$\psi_{nlm}(\vec{r}) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

and eigen-energies

$$E_{nlm} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \cdot \frac{Z^2}{n^2} = \frac{-Z^2}{2n^2}\ E_h = \frac{-Z^2}{n^2}\ \text{Ryd} \approx \frac{-Z^2}{n^2}(13.6\ \text{eV})$$

# Atomic quantum numbers

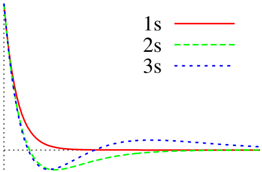
- For the box, we has $n_x$, $n_y$ and $n_z$
- Now in spherical coordinates, so correspond to $r$, $\theta$ and $\phi$
- Principal quantum number $n = 1, 2, \ldots$ is for the radial $r$ direction
- Angular quantum number $l = 0, 1, 2, \ldots, n-1$ is for the $\theta$ direction
- Azimuthal quantum number $m_l = -l, -l+1, \ldots, +l$ is for the $\phi$ direction
- But energy $E_{nlm_l} \propto n^{-2}$ only depends on $n$
- States of various $l$ and $m_l$ at same $n$ are 'degenerate' i.e. have same energy

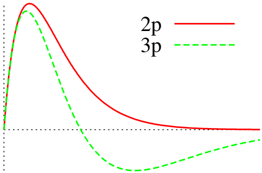
# Radial wavefunctions

- Radial functions of the form

$$R_{nl}(r) \propto \exp\left(\frac{-2Zr}{na_0}\right) \cdot r^l \cdot p^{(l)}_{n-l-1}(r)$$

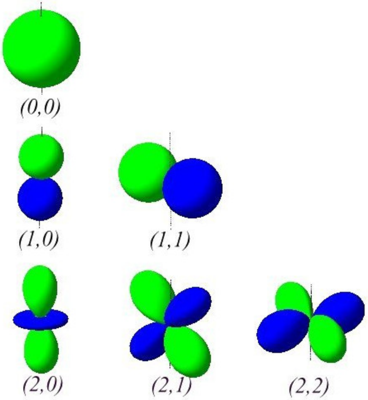
  where $a_0 = 4\pi\epsilon_0\hbar^2/(me^2) \approx 0.529$ Å is the Bohr radius
- Typical radial extent $\sim na_0/Z$
- Polynomial degree $n-l-1$: first $n$ of given $l$ has no nodes, next has one node etc.
- Remember $l = 0, 1, 2, 3$ denoted by $s$, $p$, $d$, $f$
- 1s has no nodes, 2s has 1 node etc.
- 2p has no nodes, 3p has 2 nodes etc.



# Angular wavefunctions

- Spherical harmonics $Y_{lm_l}(\theta, \phi) = P_l^{m_l}(\cos$
- Characteristic orbital shapes used in chemistry (typically Re$Y_{lm}$ and Im$Y_{lm}$)
- $l$ controls number of lobes
- $m_l$ controls number in $xy$-plane
- All $m_l$ related by spherical symmetry



# Electronic configuration of atoms

- Pauli exclusion principle: one electron per state (Fermi-Dirac statistics)
- Spin: $m_s = \pm 1/2$ (2 states)
- Azimuthal: $m = -l, -l+1, \ldots, +l$ ($2l+1$ states)
- Per $n$ and $l$: $2(2l+1)$ states
- Periodic table by orbital being filled ($Z$ range):

| | | | |
|---|---|---|---|
| 1s (1-2) | | | |
| 2s (3-4) | | | 2p (5-10) |
| 3s (11-12) | | | 3p (13-18) |
| 4s (19-20) | | 3d (21-30) | 4p (31-36) |
| 5s (37-38) | | 4d (39-48) | 5p (49-54) |
| 6s (55-56) | 4f (57-70) | 5d (71-80) | 7p (81-86) |
| 7s (87-88) | 5f (89-102) | | |

# The size of atoms

- Orbital size $\sim na_0/Z$
- Hydrogen atom $Z = 1, n = 1$: size $\sim a_0 \approx 0.53$ Å
- Sodium atom $Z = 11, n = 3$: size $\sim 3a_0/11 \approx 0.14$ Å
- Platinum atom $Z = 78, n = 6$: size $\sim 6a_0/78 \approx 0.04$ Å
- What's wrong?
- Hydrogenic orbitals are for one electron systems only!
- When more than one electron, electron-electron repulsion matters
- Effective charge seen by outer electrons is approximately that of nucleus + inner electrons

# Many-electron Schrodinger equation

- So far, we discussed wavefunction $\psi(\vec{r})$ satisfying

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

which is strictly a one-electron theory only.

- For $N$ electrons, need to keep track of all $N$ electronic coordinates with a wavefunction $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$
- Corresponding Schrodinger equation with e-e interactions:

$$\underbrace{-\frac{\hbar^2}{2m}\sum_i \nabla^2_{\vec{r}_i}\psi}_{\text{Kinetic}} + \underbrace{\sum_i V(\vec{r}_i)\psi}_{\text{e-nuc}} + \underbrace{\sum_{i\neq j}\frac{e^2}{4\pi\epsilon_0|\vec{r}_i - \vec{r}_j|}\psi}_{\text{e-e}} = E\psi$$

which is impossible to solve exactly beyond special $N = 2$ cases

# Many-electron non-interacting case

- Without e-e interactions:

$$\underbrace{-\frac{\hbar^2}{2m}\sum_i \nabla^2_{\vec{r}_i}\psi}_{\text{Kinetic}} + \underbrace{\sum_i V(\vec{r}_i)\psi}_{\text{e-nuc}} = E\psi$$

  which is *separable* in each $\vec{r}_i$.
- Therefore solution must be consist of products

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \sim \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\cdots\phi_N(\vec{r}_N)$$

- Each 'orbital' $\phi_i$: $N = 1$ Schrodinger equation with orbital energy $\varepsilon_i$
- Total energy $E = \sum_i \varepsilon_i$
- Strictly, fermionic wavefunctions need to be antisymmetric

$$\Rightarrow \psi = \det[\phi_i(\vec{r}_j)]$$

  (Slater determinant)

# Kohn-Sham density functional theory (DFT)

- A single-particle theory

$$-\frac{\hbar^2}{2m}\nabla^2\phi_i(\vec{r}) + V_{\mathrm{KS}}(\vec{r})\psi = \varepsilon_i\phi_i(\vec{r})$$

  in an effective potential $V_{\mathrm{KS}}(\vec{r})$
- $V_{\mathrm{KS}}(\vec{r}) = V(\vec{r})$ + contribution from electron density $n(\vec{r})$
- Total energy $E = \sum_i \varepsilon_i$ + contribution from electron density $n(\vec{r})$
- Electron density $n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2$ made self-consistent
- DFT works surpisingly well even for strongly interacting electrons
- When DFT does not work, material called 'strongly-correlated'!

# Atoms revisited

- Orbital energies are those from effective potential (not hydrogenic)
- For spherical atoms, still degenerate in $m$ and $m_s$, but not in $l$
- At same $n$, energy increases with $l$
- In particular, energy of $(n+1)$s $<$ $(n-1)$f $<$ $n$d $<$ $(n+1)$p $\Rightarrow$

| | | | |
|---|---|---|---|
| 1s (1-2) | | | |
| 2s (3-4) | | | 2p (5-10) |
| 3s (11-12) | | | 3p (13-18) |
| 4s (19-20) | | 3d (21-30) | 4p (31-36) |
| 5s (37-38) | | 4d (39-48) | 5p (49-54) |
| 6s (55-56) | 4f (57-70) | 5d (71-80) | 7p (81-86) |
| 7s (87-88) | 5f (89-102) | | |

# Operators and expectation values

- $|\psi(\vec{r})|^2$ probability distribution of $\vec{r}$
- Average value of $\vec{r}$:

$$\langle\vec{r}\rangle \equiv \int \mathrm{d}\vec{r} |\psi(\vec{r})|^2 \vec{r}$$

Expectation value of operator $\vec{r}$ in state with wavefunction $\psi$

$$\langle\psi|\vec{r}|\psi\rangle \equiv \int \mathrm{d}\vec{r}\ \psi^*(\vec{r})\ \vec{r}\ \psi(\vec{r})$$

- Expectation value of $r^2$:

$$\langle r^2\rangle \equiv \langle\psi|r^2|\psi\rangle \equiv \int \mathrm{d}\vec{r}\ \psi^*(\vec{r})\ r^2\ \psi(\vec{r})$$

- Uncertainty in $x$, $\Delta x \equiv \sqrt{\langle x^2\rangle - \langle x\rangle^2}$

# Momentum operator

- For a free particle with momentum $\vec{p} = \hbar\vec{k}$, $\psi = e^{i\vec{k}\cdot\vec{x}}/\sqrt{L}$
- Consider expectation value of gradient

$$\begin{aligned}\langle\psi|\nabla|\psi\rangle &\equiv \int \mathrm{d}\vec{r}\; \psi^*(\vec{r})\ \nabla\ \psi(\vec{r}) \\ &= \frac{1}{L}\int \mathrm{d}\vec{r}\; e^{-i\vec{k}\cdot\vec{x}}\ \nabla e^{i\vec{k}\cdot\vec{x}} \\ &= \frac{1}{L}\int \mathrm{d}\vec{r}\; e^{-i\vec{k}\cdot\vec{x}}\ i\vec{k}e^{i\vec{k}\cdot\vec{x}} \\ &= i\vec{k}\end{aligned}$$

- Momentum operator $\hat{\vec{p}}$ defined by $\langle\vec{p}\rangle = \langle\psi|\hat{\vec{p}}|\psi\rangle$
- So the momentum operator is

$$\hat{\vec{p}} = -i\hbar\nabla$$

# Hamiltonian operator

- If we define the Hamiltonian operator as

$$\hat{H} \equiv \frac{\hbar^2 \nabla^2}{2m} + V(\vec{r}) = \frac{\hat{\vec{p}}^2}{2m} + V(\vec{r})$$

  the Schrodinger equation becomes $\hat{H}\psi = E\psi$
- Expectation value of the Hamiltonian is $\langle \psi | \hat{H} | \psi \rangle = \mathrm{E}$
- What about time dependence? Remember $\psi(\vec{r}, t) = \psi(\vec{r}) e^{-iEt/\hbar}$

$$\begin{aligned}
\langle \psi | \hat{H} | \psi \rangle &\equiv \int \mathrm{d}\vec{r} \psi^*(\vec{r}, t) \hat{H} \psi(\vec{r}, t) \\
&= \int \mathrm{d}\vec{r} \psi^*(\vec{r}) e^{iEt/\hbar} \hat{H} \psi(\vec{r}) e^{-iEt/\hbar} \\
&= \int \mathrm{d}\vec{r} \psi^*(\vec{r}) \hat{H} \psi(\vec{r}) \\
&= \int \mathrm{d}\vec{r} \psi^*(\vec{r}) E \psi(\vec{r}) \\
&= E
\end{aligned}$$

# Time dependence due to perturbations

- Let Hamiltonian $\hat{H}$ have two eigenstates $H\psi_1 = E_1\psi_1$ and $H\psi_2 = E_2\psi_2$
- Eigenstates are orthogonal $\int \psi_1^* \psi_2 = 0$ and complete: any $\psi = c_1\psi_1 + c_2\psi_2$
- Say apply electric field $\vec{E}e^{-i\omega t}$, changes Hamiltonian to $\hat{H} + \hat{H}'e^{-i\omega t}$ with $\hat{H}' = -e\vec{E}\cdot\vec{r}$
- Time-dependent Schrodinger equation $(\hat{H} + \hat{H}'e^{-i\omega t})\psi = i\hbar\frac{\partial\psi}{\partial t}$
- Substitute expansion $\psi(t) = c_1(t)e^{-iE_1t/\hbar}\psi_1 + c_2(t)e^{-iE_2t/\hbar}\psi_2$

$$(\hat{H} + \hat{H}'e^{-i\omega t})(c_1e^{-iE_1t/\hbar}\psi_1 + c_2e^{-iE_2t/\hbar}\psi_2) \\ = (i\hbar\dot{c}_1 + E_1c_1)e^{-iE_1t/\hbar}\psi_1 + (i\hbar\dot{c}_2 + E_2c_2)e^{-iE_2t/\hbar}\psi_2$$

- Rewrite using eigenvalues of $\hat{H}$

$$c_1e^{-i(E_1+\hbar\omega)t/\hbar}\hat{H}'\psi_1 + c_2e^{-i(E_2+\hbar\omega)t/\hbar}\hat{H}'\psi_2 \\ = i\hbar\dot{c}_1e^{-iE_1t/\hbar}\psi_1 + i\hbar\dot{c}_2e^{-iE_12/\hbar}\psi_2$$

# Time dependence due to perturbations (contd.)

- Equation in terms of expansion $\psi(t) = c_1(t)e^{-iE_1t/\hbar}\psi_1 + c_2(t)e^{-iE_2t/\hbar}\psi_2$

$$c_1 e^{-i(E_1+\hbar\omega)t/\hbar}\hat{H}'\psi_1 + c_2 e^{-i(E_2+\hbar\omega)t/\hbar}\hat{H}'\psi_2$$
$$= i\hbar\dot{c}_1 e^{-iE_1t/\hbar}\psi_1 + i\hbar\dot{c}_2 e^{-iE_12/\hbar}\psi_2$$

- Now integrate equation $\int \psi_2(\vec{r},t)^*$ to get

$$c_1\langle\psi_2|\hat{H}'|\psi_1\rangle e^{i(E_2-E_1-\hbar\omega)t/\hbar} + c_2\langle\psi_2|\hat{H}'|\psi_2\rangle e^{-i\omega t} = i\hbar\dot{c}_2$$

- If we start at $t = 0$ in state $\psi_1$ i.e. $c_1(0) = 1$, $c_2(0) = 0$, then at $t = 0$

$$i\hbar\dot{c}_2 = \langle\psi_2|\hat{H}'|\psi_1\rangle e^{i(E_2-E_1-\hbar\omega)t/\hbar}$$

  which is the rate at which state $\psi_2$ starts appearing
- $c_2(t)$ oscillates in time with zero average value as long as $E_2 \neq E_1 + \hbar\omega$ (Energy conservation)
- If $E_2 = E_1 + \hbar\omega$, then $c_2(t)$ grows in time

# Fermi's Golden rule

- Upon applying a perturbation Hamiltonian $H' e^{i\omega t}$,

$$\Gamma_{1\to 2} = \frac{2\pi}{\hbar} |\langle \psi_2 | \hat{H}' | \psi_1 \rangle|^2 \delta\left(E_2 - (E_1 + \hbar\omega)\right)$$

  is the rate of transitioning from $\psi_1$ to $\psi_2$

- More generally,

$$\Gamma_i = \frac{2\pi}{\hbar} \sum_f |\langle \psi_f | \hat{H}' | \psi_i \rangle|^2 \delta\left(E_f - (E_i + \hbar\omega)\right)$$

  is the rate of transitioning out of initial state $\psi_i$

- Fundamental equation of 'quantum kinetics'
  (say analogous to Arrhenius equation)

# Orbital angular momentum

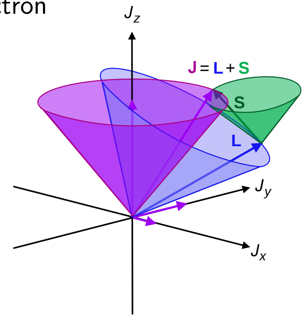
- Classical picture: electrons revolving around nuclei with $\vec{L} = \vec{r} \times \vec{p}$
- In quantum picture, $\hat{\vec{L}} = \vec{r} \times \hat{\vec{p}} = -i\hbar \vec{r} \times \nabla$
- In particular $\hat{L}_z = -i\hbar(x\partial_y - y\partial_x) = -i\hbar\partial_\phi$
- In atomic orbitals, angular dependence $Y_{lm_l}(\theta, \phi) = P_l^{m_l}(\cos\theta)e^{im_l\phi}$
- Azimuthal angular momentum $\langle \hat{L}_z \rangle = m_l \hbar$
- Account for all directions, magnitude of angular momentum

$$\langle \hat{L}^2 \rangle = l(l+1)\hbar^2$$

- Number of projections quantized to $2l + 1$ (number of allowed $m_l$)

# Spin angular momentum

- Electrons have spin $s = 1/2$
- Corresponding $m_s = \pm 1/2$ ($2 = 2s + 1$ values)
- Projected angular momentum $S_z = m_s \hbar$
- Angular momentum magnitude $S^2 = s(s+1)\hbar^2$
- Both orbital and spin angular momentum for electron
- Total angular momentum $\vec{J} = \vec{L} + \vec{S}$
- Also quantized, with quantum numbers $j, m_j$
- $j = |l - s|$ to $l + s$ in increments of 1
- $m_j = -j, -j+1, \ldots, +j$
- Projected angular momentum $J_z = m_j \hbar$
- Angular momentum magnitude $J^2 = j(j+1)\hbar^2$



# Angular momentum consequence: magnetic moments

- Consider particle with charge $q$ and mass $m$ moving with speed $v$ in circle of radius $r$
- Angular momentum $L = mvr$
- Current $I = \frac{qv}{2\pi r}$
- Magnetic moment $\mu = \frac{1}{2}\oint \vec{r} \times \mathrm{d}\vec{l} I = \frac{1}{2} r(2\pi r)\frac{qv}{2\pi r} = qvr/2$
- Classical particle $\mu = \frac{q}{2m} L$
- Exactly true for orbital angular momentum

  $$\mu_z = \frac{-e}{2m} m_l \hbar = -m_l \mu_B$$

  where $\mu_B \equiv \frac{e\hbar}{2m}$ is the Bohr magneton
- What about spin?

  $$\mu_z = -g_e m_s \mu_B$$

  where $g_e \approx 2.0023 = 2 + \frac{e^2}{4\pi\epsilon_0 hc} + \cdots$ is called the gyromagnetic ratio (Relativity $\Rightarrow g_e = 2$, rest quantum correction)

# Angular momentum conservation: selection rules

- Light absorption: photon excites electron from lower state $nlm_l$ to higher state $n'l'm_l'$
- Dominant electron-photon interaction through electric field $\Rightarrow$ involves only $L$ of electron (not $S$)
- Initial angular momentum $s = 1$ in photon and $l$ of electron $\Rightarrow j = l - 1, \ldots, l + 1$
- Projection $m_j = m_s + m_l = m_l - 1, \ldots, m_l + 1$
- Angular momentum conservation $(l', m_l')$ must equal $(j, m_j)$
- Process allowed only if $\Delta l = 0, \pm 1$ and $\Delta m_l = 0, \pm 1$
- More careful analysis $\Delta l = 0$ disallowed (because $\langle \psi_2 | \hat{H}' | \psi_1 \rangle = 0$), $\Rightarrow \Delta l = \pm 1$ and $\Delta m_l = 0, \pm 1$