

351: Physics of Materials I

MSE Faculty

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1 Catalog Description (351-1,2)

Quantum mechanics; applications to materials and engineering. Band structures and cohesive energy; thermal behavior; electrical conduction; semiconductors; amorphous semiconductors; magnetic behavior of materials; liquid crystals. Lectures, laboratory, problem solving. Prerequisites: GEN ENG 205 4 or equivalent; PHYSICS 135 2,3.

2 Course Outcomes

3 351-1: Quantum Mechanics

At the conclusion of 351-1 students will be able to:

- 1) Solve the time-independent Schrödinger equation for simple one-dimensional potentials.
- 2) Calculate probabilities of reflection and transmission for 1-D potential barriers or wells.
- 3) Use the wavefunctions and energies of the hydrogen atom to determine the ground and excited state energies of hydrogenic systems.
- 4) Describe models of bonding, including ionic, covalent, metallic, and Van der Waals, using quantum mechanical concepts of energy minimization.
- 5) Calculate the specific heat for fermions (e.g. electrons) and bosons (e.g. phonons) in 1, 2, and 3 dimensions, given the density of states.

- 6) Describe the impact of Fermi statistics on the electrical properties of metals.
- 7) Use simple models of band-structure, such as the Feynman model and the Krönig-Penney model, to relate the properties of local atomic states to delocalized states (bands) in a material.
- 8) Given the dispersion relationship, calculate the effective mass and density of states in the nearly free electron approximation.
- 9) Determine the intrinsic and/or extrinsic carrier concentration in a semiconductor given the temperature, doping level, and other relevant quantities.

4 Why Do We Need Quantum Mechanics?

4.1 Classical (Planetary) Picture of the Hydrogen Atom

Consider a classical analysis of the hydrogen atom, where the electron can be viewed as a charge $-e$ that is orbiting around a proton of charge e .

The Coulomb attraction force F_{coul} between the proton and the electron is given by the following formula:

$$F_{coul} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad (4.1)$$

Suppose that the electron is moving with a velocity of v in a circular orbit with a radius of r . The electrons are being accelerated toward the center of the orbit by v^2/r . In the classical picture the relationship between r and v is determined by Newton's second law relating the Coulomb force from Eq.4.1 to the acceleration:

$$F = m_e a = m_e \frac{v^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad (4.2)$$

Solving this equation for r results in the following expression for the radius:

$$r = \frac{e^2}{4\pi\epsilon_0 m_e v^2} \quad (4.3)$$

Classically, v is continuous suggesting that r can be anything. This implies that the Hydrogen atom does not have a fixed size, which doesn't really make sense.

4.2 The Bohr Atom

How can this issue of an indeterminate size of the hydrogen atom be fixed? Suppose certain orbits are preferred, and that only orbits meeting the following condition are allowed (we'll justify this assumption later):

$$m_e v r = h/2\pi \quad (4.4)$$

Here m_e is the **electron mass** and h is **Planck's constant**. If we use Eq.4.4 to eliminate v from Eq.4.3 and then solve for r we obtain:

$$r = \frac{4\pi\epsilon_0}{m_e e^2} \hbar^2 \equiv a_o \quad (4.5)$$

Where a_o is the Bohr radius. If we generalize so that the allowed radii are $r_n = n^2 a_o$, where $n = 1, 2, 3, \dots$ as shown in Figure we can account for key features of hydrogen spectra.

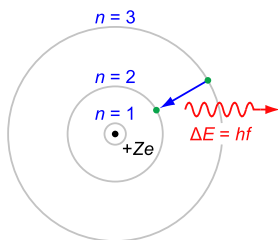


Figure 4.1: The Bohr atom[?].

4.3 Units and Magnitude of h

$$\hbar = h/2\pi \quad \hbar = 2\pi\hbar$$

$$\text{Let } a_o \simeq 0.5\text{\AA} = 0.5 \times 10^{-10} m.$$

$$\hbar^2 = \frac{h^2}{(2\pi)^2} = \frac{m_e e^2}{4\pi\epsilon_0} r_o$$

$$h^2 = \frac{\pi (9.109 \times 10^{-31} kg)}{8.85 \times 10^{-12} \frac{C^2}{Jm}} (1.6 \times 10^{-19} C)^2 (0.5 \times 10^{-10} m) \quad (4.6)$$

Checking units:

$$\frac{Jm}{C^2} (kg) (C^2) (m) = Jm^2 kg = J \left(\frac{kgm^2}{s^2} \right) s^2 \quad (4.7)$$

$$h = 6.43 \times 10^{-34} J \cdot s$$

The Bohr Radius is actually 0.529\AA .

- Note that Rutherford established that the diameter of the electron cloud as: $d_{e-cloud} \approx 10^{-10} m$.
- h had been showing up in other contexts, as we'll see.

From classical electrodynamics, orbits should **not** be stable because accelerating point charges radiate energy.

This is described by the **Larmor Formula**:

$$P_{RAD} = \frac{dE_{RAD}}{dt} = \frac{e^2 a^2}{6\pi\epsilon_0 c^3} \quad (4.8)$$

Where E_{RAD} is the radiated energy, P_{RAD} is the radiated power, c is the speed of light and a is the acceleration.

Note:

$$P_{RAD} = \frac{dE_{RAD}}{dt} = \frac{e^2 a^2}{6\pi\epsilon_0 c^3} > 0$$

For the Planetary Atom,

$$E_{ATOM} = KE + PE = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad (4.9)$$

But, recall that

$$v^2 = \frac{e^2}{4\pi\epsilon_0 m_e r} \quad (4.10)$$

$$E_{ATOM} = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = -\frac{e^2}{8\pi\epsilon_0 r} < 0 \quad (4.11)$$

Conservation of Energy:

$$E_{ATOM} + E_{RAD} = Constant$$

$$\frac{dE_{ATOM}}{dt} + \frac{dE_{RAD}}{dt} = 0 \Rightarrow \frac{dE_{ATOM}}{dt} = -\frac{dE_{RAD}}{dt} \quad (4.12)$$

Since

$$\frac{dE_{RAD}}{dt} > 0 \Rightarrow \frac{dE_{ATOM}}{dt} < 0$$

E_{ATOM} becomes more negative with time and r decreases as the electron radiates.

As the orbiting electron radiates, it spirals into the nucleus.

But, we know that atoms are stable and do not radiate.

The Planetary Model fails catastrophically! (See homework #1).

We need quantum mechanics to understand atomic (and solid state) physics!

5 Origins of Quantum Theory

Prior to 1900, most experiments were well-explained or consistent with the beliefs that:

- 1) Matter consists of particles obeying Newton's Laws.
- 2) Radiation consists of waves obeying Maxwell's Laws.

These laws were incredibly successful at explaining numerous phenomena, however new concepts were needed to explain new (and old) experiments:

- 1) Relativistic Mechanics (Einstein)
- 2) Quantization of Observed Physical Quantities (e.g. E)
- 3) Particle Properties of Radiation
- 4) Wave Properties of Matter

Quantization is a consequence of attempts to reconcile the particle and wave picture.

5.1 Black Body Radiation

A Blackbody is a perfect emitter/ absorber of radiation.

In 1879, J. Stefan found the **empirical** relationship between total emissive power R and T :

$$R(T) = E\sigma T^4 \quad (5.1)$$

Stefan-Boltzmann Law (Boltzmann derived this in 1884.)

E : emissivity = 1 for a blackbody

σ : $5.67 \times 10^{-8} \frac{W}{m^2 k^4}$ Stefan's Constant

Spectral Density:

$$R(T) = \int_0^\infty d\lambda R(\lambda, T)$$

Wien's Displacement Law: Max of $R(\lambda, T)$ occurs when $\lambda_{\max} T = b$, where $b = 2.898 \times 10^{-3} \text{m} \cdot \text{K}$.

(This is useful for temperature measurement, but we also want to know distance.)

Inside the cavity, energy is distributed according to spectral distribution function $\rho(\lambda, T)$, where $R(\lambda, T) = \frac{c}{4} \rho(\lambda, T)$.

From (Classical) Thermodynamics, Wein derived:

$$\rho(\lambda, T) = \lambda^{-5} F(\lambda, T)$$

$F(\lambda, T)$ cannot be derived from Thermo, but Wein proposed $F(\lambda, T) \sim e^{-\infty/\lambda T}$ (okay for short λ).

Lord Rayleigh and J. Jeans used electromagnetism to show that:

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} < E \text{ Spectral Density } >_{\lambda}$$

$\langle E \rangle_{\lambda}$ is the average energy of mode with wavelength λ (normal for long λ).

(How can we calculate this?)

From Classical Stat Mech, assuming $P_{\sigma e} \sim e^{-E/kT}$:

$$\langle E \rangle = \frac{\int_0^\infty dE E \exp(-\beta E)}{\int_0^\infty dE \exp(-\beta E)}$$

$$(\beta = \frac{1}{kT})$$

$$k = 1.38 \times 10^{-23} \text{ J/K}$$

Boltzmann's Constant

$$\langle E \rangle = -\frac{d}{d\beta} \ln \left[\int_0^\infty dE \exp(-\beta E) \right] \frac{d}{dx} f(x) = \frac{f'(x)}{f(x)}$$

$$\langle E \rangle = -\frac{d}{d\beta} \ln \left(\frac{1}{\beta} \right) = -\beta \left(-\frac{1}{\beta^2} \right) = \frac{1}{\beta} = kT$$

$$\therefore \rho(\lambda, T) = \frac{8\pi}{\lambda^4} kT \Rightarrow f(\lambda, T) = 8\pi k\lambda T$$

At long λ , this approaches experimental values.

But $\rho(\lambda, T) \rightarrow \infty$ as $\lambda \rightarrow 0$

“Ultraviolet Catastrophe”

1900 - Planck's Quantum Theory

Revolutionary Hypothesis: Radiation emitted by microscopic oscillators of frequency V that can only take on discrete values

$$nE_o, n = 0, 1, 2, \dots$$

(How does this affect the distribution function?)

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} nE_o \exp(-\beta nE_o)}{\sum_{n=0}^{\infty} \exp(-\beta nE_o)}$$

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}$$

$$\langle E \rangle = -\frac{d}{d\beta} \left[\ln \sum_{n=0}^{\infty} \exp(-\beta nE_o) \right]$$

$$\langle E \rangle = -\frac{d}{d\beta} \ln \left(\frac{1}{1 - \exp(-\beta E_o)} \right)$$

$$\frac{d}{dx} \ln f(x) = \frac{f'(x)}{f(x)}$$

$$\langle E \rangle = \frac{1 - \exp(-\beta E_o) (-1)}{[1 - \exp(-\beta E_o)]^2} [-E_o \exp(-\beta E_o)]$$

$$\langle E \rangle = \frac{E_o}{\exp(\beta E_o) - 1}$$

Therefore,

$$\rho(\lambda, T) = \frac{8\pi}{\lambda^4} \frac{E_o}{\exp(E_o/kT) - 1}$$

For Planck's Formula to satisfy Wien's Law, where $\rho(\lambda, T) = \lambda^{-5} f(\lambda, T)$:

$$E_o \propto \frac{1}{\lambda}$$

$E_o = hV = \frac{hc}{\lambda}$, where h is Planck's Constant.

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

$$\text{So } \rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{\exp(\frac{hc}{\lambda kT}) - 1} \text{ (consider extremes).}$$

This was a successful interpolation of (1) Wien's Exponential Law and (2) the Rayleigh-Jeans Law.

1) For short λ , $\rho(\lambda, T) \propto \exp(-\frac{hc}{\lambda kT})$ (goes to zero for short λ)

2) For long λ , $\exp(\frac{hc}{\lambda kT}) \simeq 1 + \frac{hc}{\lambda kT}$ (Taylor series)

$$\lambda \gg hc/kT$$

$$\rho(\lambda, T) \simeq \frac{8\pi hc}{\lambda^5} \frac{1}{1 + \frac{hc}{\lambda kT} - 1} - \frac{8\pi}{\lambda^4} kT$$

3) Can calculate h using $\lambda_{MAX} T = \text{Constant}$

Photoelectric Effect (evidence for quantum of radiation) Electrons emitted from metal surface when exposed to radiation (Hertz, Hallwachs - 1888, J.J. Thomson - 1899).

- $E_{\max} \propto \nu$, not intensity (Leonard, 1902)
- $\frac{dN_e}{dt} \propto$ intensity (Leonard, 1902)
- No current for $\nu < \nu_{TH}$ (Quant confirmed by Milikan)

1905 - Einstein explained that $E_{ph} = h\nu$ (theoretically).

- Radiation consists of Quanta (photons) of energy $h\nu$.
- Energy is transferred in discrete amounts.
- Einstein received the Nobel Prize for this work.

Electrons are bound to the surface with energy ϕ , the work function.

By conservation of energy, $E_{\max} = h\nu - \phi$.

$h\nu_{TH} = \phi$ (was a prediction)

E_{\max} has no dependence on intensity.

(HW Aside)

Work Function - work done on electron moving through potential

Suppose $F_x = -eE_x = +e \frac{dV}{dx}$

$$\int F_x dx = e \int \frac{dV}{dx} dx$$

Work = $eV = 1.6 \times 10^{-19} \text{ C} \cdot \text{J/C} = 1.6 \times 10^{-19} \text{ J}$ (an energy)

eV is the potential energy of electron in potential V .

Compton Scattering (He mentions Quantum Theory.) (1923)

Do photons behave as particles kinematically?

(Photoemission is intermediate case - no outgoing photon.)

- The electron carries momentum from incident photon.
- New photon energy is smaller.
- Photon and electron are treated as relativistic particles:

$$E = \gamma mc^2, p = \gamma mv, \text{ where } \gamma \equiv 1/\sqrt{1 - \frac{v^2}{c^2}}$$

Results:

- $\Delta\lambda = \lambda_1 - \lambda_0 = 2\lambda_c$
- $\sin^2\left(\frac{\theta}{2}\right) = \lambda_c(1 - \cos\theta)$, where $\lambda_c = \frac{h}{m_e c}$
- Compton Wavelength, confirmed by experiments \Rightarrow radiation behaves as a wave and a particle.

Matter Waves 1923 - De Broglie proposed that if matter behaved as waves, then $\lambda = h/p$.

For light:

$$E = hV = \frac{hc}{\lambda} \text{ and } E = pc$$

$$\Rightarrow \lambda = h/p$$

- not usually observed because p is large/ h is small
- need something very light, not too fast

1927 - Davisson and Germer confirm with electrons.

Consider acceleration of e^- through potential V .

$$E = \frac{1}{2}mv^2 = \frac{m^2v^2}{2m} = \frac{p^2}{2m}$$

$$p = \sqrt{2mE} \text{ use } E = eV$$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2meV}}$$

$$\lambda \simeq \frac{12.3\text{\AA}}{\sqrt{V(\text{volts})}} \text{ e.g. } V = 150 \text{ volts gives } \lambda \sim 1\text{\AA}$$

Constructive Interference of Electrons occurs when:

$$d \sin \theta = n\lambda, \text{ where } n = 1, 2, 3, \dots$$

(saw clear path after annealing oxidized Ni crystal after vacuum failure)

The same h shows up to explain particles.

Helium atom diffraction: surface science

Neutron: diffraction in solids

Mass is $\sim 1000x$ bigger. (How much smaller is λ ?)

\rightarrow Need low energy particles.

Matter behaves like waves and particles.

Classical physics does not describe:

1) Quantization

2) Wave - Particle Duality

1925 - Heisenberg, Born and Jordan develop Matrix Mechanics

1925 - Schrödinger develops Wave Mechanics (Matter Waves)

1930 - Dirac Formulation: More General + Relativity → Spin, Magnetism

6 Origins of Schrödinger Equation

Two-Slit Experiment for Electrons. (What do you expect?) Each electron is detected when it hits screen in fixed location.

→ localized particle

What about the statistical behavior?

Over time, a pattern builds up.

“Interference” Pattern builds up even if only 1 electron is in transit at any given time.

Interpretation:

- Electrons pass through both slits.
- Position is not determined until it reaches the detector.

Proof: $I \neq I_1 + I_2$

(We need to give up the possibility of knowing $x(t)$ at all times and adopt a probabilistic description of particle behavior.)

Introduce the wave function $\Psi(x, y, z, t)$ as a probability amplitude, i.e....

$$P(x, y, z, t) \propto |\Psi(x, y, z, t)|^2$$

P is the probability of finding the particle at x, y, z within volume at time t .

If slit #1 is open, $P_1 \propto |\Psi_1|^2$.

If slit #2 is open, $P_2 \propto |\Psi_2|^2$.

If both are open, $\Psi = \Psi_1 + \Psi_2$.

→ $P \propto |\Psi_1 + \Psi_2|^2 \neq |\Psi_1|^2 + |\Psi_2|^2$ (This says little about form of Ψ .)

(Observation of large numbers of particles provides a sense of what a single particle is likely to do.)

1926 - Born formulated the Wave Function.

Assume a large number of identical, independent systems that are identically prepared and subjected to the same external force.

$$P(\vec{r}, t) d\vec{r} = |\Psi(\vec{r}, t)|^2 d\vec{r} = \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) d\vec{r}$$

This is an inherently statistical description of matter. (It's probabilistic, but statistically deterministic.)

The probability of finding the particle somewhere is unity.

$$\therefore \int_{ALLSPACE} d\vec{r} |\Psi(\vec{r}, t)|^2 = 1$$

$\Psi(\vec{r}, t)$ must be normalizable, cannot diverge.
 \Rightarrow provides constraints for solving for Ψ

Ψ obeys Principle of Superposition. Assume: $\Psi = c_1\Psi_1 + c_2\Psi_2$, c_1, c_2 complex constants

$$\Psi_1 = |\Psi_1| e^{i\alpha_1} \Psi_2 = |\Psi_2| e^{i\alpha_2}$$

$$e^{ix} = \cos x + i \sin x$$

$$|\Psi^2| = \Psi^* \Psi = (c_1^* \Psi_1^* + c_2^* \Psi_2^*) (c_1 \Psi_1 + c_2 \Psi_2)$$

$$|\Psi^2| = |c_1 \Psi_1|^2 + |c_2 \Psi_2|^2 + c_1^* c_2 \Psi_1^* \Psi_2 + c_2^* c_1 \Psi_2^* \Psi_1$$

$$|\Psi^2| = |c_1 \Psi_1|^2 + |c_2 \Psi_2|^2 + 2Re \{c_1 c_2^* |\Psi_1| |\Psi_2| \exp[i(\alpha_1 - \alpha_2)]\}$$

$$2Re \{c_1 c_2^* |\Psi_1| |\Psi_2| \exp[i(\alpha_1 - \alpha_2)]\} - \text{Interference term} \neq 0 \text{ in general.}$$

Probability amplitudes **interfere**.

Note: Any complex number can be written: $A^* = |A| e^{i\phi}$.

$$A^* + A = |A| e^{-i\theta} + |A| e^{i\theta}$$

$$A^* + A = |A| (\cos\theta - i\sin\theta) + |A| (\cos\theta + i\sin\theta)$$

$$A^* + A = 2|A| \cos(\theta) = 2Re\{A\}$$

Build Ψ with Physical Characteristics Following De Broglie, assume particle has definite momentum $p = \frac{h}{\lambda}$, $E = hv$.

And define:

1) Angular Frequency $\omega = 2\pi v$

2) Wave Number $R = 2\pi/\lambda$

3) Reduced Planck Constant $\hbar = h/2\pi$

Then, $E = \hbar\omega$ and $p = \hbar\kappa$.

For photons, we know $\omega = 2\pi v = \frac{2\pi}{\lambda} \cdot c = \kappa c$.

Note that: (1) $\omega \propto \kappa$ and (2) ω/κ is a speed.

For free particles, we will see that $\omega \propto \kappa^2$.

- What is the speed of a free particle wave?

- $F(x - vt)$ represents a waveform traveling along x with speed v .
- For a free particle of mass m in moving along $+x$ axis,

$$\vec{P} = P_x \hat{x}, P_x > 0, \kappa = P_x/\hbar$$

Represent particle with definite momentum as a **Plane Wave**.

Since $\kappa = P/\hbar, \omega = E/\hbar, \Psi(x, t) = A \exp\left[\frac{i}{\hbar}(P_x X - E(P_x) t)\right]$.

Note:

1) $-i\hbar \frac{d}{dx} \Psi = P_x \Psi$

$$2) \quad i\hbar \frac{d}{dt} \Psi = E\Psi$$

And in 3-D,

$$\Psi(\vec{r}, t) = A \exp[i(\vec{K} \cdot \vec{r} - \omega(\kappa)t)]$$

$$\Psi(\vec{r}, t) = A \exp\left[\frac{i}{\hbar}(\vec{p} \cdot \vec{r} - E(p)t)\right]$$

We have:

$$1) \quad -i\hbar \nabla \Psi = \vec{p}\Psi \quad ; -i\hbar = \text{pop} \quad ; \nabla: \text{gradient}$$

$$2) \quad i\hbar \frac{\delta}{\delta t} \Psi = E\Psi \quad ; i\hbar \frac{d}{dt} = E_{op}$$

Postulate: The differential operators give \vec{p} and \vec{E} even in the presence of a potential. (Particles may not be free.)

Classically, $E_{tot} = \frac{p^2}{2m} + V(\vec{r}, t)$.

1926: Schrödinger proposes that $E_{op} \Psi(\vec{r}, t) = \left[\frac{p_{op}^2}{2m} + V(\vec{r}, t) \right] \Psi(\vec{r}, t)$.

From the above postulate, it follows that $i\hbar \frac{d}{dt} \Psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \Psi(\vec{r}, t)$.

This is the time dependent **Schrödinger Equation**.

It:

- 1) Describes non-relativistic quantum mechanics.
- 2) Is not derived, but is physically plausible (can be related to Hamiltonian classical mechanics).
- 3) Correctly predicts experiments to date.

Define:

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

The Schrödinger Equation can then be written:

$$i\hbar \frac{d}{dt} \Psi(\vec{r}, t) = H \Psi(\vec{r}, t)$$

In MSE 351-1, we will solve this equation for:

- 1) Free Particles ($V = 0$)
- 2) Potential Wells and Barriers in 3-D (tunneling): $E < V$ and $E > V$
- 3) Coulomb Potential in 3-D (periodic table) ($V \sim -\frac{1}{r}$)
- 4) Periodic Potentials: $V \sim \sin x$ (as in solids \rightarrow electronic "band" structure)

Tasks for Students

- 1) Learn to solve Schrödinger equation for these few cases.
- 2) Calculate probability distributions, energies and dispersion relationships.
- 3) Provide physical interpretations.

(from S+W 3.3)

We will consider only time-independent potentials: $V(t)$.

(Time-dependent potentials require Perturbation Theory. This is needed for transitions and optical properties in particular.)

Separation of Variables - attempted solution $\Psi(\vec{r}, t) = \psi(\vec{r})\omega(t) = \psi\omega$
 $-\frac{\hbar^2}{2m}\omega\nabla^2\psi + V\psi\omega = i\hbar\psi\frac{d\omega}{dt}$ (divide by $\psi\omega$)

- 1) $-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$ (Time-dependent Schrödinger Equation)
- 2) $i\hbar\frac{d\omega}{dt} = E\omega \Rightarrow \omega = \exp(-i\frac{E}{\hbar}t)$

A solution for time independent potentials is therefore: $\Psi(\vec{r}, t) = \psi(\vec{r})e^{-i\frac{E}{\hbar}t}$, where $\psi(\vec{r})$ is the solution of (1).

Apply to free particle in 1-D:

$$\nabla^2 \rightarrow \frac{d^2}{dx^2}, V(x) = 0$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi(x)\psi'' = \frac{-2mE}{\hbar^2}\psi, \kappa = \frac{\sqrt{2mE}}{\hbar}$$

$$\rightarrow \psi(x) = Ae^{i\kappa x} + Be^{-i\kappa x}, A, B \text{ constants: } \kappa = \frac{\sqrt{2mE}}{\hbar} \text{ (see below)}$$

$$\Psi(x, t) = Ae^{i(\kappa x + \frac{Et}{\hbar})} + Be^{-i(\kappa x + \frac{Et}{\hbar})}$$

$$\text{right-moving: } Ae^{i(\kappa x + \frac{Et}{\hbar})}$$

$$\text{left-moving: } Be^{-i(\kappa x + \frac{Et}{\hbar})}$$

These are plane waves (De Broglie Matter Waves):

$$E = \frac{p^2}{2m} = \frac{(h/\lambda)^2}{2m} = \frac{\hbar^2\kappa^2}{2m} = \hbar\omega \quad (\omega \propto \kappa^2)$$

Consider the right-moving wave discussed earlier:

$$\Psi_{\kappa}(x, t) = e^{i(\kappa x - \omega t)} \kappa = \frac{\sqrt{2mE}}{\hbar} \omega = \frac{\hbar}{2m}\kappa^2$$

If Ψ_{κ} represents 1 electron, then: $|\Psi_{\kappa}(x, t)|^2 = 1 \rightarrow$ constant for **all** x, t .

Interpretation: A particle with exact momentum is completely delocalized in space.

Normalization Condition: $\int_{-\infty}^{\infty} dx |\Psi_{\kappa}(x, t)|^2 = \int_{-\infty}^{\infty} dx = \infty - (-\infty)?!$

$\Rightarrow \Psi_{\kappa}(x, t)$ cannot represent wave function of a single particle.

Particles cannot have “perfectly defined” or exact momenta.

Approach: Represent particle as a superposition of plane waves that produces a localized, normalizable wave packet.

Wave Packets in 1-D (S+W 2.3, in part)

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int d\kappa \phi(\kappa) \Psi_{\kappa}(x, t) \text{ (Fourier Transform)}$$

$\Psi(x, t)$ - no index

Normalizable if $\phi(\kappa) \rightarrow 0$ as $\kappa \rightarrow \pm\infty$.

$$\text{Find } \phi(R): \Psi(x, 0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\kappa \phi(\kappa) e^{i\kappa x} = A e^{i\kappa_o x} \text{ for } \frac{-d}{2} \leq x \leq \frac{d}{2}$$

Approach: Multiply both sides by $e^{-i\kappa x'}$ and integrate.

Substitute $\kappa = \kappa^1$:

$$\phi(\kappa) = \sqrt{\frac{2}{\pi}} A \frac{\sin\left[\frac{(\kappa_o - \kappa) \frac{\ell}{2}}{\kappa_o - \kappa}\right]}{\kappa_o - \kappa}$$

Interpretation:

Particle is localized and moves with speed $\sim V = \frac{p_o}{m} = \frac{\hbar \kappa_o}{m}$ (we'll prove).

But there is a spread in momenta about κ_o :

For $\kappa \sim \kappa_o$, new peak, $(\kappa_o - \kappa) \frac{\ell}{2} \approx \pi$ This defines width of $\phi(\kappa) \rightarrow \Delta\kappa = \frac{2\pi}{\ell}$ (argument runs over $\sim \pi$).

$$\Delta p = \hbar \Delta\kappa \approx \hbar \frac{2\pi}{\ell} = \frac{h}{\ell}$$

$$\Delta p \Delta x \simeq \frac{h}{\ell} \cdot \ell \simeq h$$

$\Delta p \Delta x \sim h$ is the Heisenberg Uncertainty Principle that can be derived using matrix mechanics.

Comments:

- 1) Here, the relationship between uncertainties follows directly from Fourier Transforms.
- 2) Analogous relationships exist for $\omega, t(E, t)$.

Velocity of the Wavepacket Assume $\phi(\kappa)$ is peaked about κ_o , consider κ values $\sim \kappa_o$.

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\kappa \phi(\kappa) e^{i(\kappa x - \omega t)}, \text{ but } \omega(\kappa) \simeq W_o + \left. \frac{d\omega}{d\kappa} \right|_{\kappa_o} (\kappa - \kappa_o) \text{ (Taylor Series Expansion)}$$

$$\Psi(x, t) \simeq \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\kappa \phi(\kappa) \exp\left[i\left(\kappa x - \left(\omega_o + \left. \frac{d\omega}{d\kappa} \right|_{\kappa_o} (\kappa - \kappa_o) + \dots\right) t\right)\right] \text{ (Bring terms in front that do not depend on } \kappa.)$$

$$\omega = \frac{\hbar \kappa^2}{2m}, \left. \frac{d\omega}{d\kappa} \right|_{\kappa_o} = \frac{\hbar \kappa_o}{m} \rightarrow V_g = \frac{p_o}{m}$$

The center of the wavepacket travels at the group velocity $V_g = \left. \frac{d\omega}{d\kappa} \right|_{\kappa_o}$.

Individual components travel at phase velocity $\frac{\omega}{\kappa}$, which may cause wavepacket to spread out with time.

$$\text{Proof: } \Psi_{\kappa}(x, t) = e^{i(\kappa x - \omega t)} = e^{i\phi}$$

ϕ is a phase, and the equation defines a plane of constant phase (e.g. peak or trough).

$$\phi = \kappa x - \omega t = \text{constant}$$

$$x = \frac{\phi}{\kappa} + \frac{\omega}{\kappa} t$$

$$\left. \frac{dx}{dt} \right|_{\phi=\text{constant}} = +\frac{\omega}{\kappa} = V_p$$

Re-examine the Two-Split Experiment:

- Attempt to measure which slit the electron passes through.
- Use a microscope that can resolve the slits \rightarrow implies that $\lambda_\gamma < \delta$.

$$1) \Delta P_e \simeq P_\gamma = \frac{h}{\lambda_\gamma} > \frac{h}{d} \quad (\lambda_\gamma \leq d)$$

Note that $\Delta P_e d > h$.

$$2) P_e = \frac{h}{\lambda_e}$$

$$\frac{\Delta P_e}{P_e} = \frac{h \lambda_e}{d h} = \frac{\lambda_e}{d} = \frac{\Delta x}{L} \quad (\text{from above})$$

$$\Rightarrow \Delta x \simeq L \frac{\lambda_e}{d}$$

The uncertainty in position is comparable to the distance between interference maxima.

\Rightarrow No pattern is observed.

Why not? The act of measurement has “collapsed the wave function.”

7 Time-Independent Potentials: Wells and Barriers

Introduction Plane Waves: Solutions to Schrödinger Equation for Free Particle ($V = 0$)

But, this formulation usefully explains the Two-Slit Experiment.

To build up to hydrogen atom (sow of Schrödinger Equation for e-bound to proton), we start with a simpler case.

Recall that for time-independent potentials, in 1-D, solutions have the form:

$$\Psi(x, t) = \psi(x) e^{-i \frac{E}{\hbar} t}, \quad \text{where} \left[\frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E \psi(x)$$

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

$$\int_{-\infty}^{\infty} \psi^*(x) \psi(x) dx = 1$$

Note that $|\Psi(x, t)|^2 = |\psi(x)|^2$ are independent of time.

We call these stationary states of definite energy.

Because superposition holds, the general solution is: $\Psi(x, t) =$

$$\sum_{n=0}^{\infty} C_n \psi_n(x) e^{-i \frac{E_n}{\hbar} t}.$$

C_n : complex constant

E_n : definite energy

$|\Psi(x, t)|^2$ is time dependent: does not have definite E .

1-D Time-Independent Potentials: Wells & Barriers Recall time-independent Schrödinger Equation in 1-D:

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

Solutions of Schrödinger Equation with constant potential have the form:

$$\Psi(x, t) = \psi(x) e^{-i \frac{E_n}{\hbar} t}, \text{ where } \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) = E\psi(x)$$

Note that $|\Psi(x, t)|^2 = |\psi(x)|^2$ is time-dependent.

Such **stationary states** have definite energy (the region of potential sampled by electron is constant).

The Schrödinger Equation is a linear equation, so Principle of Superposition holds.

Let $\Psi_n(x, t) = \psi_n(x) e^{-i \frac{E_n}{\hbar} t}$ be the infinite.

Set of Solutions Since superposition holds, the general solution is $\Psi(x, t) =$

$$\sum_{n=0}^{\infty} C_n f_n(x) e^{-i \frac{E_n}{\hbar} t}.$$

C_n : complex constraints

E_n : definite energies

Note: $|\Psi(x, t)|^2$ is time-dependent and does not have a definite energy.

Infinite Square Well Potential Solve Schrödinger Equation for Stationary States:

Outside Box: $V = \infty \rightarrow \psi(x) = 0$

Boundary:

$$1) \psi(0) = 0$$

$$2) \psi(L) = 0$$

Inside Box: $E\psi(x) = -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} (V = 0)$

Soln: $\psi(x) = A \sin \kappa x + B \cos \kappa x, \kappa = \frac{\sqrt{2mE}}{\hbar}$

Boundary conditions provide restrictions:

$$1) \psi(0) = 0 \Rightarrow B = 0 \Rightarrow \psi(x) = A \sin \kappa x$$

$$2) \psi(L) = A \sin \kappa L = 0 \Rightarrow \kappa = \frac{\pi}{L} \cdot n, n = 1, 2, 3, \dots \text{ (discrete values)}$$

Now, E, ω are related to κ :

$$\kappa = \frac{\sqrt{2mE}}{\hbar}, E = \frac{\hbar^2 \kappa^2}{2m} \text{ (Particle is "free" inside box.)}$$

$$E = \frac{\hbar^2 \pi^2}{2m} \frac{n^2}{L^2} n = 1, 2, 3, \dots$$

Energy levels are quantized.

Observations:

1) $\psi_1(x)$ is symmetric; $\psi_2(x)$ is antisymmetric.

2) E is quantized.

- 3) $\kappa \propto \frac{1}{L}$ ($E \propto \frac{1}{L^2}$) is consistent with uncertainty principle. (The increase in ground state energy is new).

Determine A by normalization:

(Recall that this is physics, not just math).

$$\int_{-\infty}^{\infty} dx \psi^*(x) \psi(x) = |A|^2 \int_0^L dx \sin^{-2}\left(\frac{\pi n}{L}x\right) = 1$$

Change variables: $y = \frac{\pi n}{L}x, dy = \frac{\pi n}{L}dx$

$$= |A|^2 \frac{L}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$

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

Properties of $\psi_n(x)$:

- 1) Orthogonal: $\int dx \psi_m^*(x) \psi_n(x) = 0$ for $m \neq n$
- 2) Complete: Any solution $F(x)$ that satisfies the boundary conditions can be written as:

$$F(x) = \sum_n C_n \psi_n(x)$$

If particle is in particular state $\psi_m, |\Psi(x, 1)|^2 = (\psi_m)^2$ is independent of time. The Ψ_m are stationary states.

If particle is in superposition $|\Psi(x, t)|^2$ is time dependent \rightarrow does not have definite E .

If we know $F(x)$, we can calculate C_n :

If we know $\Psi(x, 0)$ at $t = 0$, we can now calculate $\Psi(x, t)$ (evolution of system).

$$\text{General Solution: } \Psi(x, t) = \sum_n C_n \psi_n(x) e^{i\frac{E_n}{\hbar}t}$$

If we know initial state of system $\Psi(x, 0)$, then $\Psi(x, 0) = \sum_n C_n \psi_n(x), C_n =$

$$\int dx \psi_n^*(x) \Psi(x, 0).$$

Put C_n back into general solution.

Finite Square Well Potential Look for bound, stationary states.

(example: $E < V_0$ "trapped")

Apply boundary conditions:

- 1) $\psi(\pm\infty) = 0$ $\psi(x)$ must be normalizable
- 2) $\psi(x)$ continuous at $x = \pm\frac{L}{2}$
- 3) $\frac{d\psi(x)}{dx}$ continuous at $x = \pm\frac{L}{2}$ (finite K.E.); This is guaranteed by Schrödinger Equation for these boundary conditions.

Outside of the Well

$$(x < -\frac{L}{2}, x > \frac{L}{2}) \quad -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = (E - V_1) \psi \quad E < V_1 \quad \frac{\partial^2\psi}{\partial\lambda^2} = \frac{2m(V_1-E)}{\hbar^2} \psi$$

Left: $\psi^l(x) = Ae^{-\gamma\lambda} + Be^{\gamma x} = Be^{\gamma\lambda} \gamma = \frac{2m(V_1-E)}{\hbar}$

Right: $\psi^r(x) = Fe^{-\gamma\lambda} + Ge^{\gamma\lambda} = Fe^{-\gamma\lambda}$

$$1) \quad \psi(\pm\infty) = 0 \Rightarrow A = 0, G = 0$$

Inside the Well:

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

$$\psi(x) = C\sin\kappa x + D\cos\kappa x \quad \kappa = \sqrt{\frac{2mE}{\hbar}}$$

(There will be symmetric and antisymmetric states.)

Sketch Solutions:

There are only a finite number of bound states (Soln with $E < V_1$).

Consider symmetric states $\psi(x) \sim \cos(\kappa_n x)$.

Apply Boundary Conditions (at $\frac{L}{2}$).

$$2) \quad \text{Continuity: } D\cos\left(\frac{\kappa L}{2}\right) = Fe^{-\gamma\frac{L}{2}}$$

$$3) \quad \text{Continuity of Derivative: } \frac{d\psi}{dx}$$

$$-\kappa D\sin\left(\frac{\kappa L}{2}\right) = -\gamma Fe^{-\gamma\frac{L}{2}}$$

Divide (3) by (2) to get: $\kappa \tan\left(\frac{\kappa L}{2}\right) = \gamma$, where $\kappa = \sqrt{\frac{2mE}{\hbar}}$ and $\gamma = \sqrt{\frac{2m(V_1-E)}{\hbar}}$.

$$\kappa \tan\left(\frac{\kappa L}{2}\right) = \gamma$$

$$\sqrt{\frac{2mE}{\hbar}} \tan\left(\frac{L}{2} \sqrt{\frac{2mE}{\hbar}}\right) = \sqrt{\frac{2m(V_1-E)}{\hbar}}$$

$$\sqrt{E} \tan\left[\left(\frac{2m}{\hbar^2} E \frac{L^2}{\psi}\right)^{\frac{1}{2}}\right] = \sqrt{V_1 - E}$$

We can solve this graphically:

- There must be one bound state given $E < V_1$.
- The same approach can be applied to antisymmetric states.

In the limit of a deep well, $V_1 \rightarrow \infty$.

$$\tan\left[\left(\frac{2m}{\hbar^2} E^2 \frac{L^2}{\psi}\right)^{\frac{1}{2}}\right] \rightarrow \infty$$

$$\left(\frac{2m}{\hbar^2} E^2 \frac{L^2}{\psi}\right)^{\frac{1}{2}} = \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \dots$$

$$E = \frac{\pi^1 \hbar^2}{2mL^2} \frac{(2n+1)^2}{n^2} \quad n=0,1,2,\dots; \quad n=1,3,5,\dots \quad \text{just as for infinite potential well}$$

Scattering from a Potential Barrier Consider electron incident on a potential step:

$$1) \psi_1(x) = Ae^{i\kappa_1 x} + Be^{-i\kappa_1 x} \quad \kappa_1 = \sqrt{\frac{-2mE - V_1}{\hbar}} = \sqrt{\frac{2mE}{\hbar}}$$

$$2) \psi_2(x) = ce^{i\kappa_2 x} + De^{-i\kappa_2 x} \quad \kappa_2 = \sqrt{\frac{2m(E - V_2)}{\hbar}}$$

What is the probability that the electron can be found in regions (1) and (2), respectively?

Interpretation:

Wave with amplitude A is partially reflected ($B > 0$) and partially transmitted (C). $D = 0$

Boundary Conditions:

$$1) \psi_1 \Big|_{x=0} = \psi_2 \Big|_{x=0} \Rightarrow A + B + C$$

$$2) \frac{d\psi_1}{dx} \Big|_{x=0} = \frac{d\psi_2}{dx} \Big|_{x=0} \Rightarrow i\kappa_1(A - B) = i\kappa_2(C) \quad A - B = \frac{\kappa_2}{\kappa_1}C$$

$$\text{Add (1) and (2)} \Rightarrow 2A = C \left(1 + \frac{\kappa_2}{\kappa_1}\right) \left[\frac{C}{A} = \frac{2\kappa_1}{\kappa_1 + \kappa_2}\right]$$

$$1) A + B = C, \frac{B}{A} = \frac{C}{A} - 1$$

$$\frac{B}{A} = \frac{2\kappa_1}{\kappa_1 + \kappa_2} - 1 = \frac{\kappa_1 - \kappa_2}{\kappa_1 + \kappa_2}$$

Consider two cases:

a) $E > V_2$, so κ_2 is real.

- Oscillatory solution in Region 2

- $\left(\left|\frac{B}{A}\right| > 0\right)$ Partial reflection (does not occur classically)

Note: if we used wave packets instead of a single plane wave, reflected amplitudes would be different because the κ 's are different.

b) $E < V_2$, so κ_2 is imaginary,

- Solution decays exponentially in Region 2.

- $\left|\frac{C}{A}\right| > 0$ Finite probability of finding electron at $x > 0$

- "Tunneling" is a phenomenon that is classically "forbidden."

Homework: Consider narrow barrier.

$E < V_2$

$\kappa_1 = \kappa_3$, real

κ_2 is imaginary

There is a finite probability that the electron will tunnel into Region 3.

8 3-D Potentials

Time-independent Schrödinger Equation:

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

($\psi(\vec{r})$) are stationary states of definite energy.)

Consider particle in 3-D Box:

$V(x, y, z) = 0$ if $0 < x, y, z < L$; otherwise, it's equal to ∞ .

Inside: $-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\psi(\vec{r}) \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Solve by separation of variables:

$$\psi(\vec{r}) = \psi(x)\psi(y)\psi(z)$$

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

$$E\psi(x)\psi(y)\psi(z)$$

Divide both sides by $\psi(x)\psi(y)\psi(z)$.

$$1) \frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} = E_x\psi(x)$$

$$2) \frac{-\hbar^2}{2m}\frac{\partial^2\psi(y)}{\partial y^2} = E_y\psi(y)$$

$$3) \frac{-\hbar^2}{2m}\frac{\partial^2\psi(z)}{\partial z^2} = E_z\psi(z)$$

Note: $E_x + E_y + E_z = E$; These are the equations for the 1-D particle in a box.

From Lecture #4:

$$\psi_{n_x}(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n_x\pi}{L}x\right)E_{n_x} = n_x^2\frac{\pi^2\hbar^2}{2mL^2}$$

$\therefore \psi_{n_x n_y n_z}(\vec{r}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$ (reminder: "n" is a quantum #)

$$E_{n_x n_y n_z} = \frac{\pi^2\hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

The ground state energy $E_{111} = 3E_1$, where $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$

First excited states:

$$E_{211} = E_{121} = E_{112} = (2^2 + 1^2 + 1^2)E_1 = 6E_1$$

$E_{211} = E_{121} = E_{112}$ is a 3-fold "degeneracy" in energy .

Spherically Symmetric Potentials: $V(\vec{r}) = V(r), r = |\vec{r}|$

Spherical Coordinates: $x = r \sin \theta \cos \phi$

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$x^2 + y^2 + z^2 = r^2$$

$$d\vec{r} = r^2 \sin \theta dr d\theta d\phi$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\theta^2}$$

Solve Schrödinger Equation by separation of variables in spherical coordinates:

$$\psi(\vec{r}) = R(r) y(\theta, \phi)$$

$$\frac{-\hbar^2}{2m} \left[Y \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R + R \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y + R \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + VRY = ERY$$

Multiply by $\frac{r^2}{RY}$.

1) Radial Equation: $\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2m}{\hbar^2} r^2 (V - E) = \ell(\ell + 1)$ (We will solve this second.)

2) Angular Equation: (Multiply by $Y \sin^2 \theta$.)

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -\ell(\ell + 1) \sin^2 \theta Y$$

Solve by separation of variables:

Substitute: $Y(\theta, \phi) = H(\theta) \Phi(\phi)$

Divide by $H\Phi$.

3) $\frac{1}{H} \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial H}{\partial \theta} \right) + \ell(\ell + 1) \sin^2 \theta - m^2 = 0$

4) $\frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Rightarrow \Phi = e^{im\phi}$

In our coordinate system, $\phi \leftrightarrow \phi + 2\pi$, so $\Phi(\phi + 2\pi) = \Phi(\phi)$.

This implies that $m = 0, \pm 1, \pm 2; m$ is the Magnetic Quantum Number.

Now solve (3):

$$\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial H}{\partial \theta} \right) + [\ell(\ell + 1) \sin^2 \theta - m^2] H = 0$$

Soln: $H(\theta) = AP_\ell^m(\cos \theta)A$: Normalization Constant

$P_\ell^m(x)$ Associated Legendre Function

$$P_\ell^m(x) = (1 - x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_\ell(x)$$

$P_\ell(x)$ Legendre Polynomial (for integer ℓ)

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx} \right)^\ell (x^2 - 1)^\ell$$

$\ell = 0, 1, 2, \dots$ Azimuthal / Orbital Quantum Number

Rodrigues Formula $P_1^0 = \cos \theta$

$$P_1^1 = \sin \theta$$

$$P_2^1 = 3 \sin \theta \cos \theta$$

$$P_2^2 = 3 \sin^2 \theta$$

Magnetic Quantum Number: $|m| \leq \ell$

$$-\ell, -\ell + 1, \dots, 0, \ell - 1, \ell$$

Because $P_\ell(x)$ is a polynomial of degree ℓ , $P_\ell^m(x)$ is non-zero only for $|m| \leq \ell$.

Spherical Harmonics $Y_\ell^m(\theta, \phi) = AP_\ell^m(\cos\theta)e^{im\phi}A =$ Normalization Constant

They are normalized such that:

$$\int d\eta |Y_\ell^m|^2 = 1 \text{ where } \int d\eta = \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

E.g. $Y_1^0(\theta, \phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}$

$$Y_2^{-1}(\theta, \phi) = \frac{1}{2}\sqrt{\frac{15\sin\theta}{2\pi\cos\theta e^{-i\phi}}}$$

They are also orthogonal:

$$\int d\eta Y_\ell^{m*} Y_{\ell'}^{m'} = \delta_{\ell\ell'}\delta_{mm'} = 1 \text{ if } \ell = \ell' \text{ and } m = m'; \text{ otherwise, it is equal to } 0.$$

(On the unit sphere, any square integrable function can be expanded as a linear combination of spherical harmonics.)

Radial Equation:

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2mr^2}{\hbar^2} (V - E) R = \ell(\ell + 1) R$$

Let $v = rR$, where “ v ” is the radial wavefunction:

$$R = \frac{v}{r}, \frac{dR}{dr} = \frac{-v}{r^2} + \frac{1}{r} \frac{dv}{dr}$$

$$\frac{dv}{dr} \left(r^2 \frac{dR}{dr} \right) = \frac{d}{dr} \left(-v + r \frac{dv}{dr} \right)$$

$$\frac{dv}{dr} \left(r^2 \frac{dR}{dr} \right) = -\frac{dv}{dr} + \frac{dv}{dr} + r \frac{dv^2}{dr^2} = r \frac{d^2v}{dr^2}$$

We then have $r \frac{d^2v}{dr^2} - \frac{2mr}{\hbar^2} (V - E) v = \ell(\ell + 1) \frac{v}{r}$.

Multiply by $\frac{-\hbar^2}{2mr}$:

$$\frac{-\hbar^2}{2m} \frac{d^2v}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{1}{r^2} \ell(\ell + 1) \right] v = Ev$$

$\frac{\hbar^2}{2m} \frac{1}{r^2} \ell(\ell + 1)$ is the Centrifugal Term.

Same form as 1-D Schrödinger Equation, but with extra term that acts like a repulsive potential. (Relate to stability; radius of ψ .)

In summary, for any spherically symmetric potential, we have stationary states:

$$\Psi(r, t) = \psi(\vec{r}) e^{-iE\hbar/t}, \text{ where } \psi(\vec{r}) = R(r) Y_\ell^m(\theta, \phi)$$

θ, ϕ are spherical harmonics; $\ell = 0, 1, 2, \dots; |m| \leq \ell$

and $v = rR$, satisfying the Radial Equation

Normalization $\int d\vec{r} |\psi(\vec{r})|^2 = 1$
 $\int d\vec{r} |\psi(\vec{r})|^2 = \int_0^\infty dr r^2 \underbrace{|R|^2}_{|v|^2} \int d\eta |Y_\ell^m|^2$

$$\int d\eta |Y_\ell^m|^2 = 1$$

$$\therefore \int_0^\infty dr |v|^2 = 1, \text{ so } v \rightarrow 0 \text{ as } r \rightarrow \infty$$

9 The Hydrogen Atom

Task: Solve Radial Equation for $V(r) = \frac{-e^2}{4\pi\epsilon_0} \frac{1}{r}$.

Define $\kappa = \frac{\sqrt{2m(-E)}}{\hbar}$ for $E < 0$ (Bound State):

$$\frac{1}{\kappa^2} \frac{d^2 v}{dr^2} + \left[\frac{e^2}{4\pi E_0} \frac{2m}{\hbar^2 \kappa^2} \frac{1}{r} - \frac{1}{\kappa^2} \frac{\ell(\ell+1)}{r^2} \right] v = v$$

Define $p = \kappa r$ (Dimensionless)

$$\frac{d^2 v}{dp^2} + \left[\frac{e^2}{4\pi E_0} \frac{2m}{\hbar^2 \kappa} \frac{1}{p} - \frac{\ell(\ell+1)}{p^2} \right] v = v \frac{e^2}{4\pi E_0} \frac{2m}{\hbar^2 \kappa} = p_0$$

$$\frac{d^2 v}{dp^2} = \left(1 - \frac{p_0}{p} + \frac{\ell(\ell+1)}{p^2} \right) v$$

Considering asymptotic behavior of v , we find:

$$v(p) = p^{\ell+1} e^{-p} v(p)$$

Power Series solution gives:

$$V(p) = \sum_{j=0}^{\infty} a_j p^j \text{ AND } z(j \text{ max} + \ell + 1) - p_0 = 0 \text{ This second equation is from the}$$

Recursion Relation.

Impose $a_{j \text{ max} + 1} = 0$ so the series will terminate.

Define $n = j \text{ max} + \ell + 1$ as principle quantum number (int),

$$\text{then } p_0 = zn = \frac{e^2}{4\pi \epsilon_0} \frac{2m}{\hbar^2 \kappa} \text{ but } \kappa = \frac{\sqrt{2m(-E)}}{\hbar}$$

$$\text{Apparently, } \left[\left[E_n = - \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 \frac{m}{2\hbar^2} \cdot \frac{1}{n^2} = E_1 \cdot \frac{1}{n^2} \right] \right] E_1 = -13.61 \text{ eV} .$$

What values of the orbital quantum number ℓ are allowed for a given n ?

$$n = 1, j \text{ max} = 0 \rightarrow \ell = 0$$

$$n = 2, j \text{ max} = 0 \rightarrow \ell = 1$$

$$j \text{ max} = 1 \rightarrow \ell = 0$$

$$[[\ell \leq n - 1]] \kappa_n = \frac{\sqrt{2m(-E_n)}}{\hbar} = \frac{e^2}{4\pi \epsilon_0} \frac{m}{\hbar^2 n} = \frac{1}{an}$$

$$a \equiv \frac{4\pi \epsilon_0}{m e^2} \hbar^2 \text{ Bohr Radius}$$

$$a = 0.529 \text{ \AA}$$

Find Radial Wavefunctions Ground State: $n = 1 \rightarrow j \text{ max} = 0 \ell = 0$

$$a_0 = A a_1, a_2, a_3 \dots = 0$$

$$V(\ell) = A$$

$$\Rightarrow v(p) = A p e^{-1} (\ell = 0)$$

$$v(r) = \frac{A}{a} r e^{-r/a}, \text{ where } \kappa_n = \frac{1}{na} = \frac{1}{a} \text{ for } n = 1.$$

$$\text{Normalization: } \int_0^\infty |v(r)|^2 dr = \frac{|A|^2}{a^2} \int_0^\infty dr r^2 e^{-2r/a} = 1$$

$$\int_0^\infty |v(r)|^2 dr = 2 \cdot \frac{|A|^2}{a^2} \left(\frac{a}{2}\right)^3 = 1$$

$$\text{so } \frac{|A|}{a} = 2a^{-3/2}$$

$$\text{Note: } \int_0^\infty dr r^n e^{-2r/a} = n! \left(\frac{a}{2}\right)^{n+1}$$

$$R_{10}(r) = \frac{v(r)}{r} = 2a^{-2/3} e^{-r/a}$$

$${}_{n\ell m} \psi_{100}(r, \vec{\theta}, \phi) = R_{10}(r) Y_0^0(\theta, \phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

To generate other ${}_{n\ell m}$ Radial Wavefunctions, note that:

$$a_{j+1} = \frac{2(j+\ell-1-n)}{(j+1)(j+2\ell+2)} a_j$$

(In addition, the series must terminate, so we imposed: $a_{j_{\max}+1} = 0$ for $V(p) = \sum_{j=0}^{\infty} a_j p^j$).

Excited States where $\psi_{n\ell m} = R_{n\ell} Y_{\ell}^m$

$$\ell \leq n - 1 \quad |m| \leq \ell$$

$$E_2 = \frac{E_1}{(z)^2} = \frac{-13.6\text{eV}}{4} = -3.4\text{eV}$$

$$\text{For } \ell = 0 : R_{20}(r) = \frac{1}{\sqrt{2a^3}} \left(1 - \frac{r}{2a}\right) e^{-r/2a} \quad \# \text{ of radial nodes}$$

$$\text{For } \ell = 1 : R_{21}(r) = \frac{1}{2Ya^3} \frac{r}{a} e^{-r/2a} = n - \ell - 1$$

$$\psi_{200} = R_{20}(r) Y_0^0(\theta, \phi) = R_{20}(r) \cdot \frac{1}{\sqrt{4\pi}}$$

$$\psi_{210} = R_{21}(r) Y_1^0(\theta, \phi) = R_{21}(r) \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$\psi_{21\pm 1} = R_{21}(r) Y_1^{\pm 1}(\theta, \phi) = R_{21}(r) \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

$\ell = 0$: Spherically Symmetric Wavefunctions

$\ell = 1$: Not Spherically Symmetric

Look at Slice parallel to z axis.

The Schrödinger Equation in three-dimension:

Lecture 6: Slide Notes Questions to answer today:

- 1) What is the relationship between $R_{n\ell_1} Y_{\ell}^m$ and the probability density? (visualize)
- 2) What determines the energy levels and spectrum of the hydrogen atom?
- 3) What are the consequences of electron spin on atomic structure?

For Discussion:

- Radial Wavefunctions:
 - What are the right and left columns?
 - For $\ell = 0$, what is the trend with n ?
 - For given n , what is the trend with ℓ ?
- Spherical Harmonics:
 - What are the trends with ℓ, m ?
- Combined:
 - What are the trends in the number of nodes?
 - Why is $E_n \propto -\frac{1}{n^2}$

Hydrogen Spectrum When electron undergoes transition from excited state to lower energy state, energy can be conserved through emission of a photon with energy E_γ .

$$E_\gamma = E_i - E_f = - \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) E_r = \frac{nc}{X}$$

$$\Rightarrow \frac{1}{\lambda} = \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{4\pi\hbar^3 c} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{4\pi\hbar^3 c} \rightarrow \text{Rydberg Constant } 1.10 \times 10^7 m^{-1}$$

$n_f = 1 \rightarrow$ Lyman Series (UV)

$n_f = 2 \rightarrow$ Balmer Series (VIS)

$n_f = 3 \rightarrow$ Paschen Series (IR)

The states of the hydrogen atom can be specified by quantum numbers:

1) n : Principle Quantum # specifies the energy level $n = 1, 2, 3, \dots$

2) ℓ : Orbital Quantum # $\ell \leq n - 1$

3) m : Magnetic Quantum # $|m_\ell| \leq \ell$

4) m_s : Spin $m_s = \pm \frac{1}{2}$

From spectroscopy, we have the nomenclature:

$\ell = 0$ "s" shape

$\ell = 1$ "p" principal

$\ell = 2$ "d" diffuse

$\ell = 3$ "f" fundamental

$\ell = 4$ "g"

Physical Interpretation of ℓ, m_ℓ ℓ and m are related to the orbital angular momentum of the electron.

Classically,

$$L_x = yp_z - zp_y$$

$$L_y = zp_x - xp_z$$

$$L_z = xp_y - yp_x$$

We have previously defined quantum mechanical operators for p_x, p_y, p_z , so we can write:

$$L_x = \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad L_y = \frac{\hbar}{i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad L_z = \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

These operators do not commute, i.e.,

$$[L_x, L_y] = L_x L_y - L_y L_x \neq 0$$

They are incompatible observables - they cannot both be known with arbitrary certainty at the same time, just like x and p .

(In fact, $[x, p_x] \neq 0 \rightarrow \Delta x \Delta p = \frac{\hbar}{2}$)

It can be shown that both L_z and L^2 are compatible observables, with:

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

(See Griffiths.)

For our purposes, it will be sufficient to note that:

ℓ is a measure of $L^2 L^2 \psi = \hbar^2 \ell(\ell + 1) \psi$

m is a measure of $L_z L_z \psi = \hbar m \psi$

(The forms of these operators are given in Griffiths, p. 168 and 169.)

Spin

- **Intrinsic** angular momentum of point particle
- Purely quantum mechanical: quantum #'s s, m_s
- **Important** practically \rightarrow magnetism, optical transitions
- Profound consequences for structure of matter

Classically,

Spin can be composed into orbital momenta. This is not possible for point particles.

For electrons, protons and neutrons, $|spin| = \frac{1}{2}$.

For photons, $|spin| = 1$.

Classes of Identical Particles Suppose we represent two identical particles by the wave function $\psi(\vec{r}_1, \vec{r}_2)$:

Define:

- Bosons: $\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$ Symmetric Integer Spin
- Fermions: $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$ Antisymmetric Half-Integer Spin

Let's express $\psi(\vec{r}_1, \vec{r}_2)$ in terms of wave functions for two states a and b : $\psi_a(\vec{r}_1), \psi_b(\vec{r}_2)$.

Bosons: $\psi(\vec{r}_1, \vec{r}_2) = A [\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) + \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)]$

- Symmetric under exchange of \vec{r}_1 and \vec{r}_2
- If both particles are in state a , $\psi(\vec{r}_1, \vec{r}_2) = 2A \psi_a(\vec{r}_1) \psi_a(\vec{r}_2)$.
- Bosons can occupy the same state.

Fermions: $\psi(\vec{r}_1, \vec{r}_2) = A [\psi_a(\vec{r}_1) \psi_b(\vec{r}_2) - \psi_b(\vec{r}_1) \psi_a(\vec{r}_2)]$

- Antisymmetric under exchange of \vec{r}_1, \vec{r}_2
- Both particles **cannot** be in the same state: e.g. if both “in” a , then $\psi(\vec{r}_1, \vec{r}_2) = 0$.
- Pauli Exclusion Principle

The entire wave function must be antisymmetric with respect to exchange. This has implications for bonding (allowed configurations of electrons + energy of configurations).

We now have 4 quantum numbers to describe electron wavefunctions in spherically symmetric potentials:

Now, consider the rest of the Periodic Table, beginning with He.

Schrödinger Equation becomes:

For neutral atoms of atomic Z ,

$$H = \sum_{j=1}^Z \left[-\frac{\hbar^2}{2m} \nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0} \right) \frac{ze^2}{r_j} \right] + \frac{1}{2} \left(\frac{1}{4\pi\epsilon_0} \right) \sum_{j \neq \kappa}^Z \frac{e^2}{|\vec{r}_j - \vec{r}_\kappa|}$$

Note: This cannot be solved exactly for $Z > 1$! The $e^- - e^-$ repulsion term is the problem.

If we ignore this interpretation,

$$E_n = -13.6 \frac{Z^2}{n^2} = -54.4 eV \text{ for } n = 1$$

But the measured value is $-24.6 eV$

$\therefore e^- - e^-$ interaction is very important to electronic structure.

(If we were to ignore interactions) How many degenerate states would we have for each v ?

$$\ell \leq n - 1 \quad |m_\ell| \leq \ell m_s = \pm \frac{1}{2}$$

$2\ell + 1$ values of m_ℓ for each ℓ , 2 values of m_s

$$2 \times \sum_{\ell=0}^{n-1} (2\ell + 1) = 2n^2 \text{ (arithmetic series)}$$

Here, $m_s = 2$ and $2\ell + 1 = m_\ell$.

Recall that Pauli Exclusion forbids electrons for being in the same state.

n	#
1	2
2	8
3	18
4	32

This is not the same structure as the periodic table, however. $e^- - e^-$ interaction changes energies and influences state filling.

10 Bonding

- Basic Concepts: Mechanics of Bonding
- Bond Types: Qualitative Description
- Quantum Mechanical Description of Covalent Bond

Characteristics of a Bond:

- Negative Potential Energy
- Stable: **Energy is minimized** (E_0).
 - $F_{TOT} = F_R + F_A = 0$ at r_0
 - R refers to repulsive; A refers to attractive.
 - Alt: $F = -\frac{dE}{dr} \Big|_{r_0} = 0$ r_0 : bond length
- $E_0 = \int_{\infty}^{r_0} dr F_{TOT} = \int_{\infty}^{r_0} dr F_R(r) + \int_{\infty}^{r_0} dr F_A(r)$
 $E_0 = \int_{\infty}^{r_0} dr F_{TOT} = E_R + E_A$
- For example, E_R is the Coulomb Attraction and E_A is the Coulomb Repulsion.

Quantitatively...

Example Potential: $E(r) = \frac{A}{r^n} - \frac{B}{r^m} > m$

Bond Length r_0 typically $1.5 - 3 \text{ \AA}$

Bond Energy E_0 typically $0.1 - 10 \text{ eV}$

At finite T , $\langle r \rangle = r_0$

Influence on Mechanical Properties:

1) Elastic Modulus = $\frac{\text{Stress}}{\text{Strain}} \left(\frac{\Delta F}{\Delta x} \right)$

a) $\text{Elastic Modulus} \propto \frac{dF}{dr} \Big|_{r=r_0} \propto \frac{d^2 E}{dr^2} \Big|_{r=r_0}$ (Curvature of Potential)

2) Thermal Expansion:

- a) $\langle r \rangle$ increases with temperature:
- Smaller if bonds are strong (Deep Wells)
 - Depends on $\frac{d^3 E}{dr^3}$ (Anharmonic Terms)

3) Strong Bonds Increase T_m

Bond Types

1) Ionic

- Energy is minimized by electron transfer from electropositive to electronegative atom.
- Atoms bound by Coulomb Attraction:
 - E.g. $\text{Na}1s^22s^22p^63s^1 \rightarrow \text{Ne}$
 - E.g. $\text{Cl}1s^22s^22p^63s^23p^5 \rightarrow \text{Ar}$
 - $E(r) = \frac{A}{r^n} - \frac{e^2}{4\pi\epsilon_0 r}$ for 1 pair
 - Summing:
 - * $-6 \times \frac{e^2}{4\pi\epsilon_0 a} \quad a = r_0$
 - * $+12 \times \frac{e^2}{4\pi\epsilon_0 a\sqrt{2}}$
 - * etc.
 - Infinite Sum $\Rightarrow E(r) = \frac{A}{r^n} - \frac{Me^2}{4\pi\epsilon_0 r}$

Structure	Madelung Constant
CsCl	1.7627
NaCl	1.7476
Zincblende	1.6381

E_{typ} Few eV

2) Van Der Walls

Fluctuating dipole on one atom/molecule induces dipole on neighbor \Rightarrow Attraction.

e.g. liquid He, molecular crystals

Potential well described by Lennard-Jones Potential:

$$E(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

For a crystal, $E(r) = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r} \right)^{12} - A_6 \left(\frac{\sigma}{r} \right)^6 \right]$, where A_{12}, A_6 depend on crystal structure.

VDW bonds are weak: $\sim 0.01\text{eV}$.

3) Covalent Bonds

- Strong bonds arising from **shared** electrons
- Highly directional (unlike ionic, metallic)
- Less dense packing

Feynman's Coupled Mode Approach to Hydrogen Molecular Ion

a) $H\psi = i\hbar \frac{\partial \psi}{\partial t}$, where $H = -\frac{\hbar^2}{2m} \nabla^2 + V$

H = Hamiltonian Operator.

We attempt a general solution.

b) $\Psi(\vec{r}, t) = \sum_j w_j(t) \psi_j(\vec{r})$ $\psi_j(\vec{r})$: Stationary State

Q: How does probability of being in ψ_j vary with time?

A: According to w_j , substitute (b) into (a) to test solution:

$$\sum_j w_j H \psi_j = i\hbar \sum_j \psi_j \frac{dw_j}{dt}$$

Multiply both sides by ψ_k^* and integrate over all \vec{r} :

$$\sum_j w_j \int \psi_k^* H \psi_j d\vec{r} = i\hbar \sum_j \frac{dw_j}{dt} \int d\vec{r} \psi_k^* \psi_j = i\hbar \frac{dw_k}{dt}$$

$$\int d\vec{r} \psi_k^* \psi_j = \delta_{kj}$$

$$\text{Define } H_{kj} = \int d\vec{r} \psi_k^* H \psi_j.$$

$$\text{Then, } i\hbar \frac{dw_k}{dt} = \sum_j H_{kj} w_j$$

Consider for 2 Stationary States

a) **Example #1:** $1e^-$, $2p$ very far apart

$$i\hbar \frac{dw_1}{dt} = H_{11}w_1 + H_{12}w_2$$

$$i\hbar \frac{dw_2}{dt} = H_{21}w_1 + H_{22}w_2$$

b) For "Uncoupled" States, $H_{12} = H_{21} = 0$

$$\Rightarrow i\hbar \frac{dw_1}{dt} = H_{11}w_1, w_1(t) = \kappa_1 e^{-iH_{11}t/\hbar}$$

$$\text{Probability of being in } \psi_1 \propto |w_1(t)|^2 = |\kappa_1|^2 = \text{Constant}$$

(Physically, there is no chance of sharing electron between ψ_1, ψ_2)

If d is small, electron can tunnel ($H_{12} \neq 0$).

Associate tunneling with weak coupling - increases exponentially as d decreases

$$H_{12} = H_{21} = -A$$

$$\text{Assume: } H_{11} = H_{22} = E_0 \text{ and } H_{12} = H_{21} = -A$$

$-E_0$ is energy in absence of coupling

c) Attempt Solutions:

$$i\hbar \frac{dw_1}{dt} = E_0 w_1 - A w_2 w_1(t) = \kappa_1 e^{-iEt/\hbar}$$

$$i\hbar \frac{dw_2}{dt} = -A w_1 + E_0 w_2 w_2(t) = \kappa_2 e^{-iEt/\hbar}$$

$$\kappa_1 E = E_0 \kappa_1 - A \kappa_2 0 = (E_0 - E) \kappa_1 - A \kappa_2$$

$$\kappa_2 E = -A \kappa_1 + E_0 \kappa_2 0 = -A \kappa_1 + (E_0 - E) \kappa_2$$

	Attempt Solutions:
$i\hbar \frac{dw_1}{dt} = E_0 w_1 - A w_2$	$w_1(t) = \kappa_1 e^{-iEt/\hbar}$
$i\hbar \frac{dw_2}{dt} = -A w_1 + E_0 w_2$	$w_2(t) = \kappa_2 e^{-iEt/\hbar}$
$\kappa_1 E = E_0 \kappa_1 - A \kappa_2$	$0 = (E_0 - E) \kappa_1 - A \kappa_2$
$\kappa_2 E = -A \kappa_1 + E_0 \kappa_2$	$0 = -A \kappa_1 + (E_0 - E) \kappa_2$

A solution exists if and only if:

$$1) \begin{vmatrix} E_0 - E & -A \\ -A & E_0 - E \end{vmatrix} = 0$$

$$a) (E_0 - E)^2 = A^2 \rightarrow E = E_0 \pm A$$

Sharing \Rightarrow Energy Lowering \Rightarrow Bonding

The Hydrogen Molecule Let $\psi(\vec{r}_1, \vec{r}_2)$.

Describe $2e^-, 2p$.

For identical fermions, we must have $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$.

Consider spatially antisymmetric ψ (parallel spins).

Zero probability of electron being between protons.

\rightarrow Large repulsion

But if e^- spins are antiparallel, spatial wavefunction must be symmetric for $\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$.

Probability of finding e^- between protons **lowers** the energy.

Spins	Total Spin	Spatial Symmetry	Energy	Name
Anti-parallel	$\frac{1}{2} + (-\frac{1}{2}) = 0$ $m_s = 0$	Symmetric	Lower; "Bonding"	Singlet, $s = 0$
	$(\frac{1}{2}, -\frac{1}{2}) - (-\frac{1}{2}, \frac{1}{2})$	Symmetric	Lower; "Bonding"	Singlet, $s = 0$
Parallel	$m = 1; \frac{1}{2} + \frac{1}{2} = 1$	Antisymmetric	Higher; "Anti-Bonding"	Triplet, $s = 1$
	$m = 0; (\frac{1}{2}, -\frac{1}{2}) + (-\frac{1}{2}, \frac{1}{2}) = 1$	Antisymmetric	Higher; "Anti-Bonding"	Triplet, $s = 1$
	$m = 0; \frac{1}{2} + (-\frac{1}{2}) = 0$	Antisymmetric	Higher; "Anti-Bonding"	Triplet, $s = 1$
	$m = -1; -\frac{1}{2} + (-\frac{1}{2}) = -1$	Antisymmetric	Higher; "Anti-Bonding"	Triplet, $s = 1$

2) Metallic Bonding

- Valence electrons delocalized throughout lattice.
- Electrons are like free electrons (**Free Electron Theory of Metals**).

Consequences

- 1) High electrical conductivity
- 2) High thermal conductivity
- 3) High ductility & malleability

11 Supplement

The distribution of particles in allowed states is given by **the density of states times (x) probability of occupation.**

States	
Distinguishable Particles	$N_n = d_n e^{-(\alpha t \beta E_n)} = d_n F_0(E)$
Fermions	$N_n = \frac{d_n}{e^{\alpha + \beta E_n} + 1} = d_n F_{FD}(E)$
Bosons	$N_n = \frac{d_n}{e^{\alpha + \beta E_n} - 1} = d_n F_{\beta D}(E)$

Define $\beta \equiv \frac{1}{\kappa T} \alpha \equiv -M \cdot \beta$

N_n : Most probable occupation number (number within energy window dE)

d_n : Degeneracy of energy level \rightarrow Density of states $\frac{dN}{dE}, \frac{dN}{d\kappa}$

In calculations of total particle number, total energy, and quantities that depend on them, we replace discrete sums with integrals.

$$N = \sum_{n=1}^{\infty} N_n \rightarrow \int dE \frac{dn}{dE} F(E) = \int dE z(E) F(E) \text{ OR}$$

$$N = \sum_{n=1}^{\infty} N_n \rightarrow \int d\kappa \frac{dn}{d\kappa} F(\kappa) = \int dk z(\kappa) F(\kappa)$$

$z(E)$ and $z(\kappa)$ refer to the density of states.

We next learn how to calculate the density of states for electrons and phonons (and photons).

12 Modeling Metals

(S+W 6.1-6.3) (Griffiths 5.3)

Assume particles experience no forces except at impenetrable walls (non-interacting).

- $V(x, y, z) = 0, 0 < x, y, z < L$
- $V(x, y, z) = \infty$ otherwise

Solving the 3-D Schrödinger Equation, the allowed energies of the stationary states are:

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) \quad n = 1, 2, 3 \dots$$

$$E_{n_x n_y n_z} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}, \text{ where } k_{x,y,z} = \frac{\pi}{L} n_{x,y,z}.$$

13 Free Electron Gas

k values associated with these states look like a grid of points in a plot of k_x, k_y, k_z

- Each point represents a stationary state
- Each state/ cube takes up volume in k -space: $\left(\frac{\pi}{L}\right)^3 = \frac{\pi^3}{V}$
- At $T = 0$, all Bosons or classical particles would be in lowest energy state: ψ_{111}
- Electrons, being Fermions, obey the Pauli Exclusion Principle:
 \rightarrow Only 2 per state ($M_s \pm 1/2$).

N electrons fill up one octant of sphere of radius k_f :

$$\frac{1}{8} \left(\frac{4}{3} \pi k_F^3 \right) = \frac{N}{2} \left(\frac{\pi^3}{V} \right) \Rightarrow k_F = \left(3\pi^2 \frac{N}{V} \right)^{1/3}$$

At $T = 0$, all states inside this **Fermi surface** are occupied, while all outside are empty

Energy of highest occupied state

$$\text{Fermi Energy, } E_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}$$

Density of States - number of states at a specific energy

- Between E and $E+dE$

First find number N of states between k and $k + dk$

- In k -space, a shell of thickness dk contains volume $\frac{1}{8} (4\pi k^2) dk$.

- $dN = \frac{\frac{1}{8}(4\pi k^2)dk}{\frac{\pi}{V} \frac{1}{2}} = \frac{V}{\pi^2} k^2 dk$

- $\frac{dN}{dk} = \frac{V}{\pi^2} k^2$

Write in terms of energy:

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m} dk$$

$$\frac{dN}{dk} = \frac{V}{\pi^2} k^2 \text{ note: } \frac{dE}{dk} = \frac{\hbar^2}{m} k \left(E = \frac{\hbar^2}{2m} k^2 \right)$$

$$\frac{dN}{dE} = \frac{V}{\pi^2} k \frac{m}{\hbar^2} = \frac{V}{\pi^2} \sqrt{\frac{2mE}{\hbar^2}} \frac{m}{\hbar^2} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

$$\therefore g(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

At non-zero temperature: thermal excitations move some electrons to states at energies above E_F .

Described by the **Fermi-Dirac distribution function**:

$$f(E) = \frac{1}{e^{(E-\mu)/kT} + 1}$$

We first consider the simple case of $T = 0$

$$f(E) = 1, E < \nu(o)$$

$$f(E) = 0, E > \nu(o)$$

$$\nu(o) = E_f$$

$$E_{Tot} = \int_0^\infty E g(E) f(E) dE$$

$$E_{Tot} = \int_0^{E_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{1/2} E^{3/2} dE = \frac{V}{5\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{5/2}$$

$$N = \int_0^\infty g(E) f(E) dE = \int_0^{E_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E_F^{3/2}$$

Since $\langle E \rangle = \frac{E_{Tot}}{N}$, dividing the two expression above yields:

$$\langle E \rangle = \frac{3}{5} E_F$$

$$E_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} = \frac{\hbar^2}{2m} \kappa_F^2$$

Alternatively, $E_{TOT} = \frac{\hbar^2 \kappa_F^5}{10\pi^2 m} \cdot V$ (as one could also find by integrating $d\omega/d\kappa$)

What is the average energy per electron?

$$k_F = 3\pi^2 \frac{N}{V}$$

For classical particles, $\langle E \rangle = 0$ circa $T = 0, P = 0$ also:

$$\text{Here } P = -\frac{dE_{Tot}}{dV} = -\frac{d}{dV} \left[\frac{3}{5} N \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3} \right] = (3\pi^2)^{2/3} \frac{\hbar^2}{5m} \left(\frac{N}{V} \right)^{5/3}$$

(A positive change in volume decreases the energy.)

$$\text{Therefore, } P = (3\pi^2)^{2/3} \frac{\hbar^2}{5m} \left(\frac{N}{V} \right)^{5/3}$$

The pressure is non-zero even at $T = 0$ due to the Pauli Exclusion Principle.

$$B = -V \frac{\partial P}{\partial V}$$

$$B = -V \frac{\partial P}{\partial V} = -V \frac{\partial}{\partial V} \left[(3\pi^2)^{2/3} \frac{\hbar^2}{5m} \left(\frac{N}{V} \right)^{5/3} \right] = (3\pi^2)^{2/3} \frac{\hbar^2}{3m} \left(\frac{N}{V} \right)^{5/3} = \frac{2}{3} \frac{N}{V} E_F$$

What is the specific heat?

$$C_V = \frac{d}{dT} \langle E \rangle = \frac{1}{N} \frac{d}{dT} \int_0^\infty dE E \cdot z(E) F(E)$$

This integral is difficult to evaluate for $T > 0$ (See A+M Chapter 2 for Sommerfeld Expansion to get this.)

$$C_V = \frac{\pi^2}{2} \frac{\kappa_B^2 T}{E_F}$$

We can estimate the electronic contribution to specific heat by considering how many electrons will be affected by thermal excitations.

Electrons within $\sim \kappa_B T$ below E_F will be excited to states within $\sim \kappa_B T$ above E_F .

$$N \simeq \left. \frac{dN}{dE} \right|_{E=E_F} \times \kappa_B T = z(E_F) \kappa_B T$$

The additional energy stored in electronic degrees of freedom is $N \times \kappa_B T$ or $\Delta E_{TOT} \simeq z(E_F) \cdot (\kappa_B T)^2$

$$\therefore C_V = \frac{d\langle E \rangle}{dT} \simeq \frac{2z(E_F)}{N} \kappa_B^2 T$$

Note: Show $z(E_F) = \frac{3}{2} \frac{N}{E_F}$.

So $C_V \simeq \frac{3\kappa_B^2 T}{E_F}$, which is close to $\frac{\pi^2}{2} \frac{\kappa_B^2 T}{E_F}$.

For a classical "ideal" gas, $C_V = \frac{3}{2} \kappa_B$.

Electrons make a negligible contribution to C_V at 300K because $\kappa_B T \ll E_F$ (little excitation to higher states)

Experimentally, $C_V = \gamma T + AT^3$.

For a metal:

- Low Temperatures: Linear Dependence
- High Temperatures: Cubic Dependence

Low temperature specific heat is consistent with expectations of free electron model:

$$C_V = \left(\frac{\pi^2}{2} \frac{\kappa_B^2}{E_F} \right) T$$

This model fails at higher temperatures, where lattice vibrations, or phonons, become more important.

Next Steps: Apply quantum statistical mechanics to phonons.

14 Phonons: Quantized Lattice Vibrations / Elastic Waves

- 1) Transverse: Displacement perpendicular to direction of propagation (like light)
- 2) Longitudinal: Displacement parallel to direction of propagation

We will describe two models for the phonon density of states and calculate N , E_{TOT} , and C_v .

Einstein Model: Assume N atoms of lattice oscillate with frequency ω_0 .

$z(\omega) = \frac{dn}{d\omega} = 3 \times N \delta(\omega - \omega_0)$; 3 refers to "3 polarizations"

$E = \hbar\omega$, as with photons

Also, as phonons are bosons for which N is not conserved, $\alpha = 0$, and

$$N_\omega = \frac{dN}{e^{\hbar\omega/\kappa_B T} - 1} \text{ or } F(\omega) = \frac{1}{e^{\hbar\omega/\kappa_B T} - 1}$$

$$E_{TOT} = \int_0^\infty d\omega z(\omega) F(\omega) \cdot E(\omega)$$

$$E_{TOT} = \int_0^\infty d\omega \frac{3N\delta(\omega - \omega_0) \cdot \hbar\omega}{e^{\hbar\omega/\kappa_B T} - 1} = \frac{3N\hbar\omega_0}{e^{\hbar\omega_0/\kappa_B T} - 1}$$

$$C_v = \frac{d}{dT} \langle E \rangle = 3\hbar\omega_0 \frac{(-1)}{(e^{\hbar\omega_0/\kappa_B T} - 1)^2} \left(-\frac{\hbar\omega_0}{\kappa_B T^2}\right) e^{\hbar\omega_0/\kappa_B T}$$

$$C_v = 3\kappa_B \left(\frac{\hbar\omega_0}{\kappa_B T}\right)^2 \frac{e^{\hbar\omega_0/\kappa_B T}}{(e^{\hbar\omega_0/\kappa_B T} - 1)^2}$$

Rewrite with $\theta_E = \frac{\hbar\omega_0}{\kappa_B}$, so

$$C_v = 3\kappa_B \left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2}$$

At high temperatures,

$$C_v \simeq 3\kappa_B \left(\frac{\theta_E}{T}\right)^2 \cdot \frac{1}{[1 + \frac{\theta_E}{T} - 1]^2} \simeq 3\kappa_B$$

This is in agreement with high temperature data, but this does not give $C_v \propto T^3$.

Debye Model:

$$\frac{dn}{d\kappa} = \frac{3 \times \frac{1}{8} 4\pi\kappa^2}{\pi^3/v} = \frac{3}{2} \frac{V}{\pi^2} \kappa^2$$

Assume: $\kappa = \frac{\omega}{v}$ and $d\kappa = \frac{d\omega}{v}$

$\frac{dn}{d\omega} = \frac{3}{2} \frac{V}{\pi^2} \frac{\omega^2}{v^3}$, where v is the speed of sound.

Assume: There are a finite number of modes $3N$, as there are N oscillators.

How many modes are there?

$$3N = \int_0^{\omega_D} \frac{3V\omega^2}{2\pi^2 v^3} d\omega = \frac{V\omega_D^3}{2\pi^2 v^3} \Rightarrow \frac{\omega_D}{v} = \left(6\pi^2 \frac{N}{V}\right)^{1/3}$$

Where ω_D is a cut-off frequency:

$$E_{TOT} = \int_0^{\omega_D} d\omega \frac{3V}{2\pi^2} \frac{\omega^2}{v^3} \cdot \frac{1}{e^{\hbar\omega/\kappa T} - 1} \cdot \hbar\omega$$

$$z(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{v^3}$$

$$F(\omega) = \frac{1}{e^{\hbar\omega/\kappa T} - 1}$$

$$E = \hbar\omega$$

$$C_v = \frac{d\langle E \rangle}{dT} = \frac{1}{N} \frac{3V}{2\pi^2} \frac{\hbar}{v^3} \int_0^{\omega_D} d\omega \omega^3 \frac{(-1)}{(e^{\hbar\omega/\kappa T} - 1)^2} \left(\frac{-\hbar\omega}{\kappa_B T^2} \right) e^{\hbar\omega/\kappa T}$$

$$C_v = \frac{V}{N} \frac{3}{2\pi^2} \frac{\hbar^2}{v^3 \kappa T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/\kappa T}}{(e^{\hbar\omega/\kappa T} - 1)^2}$$

$$\text{Let } x = \frac{\hbar\omega}{\kappa_B T}, \omega = \frac{\kappa T}{\hbar} x, d\omega = \frac{\kappa T}{\hbar} dx, x_D = \frac{\hbar\omega_D}{\kappa_B T} = \frac{\theta_D}{T}$$

θ_D is the Debye Temperature.

$$\theta_D = \frac{\hbar\omega_D}{\kappa_B} = \frac{\hbar v}{\kappa_B} (6\pi^2 \frac{N}{V})^{1/3}$$

$$C_v = 9\kappa_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

For $T \gg \theta_D, x \rightarrow 0$, and $C_v \rightarrow 3\kappa_B$ Classical Result

(See figures.)

For $T \ll \theta_D, x_D \rightarrow \infty$

$$C_v = 9\kappa_B \left(\frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = 4\pi^4/15$$

$$C_v = \frac{12\pi^4}{h} \kappa_B \left(\frac{T}{\theta_D} \right)^3$$

\Rightarrow Debye Model gives $C_v \propto T^3$ at low T

Phonons (quantized lattice vibrations) act like waves with momentum $p = \hbar\kappa$ (crystal momentum).

We will need to consider energy and momentum conservation in interactions with other particles.

Modifications to the Free Electron Theory of Metals

- 1) **Work Function:** finite potential barrier to electron escape (recall the photoelectric effect)

Note: this doesn't affect the energy levels much.

- 2) **Thermionic Emission:** Thermal energy can also induce electron emission (high temps).

$$\text{From Free Electron Theory, } E = \frac{1}{2m} (Px^2 + Py^2 + Pz^2)$$

Assume surface normal parallel to x ,

electrons would be emitted classically if: $\frac{Px^2}{2m} > E_f + \phi$.

Quantum mechanics: finite probability of reflection from potential step

Flux: $\frac{p_x}{m} \frac{N(p_x)}{V} dp_x$ is the number/area arriving at surface with momentum between P_x and $P_x + dP_x$.

Emission Current Density:

$$J = \int_{\sqrt{2m(E_f + \phi)}}^{\infty} [1 - R(p_x)] \frac{p_x}{m} \frac{eN(p_x)}{V} dp_x$$

$p_x > \sqrt{2m(E_f + \phi)}$ is the minimum P_x needed to get past step.

$$N(p_x, p_y, p_z) dp_x dp_y dp_z = V \left(\frac{2}{h}\right)^3 \exp\left[\frac{E_F - (p_x^2 + p_y^2 + p_z^2)/2m}{k_B T}\right] dp_x dp_y dp_z$$

$$N(p_x) dp_x = V \left(\frac{2}{h}\right)^3 \exp\left[\frac{E_F - (p_x^2/2m)}{k_B T}\right] dp_x \times \int_0^{\infty} \exp\left[\frac{-p_y^2}{2mk_B T}\right] dp_y \int_0^{\infty} \exp\left[\frac{-p_z^2}{2mk_B T}\right] dp_z$$

$$N(p_x) dp_x = V \left(\frac{4\pi m k_B T}{h^3}\right) \exp\left[\frac{E_F - (p_x^2/2m)}{k_B T}\right] dp_x$$

$$J = \left(\frac{4\pi m e k_B T}{h^3}\right) [1 - R] \exp\left[\frac{E_F}{k_B T}\right] \int_{\sqrt{2m(E_f + \phi)}}^{\infty} p_x \exp\left[\frac{-p_x^2}{2mk_B T}\right] dp_x$$

We use the following to solve:

1) Free Electron Theory: $p_x = \frac{h}{2L} N_x$

a) $R(P_x) = \text{constant}$ (approximately)

b) Maxwell-Boltzmann Tail of Fermi-Dirac Distribution matters most:

$$J = A_0 (1 - R) T^2 e^{-\phi/k_B T}, A_0 = \frac{4\pi e m k_B^2}{h^3}$$

Current depends exponentially on ϕ, T .

2) **Schottky Effect:** Thermionic Emission modified by the image force and the electric field.

a) Image force modifies the potential.

b) Voltage is often applied.

\therefore The new barrier height is given by maximum of $V(x) = V_1 + V_2$

$$J = A (1 - R) T^2 e^{-\phi_{eff}/\kappa_B T} = A_0 (1 - R) T^2 \exp\left[-\left(\phi - e\sqrt{\frac{e\varepsilon}{4\pi\varepsilon_0}}\right)/\kappa_B T\right]$$

This indicates that $\ln(J) \propto \sqrt{\varepsilon}$

- 3) **Field Emission:** At high fields, lower/more narrow barrier leads to significant tunneling.

If we assume a rectangular barrier, then:

$$T = \frac{1}{1 + \frac{V_0^2 \sinh^2 2K_2 a}{4E(V_0 - E)}}$$

$$K_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

$$T \propto \exp\left(-\frac{4a\sqrt{2m(V_0 - E)}}{\hbar}\right)$$

$$T \propto \exp\left(-\frac{2\phi\sqrt{2m\phi_{eff}}}{\hbar e \varepsilon}\right)$$

$$J \sim \exp\left(-\frac{\sqrt{2m\phi_{eff}}}{\hbar} x f\right)$$

$$J \sim \exp\left[-\frac{\sqrt{2m\phi_{eff}}}{e\hbar} \frac{\phi}{\varepsilon}\right]$$

Tunneling increases exponentially with field ε , relatively insensitive to temperature.

All of these processes are important in electronic devices.

15 Band Theory of Solids

15.1 Approach:

- Build qualitative picture of electrons scattering from periodic bumps in potential.
- Introduce Bloch Waves as appropriate solution to Schrödinger Equation in periodic potential.
- Use Kronig-Penney Model to develop band structure.
- Return to coupled modes description to connect with atomic picture.

15.2 Ziman Model:

Free electron waves scatter from dips/ bumps in the potential associated with ions:

$$\psi_R \sim e^{ikx} \psi_L \sim e^{-ikx} \psi_{\pm} = \frac{1}{\sqrt{2}} (\psi_R \pm \psi_L)$$

These two combinations produce standing waves:

- $\psi_+ \propto e^{ikx} + e^{-ikx} \sim \cos kx$
- $\psi_- \propto e^{ikx} - e^{-ikx} \sim \sin kx$

Consider λ_{e-} such that $n\lambda = 2a$ (strong interference):

$$n \frac{2\pi}{k} = 2a \Rightarrow k = n \cdot \pi/a$$

Then $\psi_+^* \psi_+ \propto \cos^2\left(\frac{\pi}{a}x\right) \rightarrow$ For $n = 1$, max e ions, low energy

$\psi_-^* \psi_- \propto \sin^2\left(\frac{\pi}{a}x\right) \rightarrow$ minimum e ions, higher energy

For free electrons, $E = \frac{\hbar^2 k^2}{2m}$

Here we have $E = \frac{\hbar^2 k^2}{2m} \pm V_0 \leftarrow$ Due to ion potentials and scattering when $k \sim \pm n\pi/a$

Strong scattering modifies free electron: E vs. k

To make this picture more quantitative, we introduce:

- Correct ψ : Bloch Theorem
- Model $V(x)$: Kronig-Penney Model

15.3 What is the actual ψ ?

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

Bloch proposed that $\psi(x) = u_k(x) e^{ikx}$ where $u(x) = u(x+a)$.

(Actually, in 3-D, $\vec{r} \rightarrow \vec{r} + \vec{a}$).

This is a “Bloch” wave containing:

- Local, atomic character, $u(x)$
- Plane wave modification e^{ikx} , free electron character (reasonable, also deep)

15.4 “Proof in 1-D”:

Model infinite array of atoms by a ring with spacing a and N total atoms, i.e.,

$V(x) = V(x+na)$ where n is an integer

$\psi(x+a) = c\psi(x)$ for periodic system where $c = e^{i\alpha}$ (complex constant)

$\psi(x+a) = e^{i\kappa a}\psi(x)$ (suppose)

$\psi(x+Na) = e^{iN\kappa a}\psi(x) = \psi(x)$

$\Rightarrow e^{iN\kappa a} = 1$, or $N\kappa a = 2\pi n$

So $\kappa = \frac{2\pi}{Na} \cdot n$, where $n = 0, \pm 1, \pm 2 \dots$

Quantized values of κ arise from (periodic) boundary conditions, $\kappa \leftrightarrow$ wavenumber,

so $\psi(x) = u_\kappa(x) e^{i\frac{2\pi}{Na}nx}$ and $u_\kappa(x) = u_\kappa(x+a)$

This 1-D Bloch Wavefunction meets conditions established by potential.

15.5 Kronig-Penney Model:

Inside Wells:

$$\frac{d^2\psi}{dx^2} = -\alpha^2\psi$$

$$\alpha = \frac{\sqrt{2mE}}{\hbar}$$

Outside Wells:

$$\frac{d^2\psi}{dx^2} = \beta^2\psi$$

$$\beta = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

Impose Bloch Condition on ψ :

$$\psi(a < x < a + b) = \psi(-b < x < 0) e^{ik(a+b)}$$

We also require the usual continuity of $\psi, \frac{d\psi}{dx}$.

These conditions lead to the following equation:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a + b)$$

To simplify, we let $b \rightarrow 0$, while $V_0 \rightarrow \infty$ (δ -function barriers) with

$$P = \lim_{b \rightarrow 0; V_0 \rightarrow \infty} \left(\frac{mba}{\hbar^2} V_0 \right)$$

as a measure of the barrier (or scattering strength)

$$\Rightarrow P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

Note that $|\cos ka| \leq 1$.

For what values of α (and $E = \frac{\hbar^2 \alpha^2}{2m}$) is $-1 < LHS < 1$?

1) Plot $P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$ versus αa .

2) Solutions exist when the function is between -1 and 1 (first figure).

3) Plot $E = \frac{\hbar^2}{2m} \alpha^2$ versus ka . (There will be two values of αa that give the same ka .)

(Go to figures.)

15.6 Reduced Zone Scheme:

- Lattice is periodic $\rightarrow k$ -space is periodic
- E versus k diagram can be reduced to 1st Brillouin Zone from $k = 0$ to π/a .
- $k \pm 2\pi/a \leftrightarrow k$

15.7 More Generally:

- E versus \vec{k} : Dispersion depends on direction in the crystal.
- Potential is more complex, especially for compounds.

15.8 Feynman Model:

Interactions between atoms lead to energy level splittings:

- 2 atoms: 2 degenerate levels \Rightarrow bonding/ anti-bonding states, 2 levels
- N atoms: N energy levels (per original level)

(See Figure).

15.8.1 Consider 1-D Array:

Assume only nearest neighbor coupling:

$$i\hbar \frac{dw_j}{dt} = E_1 w_j - A w_{j-1} - A w_{j+1}$$

$$i\hbar \frac{dw_j}{dt} = E_1 w(x_j) - A w(x_{j-1}) - A w(x_{j+1})$$

$$i\hbar \frac{dw_j}{dt} = E_1 w(x_j) - A w(x_j - a) - A w(x_j + a)$$

A : coupling coefficient

E_1 : energy in absense of coupling

As before, attempt solution of the form: $w_j = \kappa_j e^{-iEt/\hbar}$

$$E\kappa_j = E_1 \kappa_j - A(\kappa_{j-1} + \kappa_{j+1})$$

Assume that κ is a function of x , since

$$E\kappa(x_j) = E_1 \kappa(x_j) - A[\kappa(x_j + a) + \kappa(x_j - a)]$$

Try solution of the form $\kappa(x_j) = e^{ikx_j}$

$$E e^{ikx_j} = E_1 e^{ikx_j} - A[e^{ik(x_j - a)} + e^{ik(x_j + a)}]$$

Divide both sides by e^{ikx_j} to get:

$$E = E_1 - A[e^{ika} + e^{-ika}] = E_1 - 2A \cos ka$$

$$E = E_1 - 2A \cos ka$$

This is an allowed energy band.

Larger $A \rightarrow$ Wider Band

Similarly, we expect $E = E_2 - 2B \cos ka$

The generation and analysis of E vs. k is rather straightforward. (Physical Interpretation)

15.8.2 In 3-D:

$$i\hbar \frac{dw(x,y,z,t)}{dt} = E_1 w(x_j, y_l, z_m)$$

$$-A_x [w(x_j - a, y_l, z_m) + w(x_j + a, y_l, z_m)]$$

$$-A_y [w(x_j, y_l - b, z_m) + w(x_j, y_l + b, z_m)]$$

$$-A_z [w(x_j, y_l, z_m - c) + w(x_j, y_l, z_m + c)]$$

Try $w(x, y, z, t) = e^{-iEt/\hbar} \exp[i(k_x x + k_y y + k_z z)]$

$$E = E_1 - 2A_x \cos k_x a - 2A_y \cos k_y b - 2A_z \cos k_z c$$

$$E_{\min} = E_1 - 2(A_x + A_y + A_z)$$

$$E_{\max} = E_1 + 2(A_x + A_y + A_z)$$

16 Implications of Band Theory

- Periodic potential modifies parabolic E vs. k .

Diagram of Free Electron

- Consider motion analogous to that of free electron.

Classically, in electric field, $F = e\varepsilon = ma = m \frac{dv}{dt}$.

In an E field, $e\varepsilon = m \frac{dv}{dt}$

Quantum mechanically, we consider electron as wave packet with $v_g = \frac{\partial \omega}{\partial k} = \frac{1}{\hbar} \frac{\partial E}{\partial k}$ as $E = \hbar \omega$.

In a semi-classical picture, then:

$$e\varepsilon = m \frac{dv_g}{dt}$$

But what is $\frac{dv_g}{dt}$?

$$\frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d}{dt} \frac{\partial E}{\partial k} = \frac{1}{\hbar} \frac{\partial^2 E}{\partial k^2} \frac{dk}{dt}$$

$$\text{But } \frac{dk}{dt} = \frac{1}{\hbar} \frac{dp}{dt} = \frac{1}{\hbar} e\varepsilon \left(F = \frac{dp}{dt} \right)$$

(Alternatively, $dE = F dx$ and $dE = F v_g dt$.)

$$\text{So } \frac{dv_g}{dt} = \frac{1}{\hbar^2} \cdot \frac{\partial^2 E}{\partial k^2} e\varepsilon$$

$$\text{Rewriting, } e\varepsilon = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1} \frac{dv_g}{dt}$$

But we stated that $e\varepsilon = m \frac{dv_g}{dt}$, implying that electron moves as if it had a mass $\hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$.

$$\text{Define effective mass: } m^* = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$$

$$\text{Check for free electron: } E = \frac{\hbar^2}{2m} k^2$$

$$\frac{\partial E}{\partial k} = \frac{\hbar^2}{m} k, \quad \frac{\partial^2 E}{\partial k^2} = \frac{\hbar^2}{m} \Rightarrow m = \hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1}$$

How does this result compare with the Free Electron Model?

To provide a qualitative answer, consider the Feynman Model:

$$E = E_1 - 2A \cos ka$$

$$\frac{\partial E}{\partial k} = 2Aa \sin ka$$

$$\frac{\partial^2 E}{\partial k^2} = 2Aa^2 \cos ka$$

$$v_g = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \frac{2Aa}{\hbar} \sin ka$$

$$m^* = \frac{\hbar^2}{2Aa^2} \sec ka$$

Notes:

- m^* depends on k
- Negative around top of band where $k = \pi/a$
- At $k = 0, m^* \propto \frac{1}{A}$
- More overlap \rightarrow Wider bands, smaller m^*

Current Flow for Electrons in a Crystal: Free Electrons:

$$I = e \cdot \frac{N}{L} \cdot v_g$$

$$\frac{dI}{dt} = e \frac{dv_g}{dt} \frac{N}{L} = \frac{e^2 \epsilon}{m} \frac{N}{L}$$

Not all electrons in crystal can be accelerated.

$$N = \int_0^\infty f(E) g(E) dE = \int_{-\infty}^\infty f(k) g(k) dk$$

From homework, $g(k) = \frac{2L}{\pi}$, for particle in box, so for QM electrons:

$$\frac{dI}{dt} = \frac{e}{L} \int_{-\infty}^\infty \frac{dv_g(k)}{dt} f(k) g(k) dk$$

$$\frac{dI}{dt} = \frac{e}{L} \frac{e\epsilon}{\hbar^2} \int_{-\infty}^\infty \frac{d^2 E}{dk^2} f(k) \frac{L}{\pi} dk$$

$$\frac{dI}{dt} = \frac{2e^2 \epsilon}{\pi \hbar^2} \int_0^{k_F} \frac{\partial^2 E}{\partial k^2} dk \text{ for } T = 0 \text{ since } f(k) = 0 \text{ for } k > k_F$$

$$\frac{dI}{dt} = \frac{2e^2 \epsilon}{\hbar^2 \pi} \left(\frac{\partial E}{\partial k} \right) \Bigg|_{k=k_F}$$

But $\frac{dI}{dt} = \frac{e^2 E}{m} \frac{N}{L}$

$$\Rightarrow N_{Eff} = \frac{2mL}{\pi \hbar^2} \left(\frac{\partial E}{\partial k} \right)_{k=k_F} \text{ (Those electrons that can be anticipated.)}$$

Observations:

1) $\left(\frac{\partial E}{\partial k} \right) \Bigg|_{k=k_F}$ is largest when E_F is in the middle of the band (Half-filled).

$\Rightarrow N_{Eff}$ maximized, high conductivity

2) $\left(\frac{\partial E}{\partial k} \right) \Bigg|_{k=k_F} \rightarrow 0$ as $E_F \rightarrow$ Band Gap (Filled Band)

$N_{Eff} \rightarrow 0$, Conductivity $\rightarrow 0$ (at $T = 0$)

3) Number of Electrons per atom will influence the filling of bands, and therefore the type of material.

For Chain of N atoms with P.B.C. (Periodic Boundary Conditions):

- $2N$ states/band (including spin)
- Atoms with even (odd) numbers of electrons will have filled (half-filled) bands.
- Some materials with even numbers are metals, however.

E.g., Be($4e^-$) and Mg($12e^-$)

We need to consider $> 1D$

\Rightarrow use Feynman Model to develop understanding

Feynman Model in 2-D

- $E = E_1 - 2A_x \cos k_x a - 2A_y \cos k_y b$

- Bandgaps occur at $k_x = \pm\pi/a, k_y = \pm\pi/b$.

Example: Choose $a = b, A_x = A_y = 0.25, E_1 = 1, E_g = 0.5$

– Observe bands “along” k_y ($k_x = 0$):

$$E_{k_y} = \cos k_y a$$

– Observe bands “along” k_{xy} ($k_x = k_y$):

$$E_{k_{xy}} = 2 \cos k_{xy} a$$

E_F	Conduction
0.15	Electrons, Band #1
1.0	Holes along k_y , Electrons along k_{xy}
1.5	Electrons in Band #2, Holes in Band #1

For a single, free electron $\frac{dI}{dt} = \frac{e \cdot e \varepsilon}{m} = e \frac{dv_g}{dt}$.

For nearly free electrons in a solid, $\frac{dI_{tot}}{dt} = e^2 \varepsilon \sum_{occ. states} \frac{1}{m_i^*}$ where $m_i^* =$

$$\hbar^2 \left(\frac{\partial^2 E}{\partial k^2} \right)^{-1} \Bigg|_{k=k_i} .$$

For a full band: $\frac{dI}{dt} = e^2 \varepsilon \sum_i \frac{1}{m_i^*} = 0$.

If certain electron j is missing at top of band:

$$\frac{dI_h}{dt} = e^2 \varepsilon \sum_{i \neq j} \frac{1}{m_i^*} = e^2 \varepsilon \sum_{i \neq j} \frac{1}{m_i^*} + e^2 \varepsilon \frac{1}{m_j^*} - e^2 \varepsilon \frac{1}{m_j^*}$$

$$\text{Note: } e^2 \varepsilon \sum_{i \neq j} \frac{1}{m_i^*} + e^2 \varepsilon \frac{1}{m_j^*} = 0$$

So $\frac{dI_h}{dt} = -\frac{e^2 \varepsilon}{m_j^*}$ But $m_j^* < 0$ around top

$\Rightarrow \frac{dI_h}{dt} = \left| \frac{e^2 \varepsilon}{m_j^*} \right|$ Remaining electrons act collectively as particle with positive charge.

“Holes” move in opposite direction with opposite charge and therefore make same contribution to current as the electrons.

- Can have **both**, e.g., semi-metals

At finite temperatures, occupation changes according to F-D Distribution, which broadens.

Materials with narrow gaps can become conducting semiconductors.

(Figure #1, Lecture 13)

17 Semiconductors

Classes of Band Structures: (see slides) [1]

- 1) Metals: E_F within one band
- 2) Semi-Metal: E_F within two overlapping bands
- 3) Insulators: E_F within large gap ($> \sim 2eV$)
- 4) Semiconductors: E_F within small gap

SemiConductor Sub-Classes: Direct or Indirect Gap [2] (See Examples of GaAs, AlAs)

Maxima and minima depend on both structure and composition [3]

Energies of Electrons Electrons move as free particles with effective mass; near band bottom; taking $E_V = 0$ and $C\kappa = 0$ for reference.

$$E_C \simeq E_g + \frac{\hbar^2 \kappa^2}{2m_n^*} E_V \simeq -\frac{\hbar^2 \kappa^2}{2m_p^*}$$

Negativem*, + charge \longleftrightarrow Positivem*, - charge

Intrinsic Semiconductors At finite $T > 0$, electrons occupy conduction band, leaving holes in the valence band.

$$n = p = n_i$$

n = density of free electrons

p = density of free holes

n_i = intrinsic carrier concentration

$n = \int g_c(E) f(E) dE$ conduction band

$p = \int g_v(E) [1 - f(E)] dE$ valence band

From Lecture #9, the D.O.S. (density of states) for free electrons:

$$g(E) = \frac{dn}{dE} = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} \sqrt{E}$$

For bottom of conduction and top of valence band:

$$g_c(E) = \frac{1}{2\pi^2} \left(\frac{2m_c^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_c} \quad g_v(E) = \frac{1}{2\pi^2} \left(\frac{2m_v^*}{\hbar^2} \right)^{3/2} \sqrt{E_V - E}$$

These states become occupied according to $f(E)$:

$$f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1} \simeq e^{-(E-E_F)/k_B T} \text{ For } E_F \text{ in gap and } E - E_F \gg \kappa T$$

(Maxwell-Boltzmann)

Examine product $g_c(E) f(E)$ graphically to inform the integration:

1) $g_c(E)$ is zero in gap.

2) $f(E)$ is zero at top of band \rightarrow only bottom will matter.

$$\text{Hence, } n \approx \frac{(2m_c^*)^{3/2}}{2\pi^2 \hbar^3} \int_{E_c}^{\infty} (E - E_c)^{1/2} e^{-(E-E_F)/k_B T} dE$$

$$\text{Let } x = \frac{E-E_c}{k_B T} dE = k_B T dx \sqrt{E - E_c} = x^{1/2} \sqrt{k_B T}$$

$$n = \frac{(2m_c^*)^{3/2}}{2\pi^2 \hbar^3} (k_B T)^{3/2} e^{-(E_c-E_F)/k_B T} \int_0^{\infty} x^{1/2} e^{-x} dx$$

$$n = N_C e^{-(E_c-E_F)/k_B T}, \text{ where } N_C = 2 \left(\frac{m_c^* k_B T}{2\pi \hbar^2} \right)^{3/2}$$

$$p = N_V e^{-(E_F-E_V)/k_B T} \quad N_V = 2 \left(\frac{m_v^* k_B T}{2\pi \hbar^2} \right)^{3/2}$$

- As E_F increases, n increases and p decreases.

- Depends on m^*

\Rightarrow develop expression for carrier concentration for intrinsic semiconductors

Need expression for E :

$$n = p = n_i \quad \text{Let } E_F = E_{F,i}$$

$$N_C e^{-(E_C - E_{F,i})/k_B T} = N_V e^{-(E_{F,i} - E_V)/k_B T}$$

$$e^{2E_{F,i}/k_B T} = \frac{N_V}{N_C} e^{(E_C + E_V)/k_B T}$$

$$\frac{2E_{F,i}}{k_B T} = \frac{E_C + E_V}{k_B T} + \frac{3}{2} \ln \frac{m_v^*}{m_c^*}$$

$$E_{F,i} = \frac{1}{2} (E_V + E_C) + \frac{3}{4} k_B T \ln \frac{m_v^*}{m_c^*}$$

$$E_{F,i} = E_V + \frac{E_G}{2} + \frac{3}{4} k_B T \ln \frac{m_v^*}{m_c^*}$$

Fermi level is approximately mid-gap for intrinsic semiconductors.

$$n = p = n_i \Rightarrow np = n_i^2$$

$$n_i^2 = N_C e^{-(E_C - E_F)/k_B T} N_V e^{-(E_F - E_V)/k_B T}$$

$$n_i^2 = N_C N_V e^{-(E_C - E_V)/k_B T} \quad E_C - E_V = E_G$$

$$\therefore n_i = \sqrt{N_C N_V} e^{-E_G/2k_B T}$$

At given temperature, smaller gap implies more carriers and a higher intrinsic carrier concentration.

Extrinsic Semiconductors Impurities (dopants) added to control n, p
 “**n - type**”: negative charge carriers

- Add atom with extra valence electron: donor
- e.g. P, As, Sb (Group V) to Si, Ge (IV).

Donor Level Energy (estimate) Electron + ionized donor is like H atom but in material with $E \neq \varepsilon_0$

$$E_C - E_D = \left(\frac{e^2}{4\pi\varepsilon} \right)^2 \frac{m^*}{2\hbar^2} = \left[\left(\frac{e^2}{4\pi\varepsilon_0} \right)^2 \frac{m_0}{2\hbar^2} \right] \frac{m^*}{m_0} \left(\frac{\varepsilon_0}{\varepsilon} \right)^2$$

$$= \frac{m^*}{m_0} \left(\frac{\varepsilon_0}{\varepsilon} \right)^2 (13.6 eV)$$

Estimate for Si: $\varepsilon \simeq 12\varepsilon_0, m^* = 0.5m_0$

$$\Rightarrow E_C - E_D \simeq 0.05 eV \quad \text{Donor Binding Energy}$$

$$\Rightarrow E_C - E_D \simeq 2k_B T \quad \text{around } T = 300K$$

$$(k_B T \simeq \frac{1}{2} (E_i - E_D) \quad \text{around } T = 300K)$$

$$\Rightarrow \text{Most donors are ionized } n \simeq N_D \quad (\text{for } N_D \gg n_i)$$

$$\text{We showed that } n = N_C e^{-(E_C - E_{F,i})/k_B T}$$

In thermal equilibrium, for $N_D \gg n_i$, but not too large:

$$n = N_C e^{-(E_C - E_F)/k_B T} \approx N_D (E_F > E_{F,i})$$

By rewriting in terms of E_i, N_i , one can show, however, that:

$$n = n_i e^{(E_F - E_{F,i})/k_B T}$$

$$p = n_i e^{(E_{F,i} - E_F)/k_B T}$$

$$\Rightarrow np = n_i^2 \quad \text{can increase the number of electrons, but there will be fewer holes.}$$

(Figure 3-16)

Law of Mass Action “p-type”: positive charge carriers

- Add atom with 1 less valence electron: acceptor
- e.g. Add B, Al, Ga (Group III) to Si, Ge (Group IV)
- $p \simeq N_A$ for $N_A \gg n_i$ at room temperature

Observations

- At very low temperatures, not all donors will be ionized. (Ionization Regime)
- At very high temperatures, n_i becomes appreciable due to thermal activation across gap. (Ionization Regime)
- More generally, both donors and acceptors may be present. **The number of free carriers is given by:**

- 1) Space-charge neutrality: $p + N_D^+ = n + N_A^-$ (in equilibrium)
- 2) Law of Mass Action: $np = n_i^2$

At room temperatures, $N_D^+ \simeq N_D, N_A^- \simeq N_A$

If, e.g., $N_D > N_A$, then $n - p = N_D - N_A$

Compensation: We have a reduced net electron concentration.

18 Current Flow in Semiconductors

(S+W, Chapter 8 and A+M, Chapter 1)

Equilibrium

- Carriers move quickly ($\sim \nu_F$), but **net** motion of charge.
- Random scattering from phonons and impurities: this randomizes momentum.

– ℓ : mean free path between collisions

– $\tau = \frac{\ell}{\nu_F}$ average time between collisions (inverse rate)

In Applied Field $\vec{\varepsilon}$ Electron feels a force $\vec{F} = \frac{d\vec{p}\varepsilon}{dt} = -e\vec{\varepsilon}$, accelerates, but collisions randomize \vec{p} .

- i.e. $\Delta \vec{p}_{col} = -\langle \vec{p} \rangle$

For an average collision, $\frac{d\vec{p}_{col}}{dt} = \frac{-\langle \vec{p} \rangle}{\tau}$.

In steady state, $\frac{d\vec{p}_e}{dt} + \frac{d\vec{p}_{col}}{dt} = 0$

$$\Rightarrow -e\vec{\varepsilon} = \frac{\langle \vec{p} \rangle}{\tau}, \nu$$

$$-e\tau\vec{\varepsilon} = m_n^* \langle \vec{\nu} \rangle$$

$$\langle \nu \rangle = -\frac{e\tau}{m_n^*} \vec{\varepsilon} \text{ where } \langle \vec{\nu} \rangle \equiv \nu_d \text{ Drift Velocity}$$

$$\langle \vec{\nu} \rangle = -\frac{e\tau}{m_n^*} \vec{\varepsilon} \text{ where } \langle \vec{\nu} \rangle \equiv \vec{\nu}_d \text{ Drift Velocity}$$

$$\vec{J} = -e \cdot n \cdot \vec{\nu}_d = \frac{ne^2\tau}{m_n^*} \vec{\varepsilon}, \text{ so we have Ohm's Law}$$

$$\vec{J} = \sigma \vec{E}, \text{ where } \sigma = \frac{ne^2\tau}{m_n^*} = ne\mu_n \text{ is the conductivity.}$$

(Note that σ is a tensor $\overleftarrow{\sigma}$.)

Also, note that $\vec{\nu}_d = -\mu_n \vec{\varepsilon}$ (simple interpretation).

$$\vec{J} = ne\mu_n \vec{\varepsilon} \text{ for electrons.}$$

Overall, the current due to drift is:

$$\vec{J} = e(n\mu_n + p\mu_p) \vec{\varepsilon} \text{ when } \vec{\nu}_d \propto \vec{\varepsilon}.$$

You may be more familiar with $V = IR$, where $R = \rho \frac{\ell}{A} = \frac{1}{\sigma} \frac{\ell}{A}$.

- ℓ refers to length; A refers to the cross-sectional area

Observations:

Conductivity is proportional to τ , inversely proportional to m^* .

What are the origins of scattering?

Scattering Mechanisms

- 1) Phonons (Lattice Scattering)

$$\tau_{Ph} \propto T^{-3/2}$$

- 2) Impurities/ Defects

$$\tau_{Imp} \propto T^{3/2} \text{ (less time near imp)}$$

- 3) Charge Carriers

(can neglect for moderately doped semiconductors)

Scattering Rate:

$$R_{Tot} = R_{Ph} + R_{Imp}$$

$$\frac{1}{\tau} = \frac{1}{\tau_{Ph}} + \frac{1}{\tau_{Imp}}$$

$$\left(\frac{1}{\mu} = \frac{1}{\mu_{Ph}} + \frac{1}{\mu_{Imp}} \right)$$

Observations:

- Doping increases σ by increasing n, p , but impurity scattering also increases.
- At high fields, additional scattering mechanisms lead to non-linear changes in $\vec{v}d$ with $\vec{\varepsilon}$.
 - Si, Ge, velocity saturation (Optical Phonon Scattering)
 - GaAs NDR for e^- (Inter-valley Scattering)

Hall Effect (skipped in 2012)

Experiment used to determine n, p, μ_n, μ_p .

$$\vec{F} = e \left(\vec{\varepsilon} + \vec{v}_x \vec{B} \right) \text{ for holes.}$$

Assume $\vec{v} = v_x \hat{x} \vec{B} = B_z \hat{z}$.

$$F_y = e(\varepsilon_y - v_x B_z)$$

Holes are deflected in $-\hat{y}$ direction until field builds up to oppose the flow.

$\implies \varepsilon_y = v_x B_z$ in steady state (**Hall Effect**)

(The Hall voltage is $\varepsilon_y w$) $\{J_x = e \cdot p \cdot v_{dx}\}$

$$\varepsilon_y = \frac{J_x}{ep} B_z = R_H J_x B_z \text{ Note: } R_H = \frac{1}{ep}$$

$$p = \frac{J_x B_z}{e \varepsilon_y} = \frac{\frac{I_x}{wt} \cdot B_z}{qV/w} = \frac{I_x B_z}{qtV_H}$$

$$\text{Also: } R = \frac{V_x}{I_x} = \frac{1}{\sigma} \cdot \frac{L}{wt}$$

$$\implies \sigma = \frac{I_x}{V_x} \cdot \frac{L}{wt} = pe\mu_p$$

$$\implies \mu_p = \frac{\sigma}{ep} = R_H \sigma$$

We can therefore determine the majority carrier type and mobility.

Additional Transport Processes: Diffusion A gradient in free carrier concentration leads to diffusion. (See figure)

Fick's First Law: (1-D) $\phi = -D \frac{dc}{dx}$

- ϕ refers to flux $\frac{1}{cm^2 \cdot s}$
- $-D$ is the diffusion coefficient cm^2/s
- $\frac{dc}{dx}$ refers to the concentration cm^{-3}

These are the diffusion currents:

$$\bullet J_n = -(-e) D_n \frac{dn}{dx} = e D_n \frac{dn}{dx}$$

$$\bullet J_p = -(e) D_p \frac{dp}{dx} = -e D_p \frac{dp}{dx}$$

In the presence of $\vec{\varepsilon} \neq 0$ and $\frac{dp}{dx}, \frac{dn}{dx} \neq 0$:

$$J_n(x) = e\mu_n n(x)\varepsilon(x) \text{ (drift)} + eD_n \frac{dn(x)}{dx} \text{ (diffusion)}$$

$$J_p(x) = e\mu_p p(x)\varepsilon(x) \text{ (drift)} + eD_p \frac{dp(x)}{dx} \text{ (diffusion)}$$

$$J_{Tot}(x) = J_n(x) + J_p(x)$$

Whereas majority carriers dominate current flow due to drift ($n \gg p$ or $p \gg n$), minority carrier diffusion currents can be substantial ($\frac{dp}{dx}, \frac{dn}{dx}$).

Consider energy band diagram in presence of applied field. (See att version.)

The energy of an electron is $E(x) = -eV(x)$ and $\varepsilon(x) = -\frac{dV}{dx}$

$$\text{So } \varepsilon(x) = -\frac{d}{dx} \left(\frac{E_i(x)}{-e} \right) = \frac{1}{e} \frac{dE_i}{dx}$$

Electrons drift “downhill.”

Holes drift “uphill.”

Variations in **concentration** also reduce fields. Consider holes:

$$J_p(x) = e\mu_p p(x)\varepsilon(x) - eD_p \frac{dp(x)}{dx} = 0 \text{ No current when } \frac{dp}{dx} \neq 0$$

$$\implies \varepsilon(x) = \frac{D_p}{\mu_p} \frac{1}{p(x)} \frac{dp}{dx} \text{ \{Q: What } p(x) \text{ would produce this? See homework.\}}$$

$$p = n_i e^{(E_i - E_F)/\kappa T} \implies \frac{dp}{dx} = n_i e^{(E_i - E_F)/\kappa T} \cdot \frac{1}{\kappa T} \left(\frac{dE_i}{dx} - \frac{dE_F}{dx} \right)$$

Note that ε refers to $\frac{dE_i}{dx}$ and $\frac{dE_F}{dx}$ is zero in the above equation.

$$\varepsilon(x) = \frac{D_p}{\mu_p} \frac{1}{\kappa_B T} \cdot e\varepsilon$$

$$\therefore \frac{D_p}{\mu_p} = \frac{\kappa_B T}{e} \text{ Einstein Relation (also holds for electrons)}$$

Concentration Gradients \rightarrow “Built-in” Fields

$$\text{Inside a semiconductor, } \varepsilon(x) = \frac{1}{e} \frac{dE_i}{dx}$$

Slope in bands indicates field

Fields result from:

- 1) Applied voltage: $\varepsilon = V/L$

- 2) Carrier concentration gradients

Consider holes in the absence of current:

$$J_p(x) = e\mu_p p(x)\varepsilon(x) - eD_p \frac{dp}{dx} = 0 \frac{dp}{dx} \neq 0$$

$$\varepsilon(x) = \frac{D_p}{\mu_p} \frac{1}{p(x)} \frac{dp}{dx} \implies \varepsilon \neq 0$$

We can relate drift to diffusion:

$$p = n_i e^{(E_i - E_F)/\kappa T} \implies \frac{dp}{dx} = n_i e^{(E_i - E_F)/\kappa T} \frac{1}{\kappa T} \left(\frac{dE_i}{dx} - \frac{dE_F}{dx} \right)$$

$$\text{Note: } \frac{dE_i}{dx} = e\varepsilon \text{ and } \frac{dE_F}{dx} = 0$$

Substituting above,

$$\varepsilon(x) = \frac{D_p}{\mu_p} \frac{1}{\kappa_B T} \frac{dE_i}{dx} = \frac{D_p}{\mu_p} \frac{1}{\kappa_B T} e\varepsilon$$

$$\text{So } \left[\frac{D_p}{\mu_p} = \frac{\kappa_B T}{e} \right] \text{ Einstein Relation (also for } e^-)$$

This assumes equilibrium.

HW Problem #8.4 (in class, 2010, 2011)

1) Consider donor doping profile:

$$n \simeq N_d = N_0 e^{-ax} (Nd \gg n_i)$$

a) What is the field?

In equilibrium, $J(x) = 0$ and $e\mu_n n(x)\varepsilon(x) + eD_n \frac{dn(x)}{dx} = 0$

$\varepsilon(x) = -\frac{D_n}{\mu_n} \frac{dn}{dx} \frac{1}{n(x)}$ Use Einstein Relation.

$$\varepsilon(x) = -\frac{\kappa T}{e} \frac{(-aN_0 e^{-ax})}{N_0 e^{-ax}} = \frac{\kappa T}{e} a$$

Field depends on temperature and rate of dopant decrease (junction abruptness).

b) $a = 1\mu m^{-1}$ $T = 300\kappa$

$$\begin{aligned} \varepsilon &= \frac{\kappa T}{a} = \frac{(1.38 \times 10^{-23} J/\kappa)(300\kappa)(1eV)}{e 1.602 \times 10^{-19} J} \frac{1}{10^{-4} cm} \\ &= 258 V/cm \end{aligned}$$

Additional Homework Solutions:

1) Parts (a) and (b):

a) $F(E_A) = \frac{1}{e^{+(E_A - E_F)/\kappa T} + 1}$

b) $(-v)n = N_c e^{-(E_i - E_F)/\kappa_B T}$

$p = N_v e^{-(E_F - E_V)/\kappa_B T}$

$p + N_D^+ = n + N_A^- N_D = 0$

2) $\sigma_n(T) = n(T_i) e\mu_n(T)$

$= n(T) \frac{e^2}{m_n^*} \tau(T)$

$\frac{\sigma(2T_1)}{\sigma(T_1)} = \frac{n(2T_1)}{n(T_1)} \cdot \frac{T(2T_1)}{T(T_1)}$

$\frac{1}{T} = \frac{1}{T_{PH}} + \frac{1}{T_{IM}}$

$n \propto T^2$

$T_{imp} = AT^{3/2}$

$T_{PH} = BT^{-3/2}$

Also: $T_{imp}(T_1) = T_{IM}(T_2)$ (Connects A with B)

$\frac{I}{A} = J = \sigma\varepsilon = \sigma \cdot \frac{V}{L}$

$I = \sigma \cdot A \cdot \frac{V}{L}$

$I = N_d$

$\nu_d = \mu\varepsilon$

$\sigma = n \cdot e \cdot \mu_n$ (n is an estimate)

$\sigma \simeq N_d \cdot e\mu_n$

$t = \frac{d}{v}$

$t = \frac{i}{\nu_d} = \frac{L}{\mu\varepsilon} = \frac{LL}{\mu V} = \frac{L^2}{\mu V}$

$$1) J_{sat} = ne \cdot \vec{\nu}_{sat}$$

$$\text{For } \nu \propto \varepsilon, J = \sigma \varepsilon$$

For high fields, $\nu \rightarrow \nu_{sat}$

$$J_{sat} = n \cdot e \cdot \nu_{sat}$$

$$J = \frac{I}{A}; \sigma = n \cdot e \cdot \mu$$

n is approximate; μ should be looked up

$$a) T(T_1) = \frac{T_{I1}T_{P1}}{T_{I1}+T_{P1}}$$

$$T_F = AT_1^{3/2}, T_{PH} = BT_1^{-3/2}, AT_1^{3/2} = BT_1^{-3/2}$$

$$\Rightarrow B = AT_1^3$$

$$\frac{1}{T_1(T_1)} = \frac{1}{AT_1^{3/2}} + \frac{1}{AT_1^3 \cdot T_1^{-3/2}} \frac{1}{AT_1^{3/2}} \left(\frac{1}{2^{3/2}} + \frac{1}{2^{-3/2}} \right)$$

$$T_1 = \frac{A}{2} T_1^{3/2} T_2 = \frac{A}{2} T_2^{3/2} = \frac{A}{2} \cdot 2^{3/2} T_1^{3/2} = A\sqrt{2} T_1^{3/2}$$

$$T(T_2) = AT_1^{3/2}$$

$$\frac{T(T_2)}{T(T_1)} = \frac{\sqrt{2}}{2}$$

$$\sigma = 4 \cdot \frac{\sqrt{2}}{2} = 2\sqrt{2}$$

$$(2^{-3/2} + 2^{3/2})^{-1} = 0.314$$

19 351-1 Problems

1) Newton's Laws Can be derived from Hamilton's equations.

- a) Identify the Hamiltonian from conservation of energy using only momentum p (for Kinetic Energy) and position x (for potential Energy):

$$H = KE + PE$$

Use the Hamiltonian for a particle in a 1-D quadratic potential like a mass on a spring. What is KE, PE ?

- b) Hamilton's equations are

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x}$$

$$\frac{dx}{dt} = \frac{\partial H}{\partial p}$$

Show these give Newton's laws of motion for the mass on a spring.

- c) Derive the 1-D differential equation of motion from Hamilton equation. For a particle of total energy E and spring constant $k, x = 0$ at $t = 0$, what is the equation of motion $x(t)$. what is $p(t)$. show the region of Phase Space (p vs x) that describes the particle throughout its motion.
- d) Use the equipartition theorem (where $\langle A \rangle$ is time average of A , and i is index for each spatial dimension):

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = \left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = k_B T$$

to derive the relationship between thermal velocity and temperature

$$\frac{1}{2} m v_{th}^2 = \frac{3}{2} k_B T$$

- e) Derive the Dulong-Petit law for atoms in a 3-D potential from the equipartition theorem:

$$\langle E \rangle = 3k_B T$$

- f) What is the heat capacity $C = dE/dT$ in this case?

2) Problem 1.1 from Solymar and Walsh:

A 10 mm cube of germanium passes a current of 6.4 mA when 10 mV is applied between two of its parallel faces. Calculate the resistivity of the sample. Assuming that the charge carriers are electrons that have a mobility of $0.39 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$, calculate the density of carriers. What is their collision time if the electron's effective mass in germanium is $0.12 m_e$ where m_e is the free electron mass?

- 3) Give a one line description of each of these experiments and their significance to modern physics: Photoelectric Effect, Compton Effect, Black Body Radiation, Rutherford Backscattering (Bohr model), Electron Diffraction, Atomic spectra.

Classical: <https://www.youtube.com/watch?v=yXsHf1XB7QM>

Bohr Atom: <https://www.youtube.com/watch?v=ydPzEZTd-98>

Wave Particle Duality - photoelectric effect: <https://www.youtube.com/watch?v=frNLtEm1glg>

Schrödinger waves: <https://www.youtube.com/watch?v=C8XGIYz1PCw>

Probability interpretation: <https://www.youtube.com/watch?v=p7xIKoBdViY>

Compton Effect: <https://www.youtube.com/watch?v=0Y648TNGAIo>

4) Problem 2.1 from Solymar and Walsh.

Find the de Broglie wavelength of the following particles, ignoring relativistic effects:

(i) an electron in a semiconductor having average thermal velocity at $T = 300K$ and an effective mass of $m_e^* = am_o$,

(ii) a helium atom having thermal energy at $T = 300K$

(iii) an α particle (He^4 nucleus) of kinetic energy 10 MeV.

Hint: See question 1. For a gas of non-interacting particles, $\frac{1}{2}mv_{th}^2 = \frac{3}{2}k_B T$.

5) A particle of mass, m , is confined to a 1-D region $0 \leq x \leq L$. In class, we derived the following stationary state wavefunctions and energies for this 1-D infinite square well potential:

$$\psi_n(x) = A \sin\left(\frac{\pi n}{L} x\right)$$

a) Normalize the wave function to find the value of A .

b) Find the Energy of these stationary states

Assuming that the initial normalized wavefunction of this particle at $t = 0$ is:

$$\Psi(x, t = 0) = \sqrt{\frac{8}{5L}} \left[1 + \cos\left(\frac{\pi}{L} x\right) \right] \sin\left(\frac{\pi}{L} x\right)$$

a) Derive an expression for the wavefunction $\Psi(x, T)$, at all later times $t > 0$.

b) Show that the probability of finding the particle in the left half of the box (i.e., in the region $0 \leq x \leq L/2$) at time $t > 0$ is: $\frac{1}{2} + \frac{16}{15\pi} \cos\left(\frac{3\pi^2 \hbar t}{2mL^2}\right)$

- 6) Assuming that $\Psi(x,t)$ is a solution of the 1-D Schrödinger Equation, the current density is defined as:

$$J(x) = -\frac{i\hbar e}{2m} \left[\Psi^* \frac{\partial \Psi}{\partial x} - \Psi \frac{\partial \Psi^*}{\partial x} \right]$$

In this problem, consider the potential barrier of height (V) and width (d) that is depicted in Fig. 3.3 of Solymar and Walsh. Assume that the electron energy (E) is less than V .

- a) By applying suitable boundary conditions and your knowledge of quantum mechanics, develop a system of equations that could be solved to determine the transmitted current through the barrier (J_t) in terms of the incident current on the barrier (J_i).
- b) By solving your system of equations from part (a), show that:

$$\frac{J_t}{J_i} = \frac{1}{1 + \frac{V^2}{4(V-E)E} \sinh^2(\gamma d)}$$

where $\gamma = \frac{\sqrt{2m(V-E)}}{\hbar}$ and $\sinh(\gamma d) = \frac{1}{2}(e^{\gamma d} - e^{-\gamma d})$

- c) In the limit where $\gamma d \gg 1$, show that: $\frac{J_t}{J_i} = \frac{16(V-E)E}{V^2} e^{-2\gamma d}$
- d) The exponential dependence of the “tunneling” current on distance is utilized for atomic resolution imaging of conductive surfaces with the scanning tunneling microscope (STM). Conservatively assume that the STM can detect changes in the tunneling current of 1%. Under typical tunneling conditions (e.g., $V - E$ 1eV, $d \sim 10$ Å), estimate the vertical spatial resolution of the STM. Hint: The answer can be expressed in picometers (10^{-12} m)!
- 7) Derive the solution of the 2-D particle in a box (particle is constrained in both x , and y directions; $V \rightarrow \infty$ at the boundaries).
- a) Solve for the energies and wave functions of the ground and first excited states.
- b) What is the degeneracy of the first excited state?
- c) Plot the probability distributions $2|\psi|^2$ of the first excited states as surface plots.
- d) Optional: plot probability distributions of the ground state, first excited states, and 2nd excited states, and comment on the evolution.
- 8) Consider the infinite spherical well: $V(r) = 0$ if $r \leq a$, $V(r) = \infty$ if $r > a$.
- a) For $l = 0$, determine the allowed energies (E_n).

b) For $l = 0$, show that the corresponding wavefunctions are:

$$\Psi_n(r) = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}$$

In class, we worked through the Schrödinger equation in spherical coordinates for spherically symmetric potentials by breaking the solution into radial and angular functions. You should be able to solve the radial equation for the conditions given here.

- 9) Consider the infinite spherical well: $V(r) = 0$ if $r \leq a$, $V(r) = V_o$ if $r > a$.
- a) For $l = 0$, show that there is no bound state if: $V_o a^2 < \frac{\pi^2 \hbar^2}{8m}$. This can be shown without resorting to numerical computation.
- b) Given $V_o = \frac{2\hbar\pi^2}{ma^2}$, find the energies of the two bound states by graphing in MATLAB or Excel. You can also use MATLAB to check your solution by solving the transcendental equation directly.

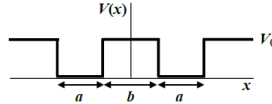
This problem is analogous to the finite square well problem solved in 3.8 of Solymar and Walsh, but in the spherical coordinate system. Through the appropriate application of boundary conditions, you should arrive at a transcendental equation whose argument can be analyzed to establish the condition for the existence of bound states.

- 10) Suppose that the nucleus of a hydrogen atom is located at a distance d from a two-dimensional infinite potential wall which, of course, tends to distort the hydrogen atom. As d approaches zero, determine the following items:
- a) The ground state wavefunction.
- b) The degeneracy of the first excited state (ignore degeneracy due to spin).
- c) The wavelength of light that is emitted upon transition between the first excited state and the ground state (express your answer in nanometers).

With the exception of part (c), this problem does not involve mathematical calculation. The proper choice of coordinate system can make the relationship between these solutions and the usual hydrogen atom solutions clear. Bear in mind that the ground state refers to the lowest energy state that exists.

- 11) Consider a double finite potential well in one dimension. Suppose that the depth V_0 and the width a are fixed such that the following equation is obeyed:

$$\beta^2 = \frac{V_0 m a^2}{2\hbar^2} = 4\pi^2$$



12) Qualitatively sketch the ground state wavefunction ψ_1 and the first excited state wavefunction ψ_2 for: (i) $b=0$, (ii) $b = a/2$, and (iii) $b \gg a$.

a) For $b = 0$, show that the ground state energy (E_1) is given by: $E_1 = \frac{\hbar^2 x_1^2}{2ma^2}$, where x_1 is the solution of the following equation: $\tan x_1 = \sqrt{\left(\frac{2\beta}{x_1}\right)^2 - 1}$. Calculate E_1 in units of $\frac{\hbar^2}{ma^2}$.

b) For $b = 0$, show that the first excited state energy (E_2) is given by: $E_2 = \frac{\hbar^2 x_2^2}{2ma^2}$ where x_2 is the solution of the following equation: $-\cot x_2 = \sqrt{\left(\frac{2\beta}{x_2}\right)^2 - 1}$. Calculate E_2 in units of $\frac{\hbar^2}{ma^2}$.

c) For $b \gg a$, estimate E_1 and E_2 in units of $\frac{\hbar^2}{ma^2}$.

d) Use the MATLAB code derived from Garcia, R., Zozulya, A. & Stickney, J. MATLAB codes for teaching quantum physics: Part 1. *arXiv physics.ed-ph*, (2007). <http://arxiv.org/pdf/0704.1622.pdf>

Consult the original publication for background on the code, which is reproduced below.

- i. What is the Heaviside function? How is it used in this code (for what purpose)?
- ii. Using the MATLAB code, generate the plots you sketched in part (a) (ground and first excited states for $b=0$, $b=a/2$, and $b \gg a$). You should have three graphs with two curves on each. Label the graphs and the wave functions.
- iii. Generate 2 more plots with intermediate barrier widths, and sketch the trends in E_1 and E_2 as a function of barrier width (you should have 5 different widths).

Note: in the code, you can change the potential profile quite easily (e.g. the quadratic harmonic oscillator potential or single square well). Parameters can be varied to develop insight into how the wavefunctions vary with the potentials.

e) Provide a physical explanation for the variation of E_1 with b that you observed in part (e).

f) The double well is a primitive one dimensional model for the potential experienced by an electron in a diatomic molecule (the two wells represent the attractive force of the nuclei). If the nuclei are free to move, they will adopt the configuration of minimum energy. In view of your conclusions in (b), does the electron in the ground state (E_1) tend to

draw the nuclei together or push them apart? What about E_2 ? Provide a physical reason for these behaviors, considering your answer to the previous question.

```

1  % Program 4: Find several lowest eigenmodes V(x) and
2  % eigenenergies E of 1D Schrodinger equation
3  % -1/2*hbar^2/m(d2/dx2)V(x) + U(x)V(x) = EV(x)
4  % for arbitrary potentials U(x)
5  % Parameters for solving problem in the interval -L < x < L
6  % PARAMETERS:
7  L = 5; % Interval Length
8  N = 1000; % No of points
9  x = linspace(-L,L,N)'; % Coordinate vector
10 dx = x(2) - x(1); % Coordinate step
11
12 % POTENTIAL, choose one or make your own
13 U = 1/2*100*x.^(2); % quadratic harmonic oscillator potential
14 %U = 1/2*x.^(4); % quartic potential
15
16 % Finite square well of width 2w and depth given
17 %w = L/50;
18 %U = -500*(heaviside(x+w)-heaviside(x-w));
19
20 % Two finite square wells of width 2w and distance 2a apart
21 %w = L/50; a=3*w;
22 %U = -200*(heaviside(x+w-a) -heaviside(x-w-a) ...
23 % + heaviside(x+w+a) -heaviside(x-w+a));
24
25 % Three-point finite-difference representation of Laplacian
26 % using sparse matrices, where you save memory by only
27 % storing non-zero matrix elements
28 e = ones(N,1); Lap = spdiags([e -2*e e],[-1 0 1],N,N)/dx^2;
29
30 % Total Hamiltonian hbar = 1; m = 1;
31 % constants for Hamiltonian H = -1/2*(hbar^2/m)*Lap + spdiags(
32 U,0,N,N);
33
34 % Find lowest nmodes eigenvectors and eigenvalues of sparse
35 matrix
36 nmodes = 3; options.disp = 0;
37 [V,E] = eigs(H,nmodes,'sa',options); % find eigs
38 [E,ind] = sort(diag(E)); % convert E to vector and sort low to
39 high
40 V = V(:,ind); % rearrange corresponding eigenvectors
41
42 % Generate plot of lowest energy eigenvectors V(x) and U(x)
43 Usc = U*max(abs(V(:)))/max(abs(U)); % rescale U for plotting
44 plot(x,V,x,Usc,'-k'); % plot V(x) and rescaled U(x)
45
46 % Add legend showing Energy of plotted V(x)
47 lgnd_str = [repmat('E = ',nmodes,1),num2str(E)];
48 legend(lgnd_str) % place legend string on plot

```

- 13) Consider a cesium chloride crystal where the potential energy per formula unit is:

$$E(r) = \frac{A}{r^n} - \frac{Me^2}{4\pi\epsilon_0 r}$$

where A is a constant, $n > 1$, r is interionic distance, and M is the Madelung constant.

- Express the binding energy (E_0) in terms of M, n, r_0 , and fundamental constants. *Hint: first express A in terms of these constants by considering the equilibrium condition.*
- The cesium chloride crystal structure consists of cations located on a simple cubic lattice (lattice constant = a) with an anion located at the center of the cube. What is the volume per formula unit (v) in terms of r ?
- From thermodynamics, the bulk modulus (B) is known to be: $B = v \frac{\partial}{\partial v} \left(\frac{\partial E}{\partial v} \right)$. Show that B_0 is of the form $B_0 = \frac{C}{r_0} \frac{d^2 E}{dr^2} |_{r=r_0}$, and find C . *Hint: use your result from the previous problem to rewrite the derivatives in terms of r .*
- Using the result from part (c), express the equilibrium bulk modulus (B_0) in terms of M, n, r_0 , and fundamental constants.
- The experimentally determined values of B_0 and r_0 for CsCl are 19.8 GPa and 3.571 Å respectively. Calculate E_0 for CsCl in eV. Note: $M = 1.7627$ for CsCl.

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