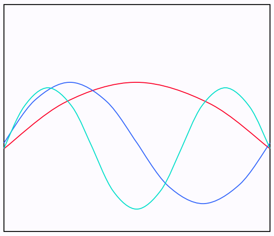
Lecture 12 - The Electron Gas

Part II - Electronic Properties of Solids
Lecture 12: The Electron Gas
(Kittel Ch. 6)



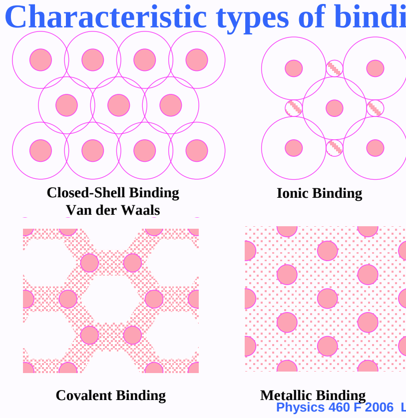
Outline

- Overview - role of electrons in solids
- The starting point for understanding electrons in solids is completely different from that for understanding the nuclei (But we will be able to use many of the same concepts!)
- Simplest model - Electron Gas
  - Failure of classical mechanics
  - Success of quantum mechanics
  - Pauli Exclusion Principle, Fermi Statistics
  - Energy levels in 1 and 3 dimensions
- Similarities, differences from vibration waves
- Density of States, Heat Capacity
- (Read Kittel Ch 6)

Role of Electrons in Solids

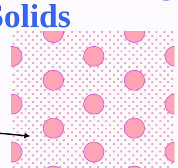
- Electrons are responsible for binding of crystals -- they are the "glue" that hold the nuclei together
  - Types of binding (see next slide)
    - Van der Waals - electronic polarizability
    - Ionic - electron transfer
    - Covalent - electron bonds
    - Metallic - more about this soon
- Electrons are responsible for important properties:
  - Electrical conductivity in metals
  - (But why are some solids insulators?)
  - Magnetism
  - Optical properties
  - . . . .

Characteristic types of binding



Starting Point for Understanding Electrons in Solids

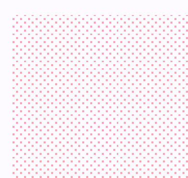
- Nature of a metal: Electrons can become "free of the nuclei" and move between nuclei since we observe electrical conductivity



- Electron Gas
  Simplest possible model for a metal - electrons are completely "free of the nuclei" - nuclei are replaced by a smooth background -- "Electrons in a box"

Electron Gas - History

- Electron Gas model predates quantum mechanics
- Electrons Discovered in 1897 - J. J. Thomson
- Drude-Lorentz Model - Electrons - classical particles free to move in a box



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Drude-Lorentz Model (1900-1905)

- Electrons as classical particles moving in a box
- Model: All electrons contribute to conductivty. Works! Still used!
- But same model predicted that all electrons contribute to heat capacity. Disaster. Heat capacity is MUCH less than predicted.

Paul Drude

Quantum Mechanics

- 1911: Bohr Model for H
- 1923: Wave Nature of Particles Proposed
  Prince Louie de Broglie
- 1924-26: Development of Quantum Mechanics - Schrodinger equation
- 1924: Bose-Einstein Statistics for Identical Particles (phonons, ...)
- 1925-26: Pauli Exclusion Principle, Fermi-Dirac Statistics (electrons, ...)
- 1925: Spin of the Electron (spin = 1/2)
  G. E. Uhlenbeck and S. Goudsmit

Schrodinger

Schrodinger Equation

- Basic equation of Quantum Mechanics

$$[- (\hbar/2m) \nabla^2 + V(\underline{r})] \Psi (\underline{r}) = E \Psi (\underline{r})$$

where
- m = mass of particle
- $V(\underline{r})$ = potential energy at point $\underline{r}$
- $\nabla^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$
- E = eigenvalue = energy of quantum state
- $\Psi(\underline{r})$ = wavefunction
- $n(\underline{r}) = | \Psi(\underline{r}) |^2$ = probability density

∇

Schrodinger Equation - 1d line

- Suppose particles can move freely on a line with position x, $0 < x < L$

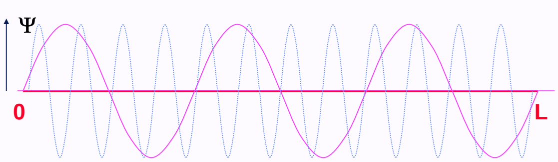
0 L

- Schrodinger Eq. In 1d with V = 0
  $- (\hbar^2/2m) d^2/dx^2 \Psi (x) = E \Psi (x)$
- Solution with $\Psi (x) = 0$ at $x = 0,L$ ← Boundary Condition
  $\Psi (x) = 2^{1/2} L^{-1/2} \sin(kx)$, $k = m \pi/L$, m = 1,2, ...
  (Note similarity to vibration waves)
  Factor chosen so $\int_0^L dx | \Psi (x) |^2 = 1$
- $E (k) = (\hbar^2/2m) k^2$

Electrons on a line

- Solution with $\Psi (x) = 0$ at x = 0,L

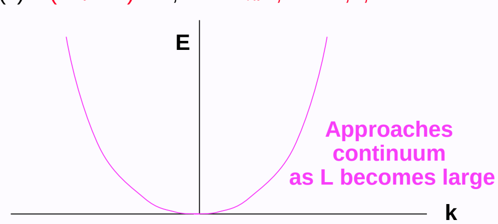
  Examples of waves - same picture as for lattice vibrations except that here $\Psi (x)$ is a continuous wave instead of representing atom displacements



Electrons on a line

- For electrons in a box, the energy is just the kinetic energy which is quantized because the waves must fit into the box

  $E (k) = (\hbar^2/2m) k^2$, $k = m \pi/L$, m = 1,2, ...



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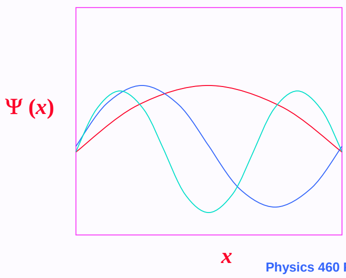
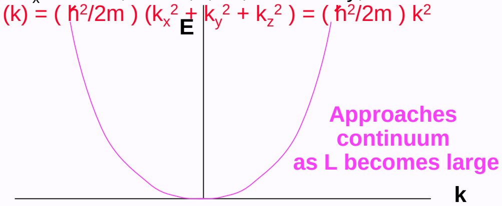
Schrodinger Equation - 1d line

- E (k) = (ħ²/2m) k ² , k = m π/L, m = 1,2, ...
- Lowest energy solutions with Ψ (x) = 0 at x = 0,L



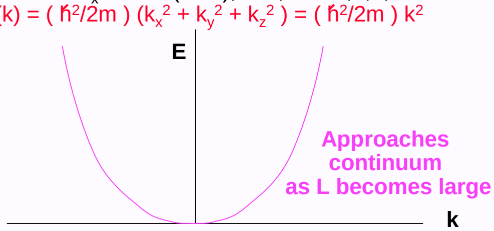
Electrons in 3 dimensions

- Schrodinger Eq. In 3d with V = 0
  $-(\hbar^2/2m)\,[d^2/dx^2 + d^2/dy^2 + d^2/dz^2]\,\Psi(x,y,z) = E\,\Psi(x,y,z)$
- Solution
  $\Psi = 2^{3/2} L^{-3/2} \sin(k_x x) \sin(k_y y) \sin(k_z z)$,
  $k_x = m\pi/L$, m = 1,2, …, same for y,z
  $E(k) = (\hbar^2/2m)(k_x^2 + k_y^2 + k_z^2) = (\hbar^2/2m)\,k^2$



Electrons in 3 dimensions

- Just as for phonons it is convenient to define Ψ with periodic boundary conditions
- Ψ is a traveling plane wave:
  $\Psi = L^{-3/2} \exp(i(k_x x + k_y y + k_z z))$,
  $k_x = \pm m\,(2\pi/L)$, etc., m = 0,1,2,..
  $E(k) = (\hbar^2/2m)(k_x^2 + k_y^2 + k_z^2) = (\hbar^2/2m)\,k^2$

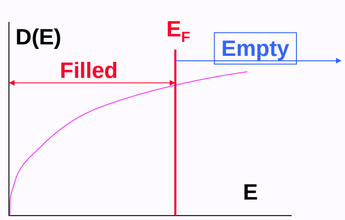


Density of States 3 dimensions

- Key point - exactly the same as for vibration waves - the values of $k_x\ k_y\ k_z$ are equally spaced - $\Delta k_x = 2\pi/L$, etc.
- Thus the volume in k space per state is $(2\pi/L)^3$ and the number of states N per unit volume $V = L^3$, with $|k| < k_0$ is
  $N = (4\pi/3)\,k_0^3 / (2\pi/L)^3 \;\Rightarrow\; N/V = (1/6\pi^2)\,k_0^3$
- ⇒ density of states per unit energy per unit volume is
  $D(E) = d(N/V)/dE = (d(N/V)/dk)\,(dk/dE)$
  Using $E = (\hbar^2/2m)\,k^2$, $dE/dk = (\hbar^2/m)\,k$
  $\Rightarrow D(E) = (1/2\pi^2)\,k^2 / (\hbar^2/m)\,k = (1/2\pi^2)\,k / (\hbar^2/m)$
  $= (1/2\pi^2)\,E^{1/2}\,(2m/\hbar^2)^{3/2}$
- (NOTE - Kittel gives formulas that already contain a factor of 2 for spin)

Density of States 3 dimensions

- $D(E) = (1/2\pi^2)\,E^{1/2}\,(2m/\hbar^2)^{3/2} \sim E^{1/2}$



What is special about electrons?

- Fermions - obey exclusion principle
- Fermions have spin s = 1/2 - two electrons (spin up and spin down) can occupy each state
- Kinetic energy = $(p^2/2m) = (\hbar^2/2m)\,k^2$
- Thus if we know the number of electrons per unit volume N_{elec}/V, the lowest energy allowed state is for the lowest $N_{elec}/2$ states to be filled with 2 electrons each, and all the (infinite) number of other states to be empty.
- Thus all states are filled up to the Fermi momentum k_F and Fermi energy $E_F = (\hbar^2/2m)\,k_F^2$ given by
  $N_{elec}/2V = (1/6\pi^2)\,k_F^3$ or $N_{elec}/V = (1/3\pi^2)\,k_F^3$
  ⇒
  $k_F = (3\pi^2 N_{elec}/V)^{1/3}$ and $E_F = (\hbar^2/2m)\,(3\pi^2 N_{elec}/V)^{2/3}$

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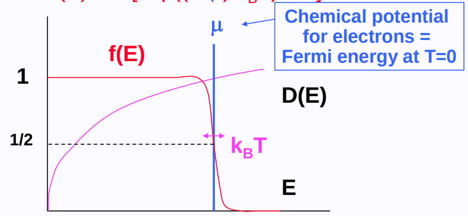
Fermi Distribution

- At finite temperature, electrons are not all in the lowest energy states
- Applying the fundamental law of statistics to this case (occcupation of any state and spin only can be 0 or 1) leads to the Fermi Distribution (Kittel appendix)

$f(E) = 1/[\exp((E-\mu)/k_BT) + 1]$



Typical values for electrons?

- Here we count only valence electrons (see Kittel table)

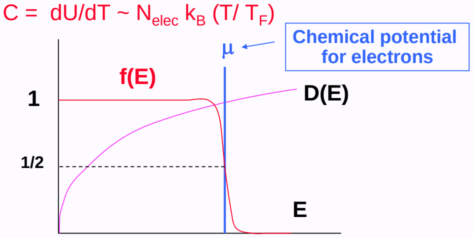
Element	N_{elec}/atom	E_F	$T_F = E_F/k_B$
Li	1	4.7 eV	5.5 x10^4 K
Na	1	3.23eV	3.75 x10^4 K
Al	3	11.6 eV	13.5 x10^4 K

- Conclusion: For typical metals the Fermi energy (or the Fermi temperature) is much greater than ordinary temperatures

Heat Capacity for Electrons

- Just as for phonons the definition of heat capacity is $C = dU/dT$ where U = total internal energy
- For $T << T_F = E_F/k_B$ it is easy to see that roughly $U \sim U_0 + N_{elec} (T/T_F) k_B T$ so that

$C = dU/dT \sim N_{elec} k_B (T/T_F)$

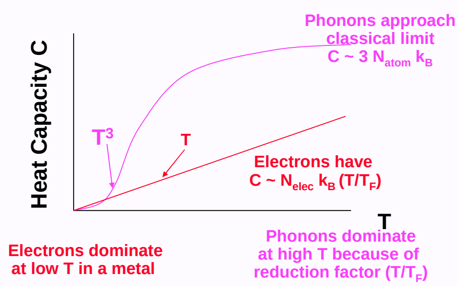


Heat Capacity for Electrons

- Quantitative evaluation:
  $U = \int_0^\infty dE\, E\, D(E)\, f(E) - \int_0^{E_F} dE\, E\, D(E)$
- Using the fact that $T << T_F$:
  $C = dU/dT = \int_0^\infty dE\, (E - E_F)\, D(E)\, (df(E)/dT)$
  $\approx D(E_F) \int_0^\infty dE\, (E - E_F)\, (df(E)/dT)$
- Finally, using transformations discussed in Kittel, the integral can be done almost exactly for $T << T_F$
  $\rightarrow C = (\pi^2/3)\, D(E_F)\, k_B^2\, T$ (valid for any metal)
  $\rightarrow (\pi^2/2)\, (N_{elec}/E_F)\, k_B^2\, T$ (for the electron gas)
  $D(E_F) = 3\, N_{elec}/2E_F$ for gas
- Key result: C ~ T - agrees with experiment!

Heat capacity

- Comparison of electrons in a metal with phonons



Heat capacity

- Experimental results for metals
  $C/T = \gamma + A\, T^2 + \ldots$
- It is most informative to find the ratio γ / γ(free) where γ(free) $= (\pi^2/2)\, (N_{elec}/E_F)\, k_B^2$ is the free electron gas result. Equivalently since $E_F \propto 1/m$, we can consider the ratio $\gamma / \gamma(\text{free}) = m(\text{free})/m_{th}^*$, where m_{th}^* is an thermal effective mass for electrons in the metal

Metal	$m_{th}^*/$ m(free)
Li	2.18
Na	1.26
K	1.25
Al	1.48
Cu	1.38

- m_{th}^* close to m(free) is the “good”, “simple metals” !

Lecture 12 - The Electron Gas

Outline

- Overview - role of electrons in solids
  - Determine binding of the solid
  - "Electronic" properties (conductivity, …)
- The starting point for understanding electrons in solids is completely different from that for understanding the nuclei (But we will be able to use many of the same concepts!)
- Simplest model - Electron Gas
  - Failure of classical mechanics
  - Success of quantum mechanics
  - Pauli Exclusion Principle, Fermi Statistics
  - Energy levels in 1 and 3 dimensions
- Similarities, differences from vibration waves
- Density of States, Heat Capacity
- (Read Kittel Ch 6)

Next time

- Continue free electron gas (Fermi gas)
- Electrical Conductivity
- Hall Effect
- Thermal Conductivity
- (Read Kittel Ch 6)
- Remember: EXAM Wednesday, October 11

Comments on Exam

- Wed. October 11
- Closed Book
  - You will be given constants, etc.
- Three types of problems:
- Short answer questions
- Order of Magnitudes
- Essay questions
- Quantitative problems – not difficult