Engineering Physics (2025)
Course code 25PY101
Unit 2: Quantum theories of solids

Course Instructor:
Dr. Sreekar Guddeti
Assistant Professor in Physics
Department of Science and Humanities
Vignan's Foundation for Science, Technology and Research

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Unit 2 Plan

1. Quantum Free Electron Theory
2. Fermi-Dirac distribution
3. Electronic specific heat of solids
4. Density of states (qualitative)
5. Success and Failures of quantum free electron theory of solids
6. E-k diagram
7. Classification of materials based on bands in solids
8. Fermi level in semiconductors- intrinsic and extrinsic

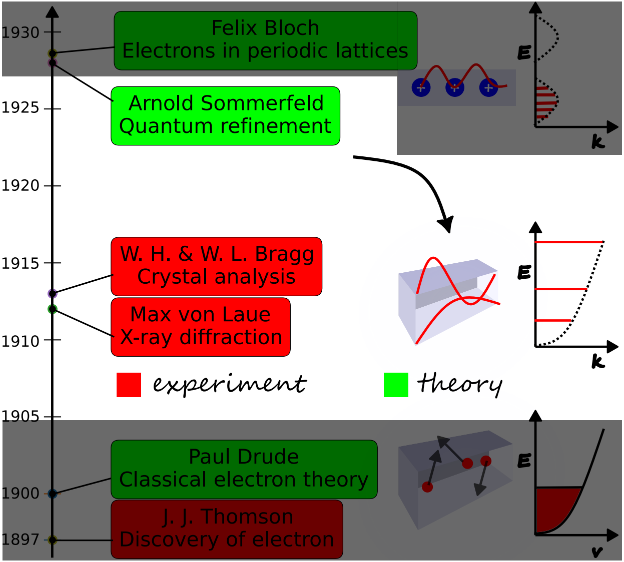
Unit 2 Plan

Summary of Classical free electron theory (CFET)

- Derived $\sigma = \dfrac{ne^2\tau}{m}$.
- Connected microscopic electron properties to macroscopic Ohm's law.
- Classical free electron theory has qualitative and quantitative agreement with experiment values of conductivity.
- However, the theory has drawbacks. Some of them are
  - Incorrect prediction for conductivity vs valency.
  - Cannot explain anomalous sign of Hall coefficient in some metals.
  - Underestimation of mean free path.
  - Cannot explain classification of materials into conductors. semi-conductors and insulators.
  - Wrong prediction of conductivity vs temperature.
  - Overestimation of heat capacity.

Electron theories of metals

1. Classical free electron theory
2. Quantum free electron theory
3. Quantum band theory



Quantum free electron theory

A. Sommerfeld, W. Pauli, E. Fermi, and P. Dirac

- Proposed by Arnold Sommerfeld in 1927.
- Considered the **matter wave nature** of electron.
- Mutual repulsion between electrons is neglected i.e. electrons are independent – **independent electron approximation**.
- Assumed "gas" is **free** i.e. not under influence of lattice – **free electron approximation**.
- Electrons obey the **Pauli exclusion principle**.
- Role of lattice is to redistribute the energy distribution that obeys **quantum** Fermi-Dirac statistics – quantum thermodynamics.
- The electron gas is called Fermi gas.

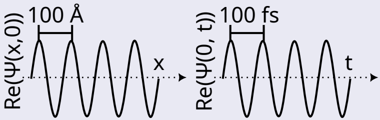
Free electron as a matter wave

Problem

Determine the wave number k, wavelength λ, angular frequency ω and period T of a wave function that describes a thermal electron at room temperature. If it is traveling along $+$ve x direction, write the expression for the wave function.

Problem

The sketches below represent the spatial and temporal parts of wave function of a thermal electron moving along x direction. Determine the temperature.



Key Insight

A matter wave is described by wave vector k and angular frequency ω.

Problem at hand

$$V(r) = +\frac{1}{4\pi\epsilon_0}\frac{1}{r} \qquad V(r) \propto -\frac{1}{r}$$

- The problem at hand is to solve the motion of interacting matter waves– electrons of the order of 10^{23} and ions of the order of 10^{23}.
- This is a tough problem. The idea is to simplify the problem by making **approximations**.

Independent electron approximation

Postulate

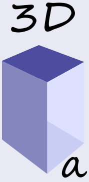
$$\xcancel{V(r) = +\frac{1}{4\pi\epsilon_0}\frac{1}{r}}$$

- Mutual repulsion between electrons is neglected i.e. electrons are independent.

Free electron approximation

Postulate

$$\cancel{V(r) \propto -\frac{1}{r}}$$



$$V(x,y,z) = \begin{cases} 0 & \begin{array}{l} 0 \le x \le a \\ 0 \le y \le a \\ 0 \le z \le a \end{array} \\ \infty & \text{otherwise} \end{cases}$$

- The interaction of electron with ions is neglected i.e. electrons are free.
- The electron is bounded within the metal by 3D infinite potential well.

Pauli's exclusion principle

Postulate

- No two electrons can occupy the same quantum state.
- No two electrons can share the same set of quantum numbers.
- Electron obeys Pauli's exclusion principle since it has spin $\frac{1}{2}$.

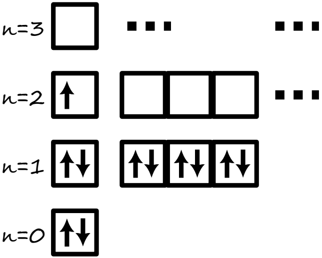
W. Pauli

Definition

A quantum state is defined by a set of quantum numbers.

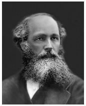
Problem

What quantum state is occupied by valence electron in Na?



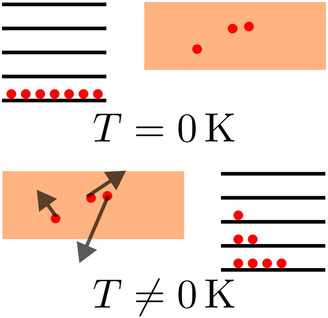
Classical thermodynamics vs Quantum thermodynamics

Boltzmann

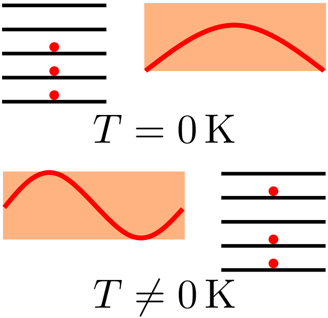


Maxwell

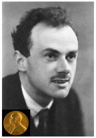
Classical thermodynamics



Quantum thermodynamics



E. Fermi



P. Dirac

- Classical thermodynamics allows electrons to share the same state.
- State is defined by velocity v.
- The occupancy of energy level is governed by Maxwell-Boltzmann statistics.

- Quantum thermodynamics is governed by Pauli exclusion principle and forbids sharing the same state.
- Quantum state is defined by wavevector k.
- The occupancy of energy level is governed by Fermi-Dirac statistics.

Sommerfeld's Quantum Free electron theory – Postulates

Postulates

1. **Waves:** Electrons are quantum waves with wavevector k, angular frequency ω.
2. **Fermion:** Electron is a spin $\frac{1}{2}$ particle and obeys Pauli's exclusion principle.
3. **Independent electron approximation:** Electrons are independent and mutual repulsion between them is ignored.
4. **Free electron approximation:** Electrons are free and move in an infinite potential well.
5. **Quantum Thermodynamics:** The thermalization is governed by Fermi-Dirac statistics.

Quantum states in a cubic box

Consider a particle of mass m confined in a cubic box of side a with infinite walls.

- Wavefunction boundary conditions lead to quantum numbers $n_1, n_2, n_3 \in \{1, 2, 3, \ldots\}$.

$$\psi_{n_1,n_2,n_3}(x, y, z) = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_1 \pi x}{a}\right) \sin\left(\frac{n_2 \pi y}{a}\right) \sin\left(\frac{n_3 \pi z}{a}\right),$$

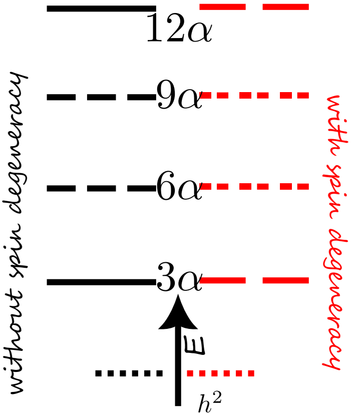
- Energy levels are given by

$$E_{n_1,n_2,n_3} = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right).$$

Quantum state vs Energy level – Degeneracy

In the 3D box, a quantum state is defined by set of three quantum numbers n_1, n_2, n_3.

n_1	n_2	n_3	E_{n_1,n_2,n_3}	degeneracy without spin	degeneracy with spin
1	1	1	$3 \cdot \frac{h^2}{8ma^2}$	1	2
2	1	1	$6 \cdot \frac{h^2}{8ma^2}$	3	6
1	2	1	$6 \cdot \frac{h^2}{8ma^2}$	3	6
1	1	2	$6 \cdot \frac{h^2}{8ma^2}$	3	6
2	2	1	$9 \cdot \frac{h^2}{8ma^2}$	3	6
1	2	2	$9 \cdot \frac{h^2}{8ma^2}$	3	6
2	1	2	$9 \cdot \frac{h^2}{8ma^2}$	3	6
2	2	2	$12 \cdot \frac{h^2}{8ma^2}$	1	2
⋮	⋮	⋮	⋮	⋮	⋮



$$\alpha = \frac{h^2}{8ma^2}$$

Quantum degeneracy

Definition

- Degeneracy is the condition when an energy level has more than one quantum state.
- If n quantum states have same energy level, then degeneracy of the energy level is n.
- Degeneracy is also called multiplicity.

Problem

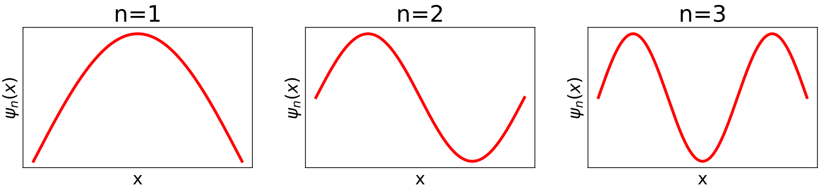
Five free electrons exist in a three dimensional potential well with all three widths equal to $a = 12\,\text{Å}$.

1. *Determine the Fermi energy level at $T = 0\,\text{K}$.*
2. *Repeat part 1 for 13 electrons.*

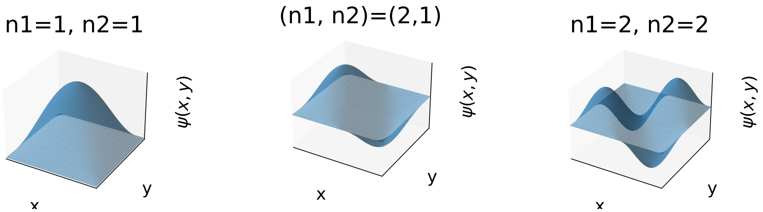
Key Insight

Quantum states can have the same energy level.

Nature of Wavefunctions – 1D, 2D

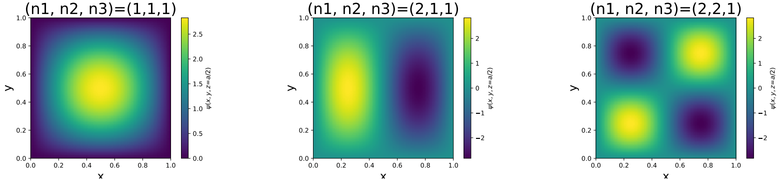


1D wave functions



2D wave functions

Nature of Wavefunctions – 3D Macroscopic atom



3D wave functions

- The above plots are called colormap plots. Each plot is a slice of the wavefunction at $z = \frac{a}{2}$.

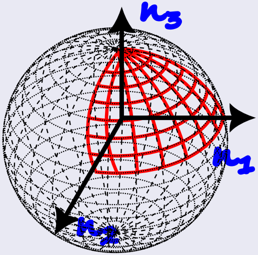
Key Insight

These wavefunctions are similar to s, p, d orbitals of hydrogen atom from chemistry.

Quantum number space

Quantum number space

- A quantum state corresponds to a point with positive integer coordinates (n_1, n_2, n_3) in the **number space**.
- This is an imaginary space.
- Quantum state lies in the positive octant of number space.



- Let us count the number of states up to energy E.
- Define $n \equiv \sqrt{n_1^2 + n_2^2 + n_3^2}$ (radial coordinate in n-space).
- The number of states with n less than some value n_0 equals the number of integer lattice points in the positive octant inside a sphere of radius n_0.
- We count the volume in n-space:

$$N(n \leq n_0) = g \times \frac{1}{8} \times \frac{4}{3}\pi n_0^3 = g\frac{\pi}{6} n_0^3, =$$

Relate n to energy

Using $E = (h^2/8ma^2)n^2$, solve for n:

$$n(E) = \frac{\sqrt{8ma^2E}}{h}.$$

Thus the total number of states with energy less than or equal to E is

$$N(E) \approx g\frac{\pi}{6}n(E)^3 = g\frac{\pi}{6}\left(\frac{\sqrt{8mL^2E}}{h}\right)^3 = g\frac{\pi}{6}\left(\frac{\sqrt{8mE}}{h}\right)^3 L^3.$$

Here, the volume $V = L^3$ and g=2.

Density of states $Z(E) = \frac{d(\frac{N}{V})}{dE}$

Definition

- Density of states $Z(E)$ [a] is defined as the rate of change of the number of states per unit volume upto energy E with respect to energy E.
- Therefore, the the number of states per unit volume from energy E to $E + \mathrm{d}E$ is given by

$$Z(E)\,\mathrm{d}E.$$

[a] In Neamen, density of states is denoted by $g(E)$.

Number of states per unit volume is

$$\rho_N(E) = \frac{N}{V} = \frac{\pi}{3}\left(\frac{\sqrt{8m}}{h}\right)^3 E^{3/2}$$

DOS in textbook form

Differentiate $\rho_N(E)$ with respect to E to get the density of states function:

$$Z(E) = \frac{\mathrm{d}\rho_N(E)}{\mathrm{d}E} = \frac{\pi}{2} \cdot \left(\frac{\sqrt{8m}}{h} \right)^3 E^{1/2}$$

$$Z(E) = \frac{\pi}{2} \cdot 8 \cdot \left(\frac{2m}{h^2} \right)^{3/2} E^{1/2}$$

$$\boxed{\therefore Z(E) = 4\pi \cdot \left(\tfrac{2m}{h^2}\right)^{3/2} E^{1/2}.}$$

Key Insight

For 3D infinite potential, $Z(E) \propto \sqrt{E}$.

Problem

Find the form of $Z(E)$ for 2D infinite potential.

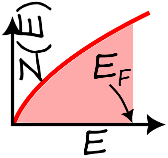
Fermi level

Definition

Fermi level of a metal is the maximum energy that an electron can have at $T = 0\,\mathrm{K}$.

At absolute zero all states are filled up to the Fermi energy E_F. The total electron density n_c (electrons per unit volume) is

$$
\begin{aligned}
n_c = \frac{N}{V} &= \int_0^{E_F} Z(E)\,\mathrm{d}E = 4\pi \cdot \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_F} E^{1/2}\,\mathrm{d}E \\
&= 4\pi \cdot \left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{2}{3} E_F^{3/2} \\
&= \frac{8\pi}{3} \left(\frac{2m}{h^2}\right)^{3/2} E_F^{3/2}.
\end{aligned}
$$



Relating Fermi energy to electron density

Invert the relation to get the Fermi energy as a function of density:

$$E_F^{3/2} = \left(\frac{h^2}{2m}\right)^{3/2} \cdot \frac{3n_c}{8\pi}.$$

$$\boxed{\therefore\ E_F = \tfrac{h^2}{2m}\ \left(\tfrac{3n_c}{8\pi}\right)^{2/3}.}$$

This is the Fermi energy of a free electron gas in three dimensions at $T = 0$.

Problem

Calculate E_F for metal with electron density $n_c = 5.8 \times 10^{28}\,\mathrm{m}^{-3}$.