Foundations of Physics 2B

Condensed Matter Physics

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Lecture 1

1.1 Describing Crystals

- ➤ regular periodic array of atoms - highly defined
- ➤ x-rays discovered in 1912
    - ➥ diffraction of x-rays key to studying crystals
- ➤ crystals classified by certain physical properties
- ➤ a perfect crystal is assumed to be a regular array of repeating points
    - ➥ we can construct a set of theoretical points in 3D (defined by vectors), called a lattice
- ➤ lattice described by unit vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$, called the lattice constants
- ➤ lattice given physical reality by placing atoms at lattice points
    - ➥ these atoms are called a basis - there can be more than one atom in a basis, e.g. NaCl
- ➤ use the relationship, where: $\underline{r}, \underline{r}'$ are points on the lattice; a_i are unit vectors; and n_i are scalar multiples -

$$\underline{r}' = \underline{r} + n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$$

- ➤ it is called a primitive lattice if this equation cannot be reduced
- ➤ think of lattices as 3D constructs for filling space
- ➤ crystals have a high degree of symmetry

1.2 Symmetry Operators

1. translation
2. rotation
3. reflection
4. inversion
5. combinations of above

- ➤ a lattice should remain invariant under specific symmetry operations
- ➤ point operators in 2D lead to 2D lattices, of which you can get different types -
    1. square
    2. hexagonal
    3. rectangular
    4. centred rectangular
    5. oblique parallelogram
    - ➥ cannot get a five-fold symmetry shape

1.3   Three-Dimensional Lattices

➤ there are seven basic crystal systems
  1. triclinic
  2. monoclinic
  3. orthorhombic
  4. tetragonal
  5. rhombohedral (trigonal)
  6. hexagonal
  7. cubic
➤ use parameters to define these -
  ➥ p - primitive
  ➥ i - interstitial
  ➥ f - face-centred
  ➥ c - base-centred
➤ by varying the parameters for each basic type (see table in lecture summary), get 14 Bravais lattices in 3D
  ➥ these are the basic building blocks of all crystals

1.4   Miller Indices

➤ **key concept for categorising crystals**
➤ describe a particular crystallographic plane or orthogonal direction in crystal
➤ effectively describes crystals as families of parallel planes
➤ method for determining the index:
  1. find the intercepts of plane on crystal axes - the three lattice constants
  2. take the reciprocal of these constants
  3. reduce to 3 integers with the same ratio
  4. this gives the index of the plane, using the notation (hkl), or $(\nu_1\nu_2\nu_3)$ in Kittel
  5. if one of the indices is negative, put a bar above the magnitude
➤ separation between planes:

$$d = \frac{1}{\sqrt{\frac{h^2}{a_1^2} + \frac{k^2}{a_2^2} + \frac{l^2}{a_3^2}}}$$

➤ For a cubic, this reduces to

$$d_{hkl} = \frac{a}{\sqrt{N}}$$

Lecture 2

2.1   X-Ray Diffraction

➤ crystal is defined by a set of parallel planes separated by distance d
➤ waves incident on crystals will be diffracted - developed by Bragg and lead to the law of x-ray diffraction
➤ for each wave will experience specular reflection - small reduction in intensity
➤ path length difference $A \to B \to C = 2d\sin\theta$
➤ if path length is equal to an integer multiple of the wavelength of wave, get constructive interference
➤ Bragg Law:

$$2d\sin\theta = n\lambda$$

➤ typically, $\lambda \approx 0.15\,nm$ for x-rays
➤ it is observed that each plane of atoms reflects $10^{-3} - 10^{-5}$ of the intensity
➤ Bragg law is a consequence of periodic structure of crystals
➤ Fourier analysis is used

2.2 Electron Density

➤ crystal lattice is defined by translation vector,

$$\underline{T} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$$

➤ crystal is invariant under $\underline{T}$ translation
➤ many physical properties related to electron density, $n(\underline{r})$
➤ crystal symmetry $\implies n(\underline{r}) = n(\underline{r} + \underline{T})$, local electron environment is also invariant under $\underline{T}$
➤ consider electron density in one dimension:

$$n(x) = n_0 + \sum_p \left[c_p \cos\left(\frac{2\pi x p}{a}\right) + s_p \sin\left(\frac{2\pi x p}{a}\right) \right]$$

➤ $p \in \mathbb{N}$; a = the lattice constant; and x = distance
➤ crystal symmetry also $\implies n(x) = n(x + a)$

2.3 Reciprocal Lattice Points

➤ arguments of sin and cos are called reciprocal lattice points
  ➥ there is a factor of $\frac{2\pi}{a}$ - requires functions to have correct periodicity
  ➥ units - $\cos, \sin$ are dimensionless; $\frac{2\pi p}{a}$ is the basis of summation
  ➥ only certain values are allowed by the relationship above

$$n(x) = \sum_p n_p e^{\frac{i2\pi p x}{a}}$$

➤ allowed points in sin() and cos() are equivalent to families of planes described by Miller indices (hkl)
➤ in 3D:

$$n(\underline{r}) = \sum_G n_G e^{\underline{G}\cdot\underline{r}}, \ G = \text{reciprocal lattice vectors}$$

➤ G is defined as the family of reciprocal lattice points in 3D - each describing a family of crystal planes
➤ b_1, b_2, b_3 are the reciprocal lattice unit vectors, units of frequency

$$b_1 = 2\pi \frac{\underline{a}_2 \times \underline{a}_3}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)} \ ; \ b_2 = 2\pi \frac{\underline{a}_3 \times \underline{a}_1}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)} \ ; \ b_3 = 2\pi \frac{\underline{a}_1 \times \underline{a}_2}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)}$$

➤ a_i are unit vectors of crystal
➤ $a_i \cdot b_j = 2\pi \delta_{ij}$ - delta function

$$\underline{G} = \nu_1\underline{b}_1 + \nu_2\underline{b}_2 + \nu_3\underline{b}_3$$
$$n(\underline{r} + \underline{T}) = \sum_G n_G e^{i\underline{G}\cdot\underline{r}} \underbrace{e^{i\underline{G}\cdot\underline{T}}}_{2\pi \times p}$$

Lecture 3

3.1 X-Ray Diffraction

➤ incident electromagnetic wave on crystal - $\exp[9(\underline{k} \cdot \underline{r})]$
  ➥ $\underline{k}$ is the wavevector of the x-ray
➤ elastic process - conservation of energy
➤ assume interaction between electric field of wave and electrons in atom
➤ electron density - $n(\underline{r})$

➤ scattered wave is described by

$$F = \int n(\underline{r}) \exp\left[i((\underline{k} - \underline{k}') \cdot \underline{r})\right] \, dV$$

$$= \int n(\underline{r}) \exp\left[i(\Delta\underline{k} \cdot \underline{r})\right] \, dV$$

➤ $\Delta\underline{k} = \underline{k} - \underline{k}'$
➤ elastic scattering - $|\underline{k}| = |\underline{k}'|$
➤ $\Delta\underline{k}$ - scattering vector
  ➥ for Bragg condition - $\Delta\underline{k} = \underline{G}$

$$F = \sum_G \int n_G \exp\left[i(\underline{G} - \Delta\underline{k}) \cdot \underline{r}\right]$$

➤ alternative formulation of Bragg condition -

$$\underline{k} + \underline{G} = \underline{k}'$$
$$\implies (\underline{k} + \underline{G})^2 = |\underline{k}|^2$$
$$2\underline{k} \cdot \underline{G} + |\underline{G}|^2 = 0$$
$$\implies 2\underline{k} \cdot \underline{G} = |\underline{G}|^2$$

➤ n.b. $\Delta\underline{k}$ has equivalent positive and negative values

3.2 Brillouin Zones

➤ analogy to unit cells in reciprocal space
➤ first Brillouin zone is Wigner-Seitz primitive cell in reciprocal lattice
  ➥ used to describe a wide range of physical properties
➤ construct Brillouin zone:
    1. select origin in reciprocal space
    2. draw reciprocal lattice vector to all nearest neighbours
    3. perpendicular bisectors enclose first Brillouin zone

Examples of Reciprocal Lattices

➤ simple cubic lattice:

$$\underline{a}_1 = a\hat{x} \qquad\qquad \underline{a}_2 = a\hat{y}, \qquad\qquad \underline{a}_3 = a\hat{z}$$
$$\underline{b}_1 = \frac{2\pi}{a}\hat{x} \qquad\qquad \underline{b}_2 = \frac{2\pi}{a}\hat{y} \qquad\qquad \underline{b}_3 = \hat{z}$$

➤ reciprocal lattice is a simple cube with lattice constant $\frac{2\pi}{a}$
➤ body centred cubic lattice:

$$\underline{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) \qquad \underline{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) \qquad \underline{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$
$$\underline{b}_1 = \frac{2\pi}{a}(\hat{y} + \hat{z}) \qquad\qquad \underline{b}_2 = \frac{2\pi}{a}(\hat{x} + \hat{z}) \qquad\qquad \underline{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y})$$

➤ these are primitive lattice vectors of fcc (face centre cubic) lattice
➤ similarly, reciprocal of fcc lattice is bcc lattice

3.3 Structure Factor

➤ structure factor describes intensity of Bragg peaks
  ➥ arises because Bragg law considers parallel planes but can also get interference within unit cell

➤ integral over unit cell describes total scattered intensity

$$F_G = N \int_{cell} n(\underline{r}) \exp\left[-i\underline{G} \cdot \underline{r}\right] = NS_G$$

➤ N is the total number of cells; S_G is the structure factor for a single cell
➤ define origin at $\underline{r} = 0$
➤ consider $n(\underline{r})$ as sum over all unique atoms in unit cell

$$n(\underline{r}) = \sum_{j=1}^{S} n_j(\underline{r} - \underline{r}_j)$$

$$S_G = \sum_j \exp\left[-i\underline{G} \cdot \underline{r}\right] \int n_j(\underline{\rho}) \exp\left[-i\underline{G} \cdot \underline{\rho}\right]$$

$$= \sum_j f_j \exp\left[-i\underline{G} \cdot \underline{r}_j\right]$$

$$S_G(\nu_1\nu_2\nu_3) = \sum_j f_j \exp\left[-i2\pi(\nu_1 x_j + \nu_2 y_j + \nu_3 z_j)\right]$$

➤ $\underline{\rho} = \underline{r} - \underline{r}_j, \underline{r}_j$ is position of unique atom in unit cell; f_j is atom form factor scattering of one atom
➤ $\nu_1\nu_2\nu_3 = hkl$ describing Bragg peak; (x_j, y_j, z_j) is position coordinates within unit cell
➤ for bcc lattice - have two unique atoms at coordinates $(000), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
➤ evaluate $S_G \implies S = 0$ when $\nu_1 + \nu_2 + \nu_3 =$ odd integer; $S = 2f$ when $\nu_1 + \nu_2 + \nu_3 =$ even integer
➤ fcc lattice - 4 atoms $(0, 0, 0), (0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0)$
  ➥ $S = 0$ when integers mixed
  ➥ $S = 4f$ when integers all odd or all even

Lecture 4

4.1 Crystal Bonding

➤ bonding is a stable equilibrium between attractive and repulsive force
➤ repulsive arises from electrons being fermions
  ➥ no two fermions occupy the same quantum state
  ➥ as electrons from adjacent atoms overlap, increases energy to satisfy Pauli exclusion principle
➤ different types of bonds have different attractive forces:

1. Van Der Waals bonding exists in almost all solid system - very weak force, usually only observed at low temperatures in noble gases
   ➤ attraction is between electric dipoles
     (a) permanent
     (b) permanent-induced
     (c) two induced dipoles
   ➤ spherically symmetrical atom - when brought closer to another atom, electron distribution adjusts because of Coulomb potential
   ➤ can consider movement of charge as electric dipole:
     ➥ amount of charge, q, moving distance, L, $\rightarrow$ dipole moment $= p = qL$
     ➥ electric dipole consists of charge $+q$ and $-q$ separated by L
     ➥ at arbitrary point, electric potential

$$V = \frac{Q}{4\pi\epsilon_0}\left(\frac{1}{r_b} - \frac{1}{r_a}\right)$$

     ➥ it can be shown that

$$V(r) = \frac{\underline{p} \cdot \hat{r_1}}{4\pi\epsilon_0 r^2}$$

➦ where $\underline{p}$ is the electric dipole vector, and $\hat{r}_1$ is the unit vector along $\underline{r}$
➦ show potential energy and force are

$$U(r) = \frac{A}{r^6}$$

$$F(r) = -\frac{dU}{dr} = \frac{A}{r^7}$$

➤ modelling Pauli repulsion - very complex
  ➦ approximate using empirical function
  ➦ experimental data on solid gases shows that the function is of the form $\frac{B}{r^{12}}$ fits data

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

  ➦ this is the Lennard Jones $6 - 12$ potential - models interatomic potential in Van Der Waals solids
    ➡ $4\epsilon\sigma^6 \equiv A$
    ➡ $4\epsilon\sigma^{12} \equiv B$
2. other examples of bonding
   (a) ionic bonding - crystals made of positive and negative energy
       ➤ many salts are under this (NaCl, LiF, MgCl)
       ➤ overall energy of ionic crystal - ionisation energy, electron affinity
       ➤ energy - electrostatic attraction

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

       ➤ this considers only nearest neighbours
       ➤ in ionic crystals, energy must also consider other ions - not just nearest neighbours
       ➤ interaction of all ions described by modelling constant
         ➦ face centred cube crystal has modelling constant of 1.7475
   (b) covalent crystals - sharing of electrons, generally occurs in systems of similar atoms (e.g. silicon semiconductor, diatomic gases)
       ➤ covalent bonding can only be described using QM
       ➤ two electrons, spin $= \frac{1}{2}$
         ➦ $\uparrow\downarrow \rightarrow S = 0$ - spin antisymmetric
         ➦ $\uparrow\uparrow \rightarrow S = 1$ - spin symmetric
         ➦ when spin is antisymmetric, position (wavefunction) is symmetric or vice versa
         ➦ large electron density between atoms - forms a bond

Lecture 5

➤ consider crystals as system of vibrating atoms
➤ family of excitations in solids, elastic waves - phonons
➤ range of phenomena suggests atoms vibrate
➤ describe crystal as series of parallel planes denoted by $s, s \pm 1, s \pm 2, \cdots$
➤ describe position of plane using coordinate $u_s, u_{s\pm1}, \cdots, u_s$ is the displacement from the equilibrium
➤ longitudinal and transverse waves exist
➤ physics to describe motion?
  ➦ Hooke's law - elastic wave, restoring force, linear function of u_S
➤ energy of oscillating system:

$$E = \frac{1}{2}kA^2$$

➤ spring constant - $\omega = \sqrt{\frac{k}{m}}$
➤ elastic energy is a quadratic function of displacement from mean position

➤ need to know the force exerted on individual planes
➤ *assume only nearest neighbour interactions apply*
➤ forces acting on plane s:

$$F_s = c(u_{s+1} - u_s) + c(u_{s-1} - u_s)$$

➤ c is a force constant for the nearest neighbour

$$M \frac{d^2 u_s}{dt^2} = c(u_{s+1} + u_{s-1} - 2u_s)$$

➤ Assume SHM:

$$\frac{d^2 u_s}{dt^2} = -\omega^2 u_s$$

➤ Equation relates motion of planes:

$$-M\omega^2 u_s = c(u_{s+1} + u_{s-1} - 2u_s)$$

➤ by substitution, the general form of equation is:

$$u_{s\pm 1} = U \exp\left[i(s \pm 1)ka\right] = U \exp\left(iska\right) \exp\left(\pm ika\right)$$

➤ U is the maximum amplitude, k is the wavevector of the elastic wave, and a is the spacing of adjacent planes

$$-\omega^2 M u \exp\left(iska\right) = CU \left\{\exp\left[i(s+1)ka\right] + \exp\left[i(s-1)ka\right] - 2\exp\left[iska\right]\right\}$$

$$\omega^2 M = -C\left[\exp(ika) + \exp(-ika) - 2\right]$$

$$\omega(k)^2 = \left(\frac{2c}{M}\right)(1 - \cos(ka))$$

$$\omega(k)^2 = \frac{4c}{M} \sin^2\left(\frac{1}{2}ka\right)$$

$$\implies \omega(k) = \sqrt{\frac{4c}{M}} \left|\sin\left(\frac{1}{2}ka\right)\right|$$

➤ angular frequency depends on the wavevector - phenomena is known as dispersion
➤ waves of certain wavelength or wavevector travel at different velocities

5.1 Group Velocity

➤ consider displacement of planes as a packet of elastic energy propagating through a crystal (phonons)

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

➤ velocity is related to the gradient of $\omega(k)$ dispersion curve

$$v_g = \sqrt{\frac{Ca^2}{M}} \cos\left(\frac{1}{2}ka\right)$$

➤ low wavevector waves have higher velocity, waves at boundary of Brillouin zone have zero velocity

5.2 Long Wavelength Limit

➤ applies to waves $k \approx 0$, defined by $ka \ll 1$
➤ this corresponds to sound waves in crystal
➤ when $ka \ll 1 \rightarrow \cos(ka) = 1 - \frac{1}{2}(ka)^2$
➤ dispersion relation (long wavelength):

$$\omega^2 = \left(\frac{c}{M}\right)k^2 a^2$$

$$\omega = \sqrt{\frac{c}{M}} ka$$

➤ $\omega \propto k$ at long wavelengths

Lecture 6

➤ consider two atom basis in phonon model - e.g. salts (NaCl), semiconductors (GaAs), etc
➤ use same equation of motion with M_1 and M_2 masses and $U_{s,s\pm1\cdots}, V_{s,s\pm1\cdots}$

$$M_1\frac{d^2U_s}{dt^2} = c(V_s + V_{s-1} - 2U_s) \; ; \; M_2\frac{d^2V_s}{dt^2} = c(U_{s+1} + U_s - 2V_s)$$

➤ solutions is SHM - travelling wave, different amplitudes on adjacent planes u_s, v_s
➤ we define a as the distance between identical planes (M_1 or M_2)

$$U_s = U\exp(isKa)\exp(-i\omega t) \; ; \; V_s = V\exp(isKa)\exp(-i\omega t)$$

➤ substitute travelling wave into equation of motion

$$-\omega^2 M_1 U = cv[1 + \exp(-iKa)] - 2cu$$
$$-\omega^2 M_2 V = cu[1 + \exp(iKa)] - 2cv$$

➤ only solution obtained from determinant of matrix equation

$$\begin{vmatrix} 2c - M_1\omega^2 & -c[1 + \exp(iKa)] \\ -c[1 + \exp(iKa)] & 2c - M_2\omega^2 \end{vmatrix} = 0$$

$$M_1 M_2 \omega^4 - 2c(M_1 + M_2)\omega^2 + 2c^2(1 - \cos(Ka)) = 0$$

$$\frac{c(M_1 + M_2)}{M_! M_2} \pm \frac{C(M_1 + M_2)}{M_1 M_2}\sqrt{1 - 2\frac{M_1 M_2(1 - \cos(Ka))}{(M_1 + M_2)^2}} = \omega^2$$

➤ solution gives two branches in phonon dispersion relation
➤ consider two limits to illustrate general behaviour
  1. when $Ka \ll 1$ - long wavelength limit
  2. $K = \pm\frac{\pi}{a}$ - boundary of first Brillouin zone
➤ for small Ka (long wavelength limit), $\cos(Ka) \approx 1 - \frac{1}{2}K^2a^2$
➤ two solutions of dispersion:

$$\omega^2 \approx 2c\left(\frac{1}{M_1} + \frac{1}{M_2}\right)$$

$$\omega^2 \approx \frac{\frac{1}{2}c}{M_1 M_2}K^2a^2$$

  1. ω is independent of K in the optical branch
     ➥ two atoms out of phase
  2. $\omega \propto K$ in the acoustic branch
     ➥ two atoms move in phase

6.1 Thermal Properties of Crystals

➤ phonon heat capacity:

$$C_V = \left(\frac{dU}{dT}\right)_V$$

➤ C_V used because no work done to change volume
➤ U is the total internal energy of the vibrating lattice

$$U_{tot} = \sum_k\sum_p U_{kp} = \sum_k\sum_p \langle n_{kp}\rangle\hbar\omega_{kp}$$

➤ where k is the wavevector, and p is the polarisation, and $\langle n_{kp}\rangle$

➤ $\langle n_{kp} \rangle$ described by Planck distribution function:

$$n = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

➤ number of vibrational nodes is called the density of states - number of vibrations per unit energy

$$D(\omega) = \frac{dN}{d\omega} = \left(\frac{vK^2}{2\pi^2}\right)\left(\frac{dK}{d\omega}\right)$$

➤ number of phonon nodes in a given frequency or energy range

6.2 Debye Model

➤ assumption is that velocity of sound is constant
➤ Debye model dispersion relation: $\omega = vK$
➤ density of states goes to

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3} \ ; \ D(\omega) \propto \omega^2$$

➤ maximum frequency range is Debye frequency:

$$\omega_D^3 = 6\pi^2 v^3 \frac{N}{V}$$

➤ corresponds to Debye wavevector:

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

6.3 Einstein Model

➤ assumes all phonons have the same frequency or energy

$$U = N\langle n \rangle \hbar\omega = \frac{N\hbar\omega}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}$$

➤ N is the total number of oscillators

Lecture 7

7.1 Electrical Properties of Crystals from Classical Physics

➤ assumptions:
  1. outer valence electrons are detached - free to move through the crystal
  2. electric field due to other electrons and nucleus cancel out
➤ Drude model - applied kinetic theory of gases to electrons

1. specific heat capacity of electrons
  ➤ Mean kinetic energy $E = \frac{3}{2}k_B T$
  ➤ specific heat capacity per electron: $C_V = \frac{dE}{dt} = \frac{3}{2}k_B$
2. electrical conductivity
  ➤ begin with Ohm's Law, $V = IR$
  ➤ rewrite in dimensionless form, $E = \rho J$
  ➤ $J = \sigma E$
  ➤ Drude model assumes electrons collide with something
  ➤ describe using a mean time between collision events τ
  ➤ equations of motion $\underline{v} = \underline{v_0} - \frac{|e|tE}{m_e}$
  ➤ electron velocity v_0 is random - no overall contribution

➥ considers only drift velocity in response to $\underline{E}$
➥ electron drift velocity is average of $-\frac{|e|tE}{m_e}$

$$\underline{\bar{v}} = -\frac{|e|\bar{t}\underline{E}}{m_e}, \ \bar{t} = \tau$$

$$\underline{J} = -n|e|\underline{v} = \frac{n|e|^2\tau}{m_e}\underline{E}$$

$$\implies \sigma = \frac{n|e|^2\tau}{m_e}$$

➤ this is the Drude electrical conductivity formula

3. thermal conductivity of electrons
  ➤ temp gradient $\frac{dT}{dz}$
  ➤ assume electron is in thermal equilibrium at point of collision
  ➤ consider thermal energy carried by the electron
  ➤ thermal average is $v_z^2 = \frac{k_B T}{m_e}$

$$Q = -nv_z c_V v_z \tau \frac{dT}{dx}$$

$$= -\kappa \frac{dT}{dz}$$

$$\kappa = \frac{3}{2}n\frac{k_B^2 T}{m_e}\tau$$

➤ comparison with ratio of thermal to electrical conductivity

$$\frac{\kappa}{\sigma} = \frac{3}{2}\left(\frac{k}{e}\right)^2 T$$

Lecture 8

8.1 Free Electron Model

Assumptions:

1. outer valence electrons detach - free to move around crystal
2. effects of ions and electrons cancel - electrons move in region of no potential

➤ free electron model treats metal as empty box (zero potential) of dimensions (L_x, L_y, L_z)
  ➥ inside the box, zero potential
  ➥ outside the box, infinite potential

Periodic Boundary Conditions
➤ boundary used in this model - consequence of periodicity of crystals

$$\psi(\underline{r}) = \psi(\underline{r} + \underline{L}), \underline{L} = (L_x, L_y, L_z)$$

➤ wavefunction is assumed to be periodic with dimensions of sample space, $\underline{L}$
➤ this removes any limitation on the value of $\underline{r}$

$$\psi(x, y, z) = \psi(x + L_x, y, z) + \psi(x, y + L_y, z) + \psi(x, y, z + L_z)$$

Free Electron Wavefunction
➤ potential inside box is zero, so time-independent Schrodinger is

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

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$$\psi(x, y, z) = A \exp\left[i(k_x x + k_y y + k_z z)\right], k_i = \frac{2\pi(l/m)}{L_i}$$

$$E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right)$$

➤ electron energy eigenstates are stationary (independent of time)
➤ amplitude A is constant, uncertainty in position coordinate, all energy states overlap

k-space

➤ reciprocal space
➤ can describe electrons using k-coordinate
➤ each electron has coordinate (k_x, k_y, k_z) in k-space, separated by $\frac{2\pi}{l}$ in each dimension
➤ allowed points form mesh in k-space - each within a volume $\left(\frac{2\pi}{L}\right)^3$
  ➥ "exclusion zone"
  ➥ no other allowed k-states within the volume
➤ each k-state has 2 electron spin degeneracy - Pauli exclusion principle
➤ allowing for spin, we have

$$2 \div \left(\frac{2\pi}{L}\right)^3 = \frac{L^3}{4\pi^3}$$

Fermi Energy and Surface

➤ maximum energy of system
➤ define Fermi energy as highest occupied energy level when system is in ground state (0 Kelvin)

$$E = \frac{\hbar^2 k^2}{2m_e}$$

➤ surface of constant energy is constant, k^2
➤ Fermi surface is a sphere of radius k_F
➤ $\frac{L^3}{4\pi^3}$ electron states per unit volume, so volume of sphere is $V = \frac{4}{3}\pi k_F^3$
➤ total number of electrons:

$$N = \left(\frac{4}{3}\pi k_F\right)^3 \left(\frac{L^3}{4\pi^3}\right)$$

$$k_F = \left(\frac{3N\pi^2}{L^3}\right)^{1/3} = (3\pi^2 n)^{1/3}, n = \text{ electron density}$$

$$E_F = \frac{\hbar^2}{2m_e} k_F^2 = \frac{\hbar^2}{2m_e}(3\pi^2 n)^{2/3}$$

Density of States

➤ number of electron energy states per unit energy range
➤ consider volume of k-space between k and $k + \delta k$:
  ➥ volume is surface area $\times \delta k = 4\pi k^2 \delta^2$
➤ number of states between k and $k + \delta k \rightarrow$

$$n(k)\delta k - \frac{L^3}{4\pi^3}4\pi k^2 \delta k$$

➤ express energy:

$$n(E)\delta E = \frac{L^3}{\pi^2}k^2 \delta k \implies n(E) = \sqrt{2}\frac{L^3}{\pi^2}\frac{n_e^{3/2}}{k^3}\sqrt{E}$$

Lecture 9

9.1 Fermi-Dirac Distribution

➤ Fermi energy is energy of highest occupied state at 0 Kelvin (overall ground state)
➤ Fermi function describes occupation of energy levels
➤ at 0 Kelvin, states above E_F are empty $f = 0$, states below E_F are occupied $f = 1$
➤ define an occupation number:

$$f(E) = \begin{cases} 1 & 0 < E \leq E_F \\ 0 & E > E_F \end{cases}$$

➤ can be considered a continuous distribution function

$$N = \int_0^{E_F} n(E)dE = \int_0^i nftyf(E)n(E)dE$$

➤ consider how function varies with temperature - energy range covering transition from $f = 1$ to $f = 0$ is broadened out at finite temperatures
➤ this is described by the Fermi-Dirac distribution function - derived by considering 3 constraints:
  1. Conservation of Energy
  2. Conservation of Particle Number
  3. Subject to Pauli Exclusion principle

$$f(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]}$$

➤ this is a normalised statistical distribution function
➤ describes the probability of energy state E being occupied by an electron

Behaviour of Fermi-Dirac Function

➤ at low temperatures, $k_B T \ll E_F$

1. when $E < E_F \rightarrow \frac{E - E_F}{k_B T} \rightarrow$ large and negative
2. when $E > E_F \rightarrow \frac{E - E_F}{K_B T} \rightarrow$ large and positive, $f(E) \approx 0$
3. when $E \approx E_F$, transition from $f(E) = 1 \rightarrow f(E) = 0$ occurs over narrow energy range around E_F - width is about $k_B T$ on each side of E_F

➤ in systems with low densities of electrons, $f(E) \ll 1$
  ➥ approximation, when $E_F \ll k_B T$:

$$f(E) \approx \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right] \approx \exp\left(-\frac{E}{k_B T}\right)$$

  ➥ this behaves like the classical system, very low E_F

Free Electron Heat Capacity

➤ can determine the electronic specific heat capacity using free electron model
➤ what happens when temperature is increased?
➤ only small proportions of electrons will increase their energy - those that are within $k_B T$ of E_F
➤ we require am empty electron state for the excited electron to move to
➤ electrons within region $k_B T$ of E_F will absorb thermal energy
➤ assume number of electrons with energy close to E_F is given by $n(E_F)k_B T$
➤ extra energy acquired by electron is $k_B T$

$$U(T) - U(0) = n(E_F)(k_B T)^2 - \text{ only for electrons}$$

➤ $n(E_F)$ is the density of states at Fermi energy

$$C_V = \frac{dU}{dT} \approx 2n(E_F)k_B^2 T$$

➤ note that this assumes $n(E_F)$ is constant over energy range

$$n = \frac{(E_F 2m_e)^{3/2}}{3\pi^2 \hbar^3}$$
$$N = n(E_F)E_F V$$
$$n(E_F) = \frac{3}{2}\frac{N}{E_F}$$
$$C_V \approx \frac{3}{2}k_B T \left(\frac{2k_B T}{E_F}\right)$$

➤ specific heat capacity is modified from classical value by bracketed factor
➤ electronic specific heat capacity is proportional to temperature

Lecture 10

10.1 Magnetic Properties of Free Electrons

➤ Free electron model can predict magnetic properties
➤ how does metal respond when placed in magnetic field?

Magnetic Susceptibility of Metals
➤ metals develop an induced magnetic moment in magnetic fields
➤ interactions between B-field and electron spin
➤ it is known all materials show a weak paramagnetism which is independent of temperature
   ➥ this is parallel to applied field
➤ use free electron model to demonstrate this observed effect
➤ electrons have a magnetic moment due to spin:

$$\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}\, J\,T^{-1}$$

➤ energy of electron will change in field by $\pm\mu_B$ depending on spin
➤ assume equal numbers of $\pm$ spin for electrons
   ➥ parallel
   ➥ anti-parallel
➤ when B field applied:
   ➥ half of electrons increase energy by:

$$+\frac{e\hbar}{2m_e}B \text{ - antiparallel}$$

   ➥ half of electrons reduce energy by:

$$-\frac{e\hbar}{2m_e}B \text{ - parallel}$$

➤ total energy of system can be reduced if some electrons reverse spins
➤ a proportion of electrons with antiparallel spins can reverse spins to reduce overall energy
➤ how many electrons reverse spin?
   ➥ need to have the same Fermi energy for spin up and spin down electrons
➤ density of states function evaluated at E_F multiplied by change in energy gives number of electrons
➤ number of electrons within $\mu_B B$ of the original Fermi energy: $ne = \frac{1}{2}n(E_F)\mu_B B$
➤ difference in population: $n(E_F)\mu_B B$ - number of electrons with spin up increased by this amount

➤ net magnetic moment: $n(E_F)\mu_B^2 B$ - produces net magnetic moment per unit volume

$$M = \frac{\mu_B^2 B n(E_F)}{V}$$

➤ paramagnetic susceptibility, a measure of how easy it is to magnetise system:

$$\chi = \frac{\partial M}{\partial H}, H = \frac{M}{\mu_0}\chi \qquad\qquad = \mu_0\mu_B^2 \frac{n(E_F)}{V}$$

➤ this is called the Pauli Paramagnetism - it is independent of temperature
➤ at finite temperatures, temperature dependence of Fermi distribution will lead to a small temp dependence

10.2   Hall Effect

➤ observed in 1879
➤ consider current density, j, flowing along bar in x direction:
➤ apply perpendicular magnetic field, B
➤ electrons experience Lorentz force - $F = e(v \times B + E)$
➤ electrons are pushed to one side of metal bar by this force
➤ electric field will compensate for motion due to Lorentz force - $eE_y = -F \implies E_y = -v \times B$
➤ current density, $j = nev$

$$E_y = -\frac{1}{ne}j \times B, \frac{1}{ne} = R_H$$

➤ R_H is the Hall coefficient
➤ the sign of the Hall coefficient shows the charge on the carriers
　➥ some metals, however, have positive Hall coefficient

Lecture 11

11.1   Nearly Free Electron Model

➤ free electron model - ignored some interactions:
　　1. electron-atoms - free electron approximation
　　2. electron-electron - independent electron approximation
➤ nearly free electron model includes electron-atom interactions
➤ failures of free electron model:
　➥ temperature dependence of conductivity
　➥ some metals have a positive Hall coefficient
➤ interaction between electrons and crystal lattices?
　➥ lattice $\underline{R} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$, where $\underline{a}_1, \underline{a}_2, \underline{a}_3$ are lattice vectors

11.2   Bloch Theorem

➤ this is a consequence of periodic properties of crystals
　➥ provides insights into behaviour of electrons in periodic potential Bloch states
　➥ describes electrons moving in periodic potential
➤ consider a 10 crystal (line of atoms). $\psi(x)$ is solution satisfying time-independent Schrodinger equation
　➥ Schrodinger equation has periodic potential $V(x)$ representing atoms
　➥ energy eigenvalues, σ
➤ Schrodinger equation evaluated at $(x + R)$ must give same solution as as (x)
　➥ local electronic environment at x and $x + R$ are identical
　➥ have second solution $\phi(x)$ which also satisfies the Schrodinger equation with energy E
　➥ Assume ψ and ϕ are unique solutions, can write $\phi(x) = \psi(x + R)$

- ➥ R is lattice vector $= na$
- ➥ $\psi(x + R) = c(R)\psi(x)$ where $c(R)$ is a constant equal to 1
- ➤ using series of lattice translations, $c(R_1 + R_2) = c(R_1)c(R_2)$
  - ➥ therefore $c(nR) = [c(R)]^n,\ n \in \mathbb{N}$
- ➤ wavefunction must satisfy boundary conditions (periodic over M lattice translation where $Ma = l$, the length of 10 crystals)
- ➤ Bloch theorem brings together two requirements to satisfy both periodic bonding conditions and lattice translation by $n_1 a_1$ where n_1 is an integer
- ➤ from this we have $\psi(x + Ma) = \psi(x) \implies [c(a)]^M = 1$
  - ➥ a functions that satisfies replacement for $c(a) = \exp[ika]$, where $ka = \frac{2\pi l}{M}$ $(l \in \mathbb{Z})$
- ➤ for any lattice translation, $\underline{R} = m\underline{a}$ $(m \in \mathbb{Z}, \underline{a}$ is lattice constant)
  - ➥ $c(R) = [c(a)]^M \equiv \exp[iMka] = \exp[ikR], R = \frac{2\pi l}{L}$ - $l \in \mathbb{Z},$ L is the total dimension of sample
- ➤ these statements set out Bloch's theorem - they explain the difference between free electron and nearly free electron models
- ➤ free electron model $\psi(x) = C\exp[ikx]$ - plane wave with constant energy E, k is the electron wavevector
- ➤ nearly free electron model $\psi(x + R) = C\exp[ik(x + R)] = C\exp[ikR]\psi(x) = Cu_k(R)\psi(x),\ u_k(R)$ is the Bloch function
- ➤ the Bloch theorem tells us that nearly free electron wavefunctions (weak periodic potential) are composed of two parts:
  1. plane wave free electron behaviour, $C\exp[ikx]$
  2. modulated in intensity by Bloch function, $u_k(R)$, has periodicity of lattice
  - ➥ fundamental nature of ψ is still free electron behaviour, but with a modification

Consequences of Bloch Theorem
- ➤ adding multiples of $\frac{2\pi}{a}$ to Bloch wavevectors does not alter solution ψ
  - ➥ only k values in $\frac{2\pi}{a}$ range are physically distinct
  - ➥ all other values can be mapped into unique range
- ➤ convention is to define this as $-\frac{\pi}{a} \to \frac{\pi}{a}$
  - ➥ this corresponds to the first Brillouin zone

Energy Band Diagrams
- ➤ shows electron behaviour in terms of energy and wavevector - free electron model $E = \frac{\hbar^2 k^2}{2m_e}$
- ➤ branches of $E(k)$ curve are moved into first Brillouin zone

Lecture 12

12.1 Nearly Free Electron Energy Bands

- ➤ physical origin of energy gaps and energy bands:
  1. Bragg reflection - electron waves can scatter from planes of atoms. Weak periodic potentiation Schrodinger equation. Gives corresponding values for energy gaps at $k = \frac{n\pi}{a}$
  2. interference at certain wavelengths, get interference between electron waves and atoms

Energy Bands
- ➤ describe relationship between energy and wavevector
- ➤ electrons of different 'k' propagate at different velocities - dispersion
- ➤ travelling wave group velocity: $v_g = \frac{d\omega}{dk}$
- ➤ For electron: $v_g = \frac{1}{\hbar}\frac{dE(k)}{dk}$

➤ velocity of Block electrons (know $E = \frac{\hbar^2 k^2}{2m_e}$). This gives:

$$v_g = \frac{1}{\hbar} \frac{d}{dk} \left(\frac{\hbar^2 k^2}{2m_e} \right) = \frac{\hbar k}{m_e} = \frac{p}{m} = vk$$

➤ $\hbar k$ *is the crystal momentum*
➤ crystal momentum is the momentum an electron has as a result of interacting with periodic potential
➤ exhibits different physical parameters

Current Carried by Energy Bands

➤ we know that the current density is $j = ne\langle v \rangle$, where $n \equiv$ electron density, $\langle v \rangle \equiv$ average velocity

$$\langle v \rangle = \frac{1}{\hbar} \int_{k=-\frac{\pi}{a}}^{k=\frac{\pi}{a}} \frac{dE}{dk} dk \frac{a}{2\pi}$$

➤ consider $k = \frac{\pi}{a}$ nd $k = -\frac{\pi}{a}$, these are physically equivalent states (from Block theorem)
  ➥ tells us that $E\left(\frac{\pi}{a}\right) = 0 = E\left(-\frac{\pi}{a}\right)$
$$\langle v \rangle = \frac{a}{2\pi\hbar} \left[E\left(\frac{\pi}{a}\right) - E\left(-\frac{\pi}{a}\right) \right] = 0$$

➤ above implies average velocity of fulled energy band is zero, as is current density
➤ completely filled energy band carries no electrical current (insulators)
➤ current carried by partially filled bands (metals or semiconductors)

12.2 Equation of Motion for Bloch Electrons

➤ consider force F applied to electron - $Fv_g =$ rate of work being done

$$Fv_g = \frac{dE}{dt} = \frac{dE}{dk} \times \frac{dk}{dt}$$
$$v_g = \frac{1}{\hbar} \frac{dE}{dk} \implies F = \hbar \frac{dk}{dt}$$

➤ can predict how electron will respond in electric field

12.3 Effective Mass

➤ electrons in Bloch states move as though the mass of electron is different form free electron masses
➤ consider $E(k)$ relationship near band edge at $k = k_0$ where $\frac{dE}{dk} = 0$ (i.e. zero group velocity)
➤ general form given by $E = E(k_0) + \frac{1}{2}A(k - k_0)^2$
➤ group velocity: $v_g(k) = \frac{A(k-k_0)}{\hbar}$ - compare with free electrons, where we have $v_{free} = \frac{p}{m_e} = \frac{\hbar k}{m_e}$
➤ electrons behave as though they have an effective mass of $m_{eff} = \frac{\hbar^2}{A}$
➤ from Taylor's theorem, we can show that $A = \frac{d^2 E}{dk^2}\Big|_{k=k_0}$

$$m_{eff} = \hbar^2 \left[\frac{d^2 E}{dk^2} \right]_{k=k_0}^{-1}$$

➤ second derivative is curvature - when $E \propto k^2$ then m_{eff} is constant
➤ some regions of m_{eff} are positive, some regions are negative
➤ negative mass $\implies$ electrons slow down in electric field, force is in opposite direction

12.4 Electrons and Holes

➤ an energy band which is nearly filled has some vacant energy states near top of energy band
➤ consider vacant states of holes - charge of $+e$, equivalent to negative effective mass
➤ hole wavevector $k_h = -k_e$, energy $E(k_h) = -E(k_e), v_h = v_e$

1. if energy band is full there is no current
2. if energy band is partially full then electrons with m_{eff} describe electrical response
3. if energy band is almost completely filled, then holes with negative m_{eff}, positive charge

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