

Foundations of Physics B

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Chapter 1

Condensed Matter Physics

Lecture 2

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 $\vec{a}_1, \vec{a}_2, \vec{a}_3$, 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: \vec{r}, \vec{r}' are points on the lattice; \vec{a}_i are unit vectors; and n_i are scalar multiples

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

- 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

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

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

milller 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 3

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 $A \rightarrow B \rightarrow C = 2d \sin \theta$
- 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, $\lambda \approx 0.15 \text{ nm}$ 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

electron density

- crystal lattice is defined by translation vector,

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

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

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

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

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

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

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

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

- 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

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

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

$$\underline{G} = \nu_1 \vec{b}_1 + \nu_2 \vec{b}_2 + \nu_3 \vec{b}_3$$

$$n(\vec{r} + \underline{T}) = \sum_G n_G e^{i\vec{G} \cdot \vec{r}} \underbrace{e^{i\vec{G} \cdot \underline{T}}}_{2\pi \times p}$$

Lecture 4

x-ray diffraction

- incident electromagnetic wave on crystal - $\exp[i(\vec{k} \cdot \vec{r})]$
 - \vec{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 - $n(\vec{r})$
- scattered wave is described by

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

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

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

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

- alternative formulation of Bragg condition -

$$\vec{k} + \vec{G} = \vec{k}'$$

$$\implies (\vec{k} + \vec{G})^2 = |\vec{k}|^2$$

$$2\vec{k} \cdot \vec{G} + |\vec{G}|^2 = 0$$

$$\implies 2\vec{k} \cdot \vec{G} = -|\vec{G}|^2$$

- n.b. $\Delta \vec{k}$ has equivalent positive and negative values

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:

$$\vec{a}_1 = a\hat{x} \quad \vec{a}_2 = a\hat{y}, \quad \vec{a}_3 = a\hat{z}$$

$$\vec{b}_1 = \frac{2\pi}{a}\hat{x} \quad \vec{b}_2 = \frac{2\pi}{a}\hat{y} \quad \vec{b}_3 = \frac{2\pi}{a}\hat{z}$$

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

$$\vec{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z}) \quad \vec{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z}) \quad \vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y} + \hat{z}) \quad \vec{b}_2 = \frac{2\pi}{a}(\hat{x} + \hat{z}) \quad \vec{b}_3 = \frac{2\pi}{a}(\hat{x} + \hat{y})$$

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

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

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

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

$$\begin{aligned} n(\vec{r}) &= \sum_{j=1}^S n_j(\vec{r} - \vec{r}_j) \\ S_G &= \sum_j \exp \left[-i\vec{G} \cdot \vec{r} \right] \int n_j(\vec{\rho}) \exp \left[-i\vec{G} \cdot \vec{\rho} \right] \\ &= \sum_j f_j \exp \left[-i\vec{G} \cdot \vec{r}_j \right] \\ S_G(\nu_1 \nu_2 \nu_3) &= \sum_j f_j \exp \left[-i2\pi(\nu_1 x_j + \nu_2 y_j + \nu_3 z_j) \right] \end{aligned}$$

- $\vec{\rho} = \vec{r} - \vec{r}_j$, \vec{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 $\nu_1 + \nu_2 + \nu_3 = \text{odd integer}$; $S = 2f$ when $\nu_1 + \nu_2 + \nu_3 = \text{even integer}$
- 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 5

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
 1. permanent
 2. permanent-induced
 3. 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

$$V(r) = \frac{\vec{p} \cdot \hat{r}_1}{4\pi\epsilon_0 r^2}$$

- where \vec{p} is the electric dipole vector, and \hat{r}_1 is the unit vector along \vec{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

1. 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

2. 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 6

- 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 $s, s \pm 1, s \pm 2, \dots$
- describe position of plane using coordinate $u_s, u_{s \pm 1}, \dots$, 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:

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

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

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

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

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

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

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

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

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

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 7

- 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 $U_{s,s\pm 1}, V_{s,s\pm 1}$

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

- 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

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

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

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

- 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:

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

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

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

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

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:

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

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 8

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 $\underline{v} = \underline{v}_0 - \frac{|e|\underline{t}\underline{E}}{m_e}$
- electron velocity v_0 is random - no overall contribution
 - considers only drift velocity in response to \underline{E}
 - electron drift velocity is average of $-\frac{|e|\underline{t}\underline{E}}{m_e}$

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

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

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

- 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 $v_z^2 = \frac{k_B T}{m_e}$

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

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

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

- comparison with ratio of thermal to electrical conductivity

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

Lecture 9

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

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

- wavefunction is assumed to be periodic with dimensions of sample space, \vec{L}
- this removes any limitation on the value of \vec{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

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\vec{r}) + V(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r}) \psi(x, y, z) = A \exp[i(k_x x + k_y y + k_z z)], k_i = \frac{2\pi(l/m)}{L_i} E = \frac{\hbar^2}{2m_e} (k_x^2 + k_y^2 + k_z^2)$$

- 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 $\times \delta k = 4\pi k^2 \delta k$
- 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 10

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

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

- 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 an 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 11

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:

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

- 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:

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

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

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 12

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

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 1D 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 at (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 1D crystal)
- bloch theorem brings together two requirements to satisfy both periodic boundary 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 function 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 $\psi(x + R) = C \exp[ik(x + R)] = C \exp[ikR] \psi(x) = C u_k(R) \psi(x)$, $u_k(R)$ 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 $-\frac{\pi}{a} \rightarrow \frac{\pi}{a}$
 - 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 13

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 potential 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 Bloch 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 $k = \frac{\pi}{a}$ and $k = -\frac{\pi}{a}$
these are physically equivalent states (from Bloch 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 filled 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)

equation of motion for block electrons

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

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

- can predict how electron will respond in electric field

effective mass

- electrons in block states move as though the mass of electron is different from 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 $A = \left. \frac{d^2E}{dk^2} \right|_{k=k_0}$

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

- 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

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 $E(k_h) = -E(k_e)$, $v_h = v_e$
- if energy band is full there is no current
 - if energy band is partially full then electrons with m_{eff} describe electrical response
 - if energy band is almost completely filled, then holes with negative m_{eff} , positive charge