

# Intro to Solid State Physics: Li Yang

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# Chapter 1: Crystal Structure

**Ideal crystal is constructed by the infinite repetition of identical structural groups of atoms.** A group is called the basis. Detecting crystal structure started with x-rays due to the wavelength of the x-ray ( $\approx 1$  angstrom) being comparable to the interatomic spacing in a crystal.

**What is a *lattice*?** 2D Bravais Lattices [Wikipedia](#) The famous graphene has a hexagonal (honeycomb) structure like lattice, but it does not have the center atom from the true hexagonal lattice. The primitive of this lattice is made of up two atoms than can be translated to form the lattice. Thus graphene is like a diatomic crystal.

**3D Bravais Lattices** There are 14 Bravais lattices in 3D. In both 2D and 3D, the primitive cells that make up the lattice must fill the least amount of space and have no ‘holes’ or ‘extras’ left over. The 2 most common lattices now are the Primitive Hexagonal for its symmetry and the Body Centered Cubic (BCC) which is the lattice of Silicon, the most important material today.

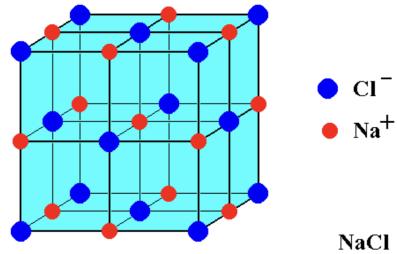


Figure 0.1: Sodium Chloride Structure (FCC)

**Example Structures** The lattice of Sodium Chloride is FCC as shown in Figure 0.1

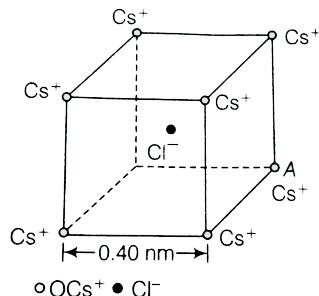


Figure 0.2: Cesium Chloride Structure (SC)

Figure 0.2 shows the lattice of Cesium Chloride which is SC.

## Chapter 2: Wave Diffraction and the Reciprocal Lattice

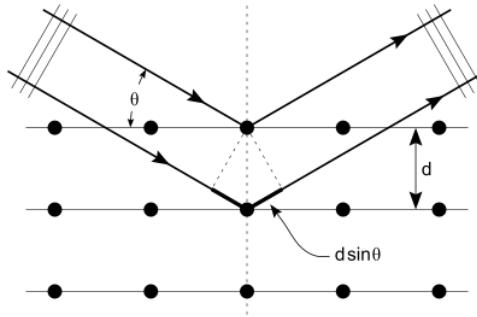


Figure 0.3: Bragg's Law

**Scattering and Bragg's Law** When two beams of same phase meet, they constructively interfere. When they are out of phase, they destructively interfere. The location of constructive interference, or path difference, is shown by the bold lines in Figure 0.3. The path difference is

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

known as Bragg's Law which is only valid for  $\lambda \leq 2d$ . In reality each lattice plane will reflect about  $10^{-3} \sim 10^{-5}$  of the incident beam. Thus only about  $10^3 \sim 10^5$  planes contribute to the diffraction. The periodicity of the lattice leads to a periodic observable...

*aside:* The electron wavefunction is not observable— $\psi$  is a complex number, but the electron density,  $\psi^* \psi$ , is observable. Read about the quantized Hall effect (Queen):) and Superconductivity (King).

$$\psi(x + T) = \psi(x) e^{i\theta} n(x + T) = n(x)$$

**Fourier Transform** The discrete Fourier transform is useful for periodic functions.

$$\begin{aligned} n(x) &= \sum_{p \geq 0} \left[ C_p \cos\left(\frac{2\pi}{a}x\right) + S_p \sin\left(\frac{2\pi}{a}x\right) \right] \\ &= \sum_p n_p e^{i\frac{2\pi}{a}px} \end{aligned}$$

or in vector notation

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_G e^{i\mathbf{G} \cdot \mathbf{r}}$$

Since  $n(x)$  is real, there is a symmetry of the complex conjugate

$$n_p = n_{-p}^*$$

### Inverse Fourier Transform

$$n_p = \frac{1}{a} \int_0^a n(x) e^{-i\frac{2\pi}{a}px} dx$$

and in vector notation

$$n_G = \frac{1}{V} \int_{cell} n(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}} dV$$

**Reciprocal Space Vectors** The basis vectors of the reciprocal lattice are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}; \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

where the denominator is the volume of the unit cell (parallelepiped)  $\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = V_c$ . Taking the dot product of a primitive vector with a reciprocal lattice vector gives

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$$

where the Kronecker delta tells us that the dot product is either  $2\pi$  or 0. With this we can write the  $\mathbf{G}$  vector as a linear combination of the reciprocal lattice vectors

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

we can also show that

$$n(\mathbf{r} + \mathbf{T}) = n(\mathbf{r})$$

which means that this is invariant under translations.

### Scattering amplitude

$$F = \int d\mathbf{r} n(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} e^{-i\mathbf{k}' \cdot \mathbf{r}}$$

where  $|\mathbf{k}| = |\mathbf{k}'|$ . In vector notation

$$\begin{aligned} F &= \int d\mathbf{r} \sum_{\mathbf{G}} n_G e^{i(\mathbf{G} - \mathbf{r}') \cdot \mathbf{r}} e^{-i\Delta\mathbf{k} \cdot \mathbf{r}} \\ &= \sum_{\mathbf{G}} n_G \int d\mathbf{r} e^{i(\mathbf{G} - \Delta\mathbf{k}') \cdot \mathbf{r}} \end{aligned}$$

where  $\Delta\mathbf{k} = -(\mathbf{k} - \mathbf{k}')$ . When  $\mathbf{G} = \Delta\mathbf{k}$  we can rewrite to

$$\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$$

in absolute value

$$|\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}'| \rightarrow |\mathbf{k} + \Delta\mathbf{k}| = |\mathbf{k}| \rightarrow |\mathbf{k} + \mathbf{G}| = |\mathbf{k}|$$

and

$$(\mathbf{k} + \mathbf{G}) \cdot (\mathbf{k} + \mathbf{G}) = \mathbf{k} \cdot \mathbf{k} \rightarrow 2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0$$

For the 1D crystal  $G = 2\pi/a$ . Since  $\mathbf{k} \cdot \mathbf{G} = 2\pi/\lambda G \sin \theta$  and  $2\mathbf{k} \cdot \mathbf{G} = \mathbf{G}^2$  We get

$$\begin{aligned} 2 \cdot \frac{2\pi}{\lambda} G \sin \theta &= \mathbf{G}^2 \\ \rightarrow \frac{4\pi}{\lambda} \sin \theta &= G \end{aligned}$$

since  $G = 2\pi/a$  we get Bragg's Law

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

For the SC the reciprocal lattice is SC, but for BCC, the reciprocal lattice is different...

## Chapter 2: cont'd

**Wigner-Seitz primitive cell:** How to create the most symmetric primitive cell.

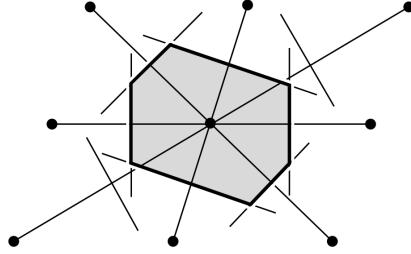


Figure 0.4: Wigner-Seitz Primitive Cell

Steps: Connect a given lattice point to all nearby lattice points. Bisect all lines. The area enclosed by the bisectors is the Wigner-Seitz primitive cell as shown in Figure 0.4.

**Reciprocal Lattice of SC** The lattice vectors (primitive translation vectors) are

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

the reciprocal lattice vectors using the formula from last lecture are

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_c} = \frac{2\pi}{a} \hat{\mathbf{x}}, \quad \mathbf{b}_2 = \frac{2\pi}{a} \hat{\mathbf{y}}, \quad \mathbf{b}_3 = \frac{2\pi}{a} \hat{\mathbf{z}}$$

**Reciprocal Lattice of BCC** The lattice vectors are

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

and the reciprocal lattice vectors are

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

**Reciprocal Lattice of FCC** The lattice vectors are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

which is the same as the reciprocal space of BCC. Thus, the reciprocal lattice of FCC is BCC!

**Brillouin Zone** The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice.

## Chapter 3: Crystal Binding and Elastic Constants

We are mostly interested in the E&M interaction between atoms on the energy scale of eV (e.g. the band gap of silicon is 1.2 eV).

**There are 4 main types of bonds:**

**Metallic Bond** Bonds between metals have weakly bound valence electrons. Hence the electrons move freely around like a fluid. This is why metals are good conductors.

**Ionic Bond** Bonds between metals and non-metals (e.g. NaCl). The opposing charges attract each other where the electrons form full shells and hence less conductivity.

**Covalent Bond** Bonds between non-metals (e.g. Si). The atomic orbitals defined by QM describes the bonds through the hybridization of the orbital wavefunctions (e.g.  $sp^3$  in diamond). This is a very difficult problem to solve.

**Van der Waals interaction** Inert gases... e.g. He is interesting as it is a liquid at very low temperatures, and it is a boson (He-4 superfluid) and fermion (He-3) depending on the number of neutrons.

**Hydrogen Bonding** is very important in biology, but not in solid state physics.

### Van der Waals interaction

Two types of energy to consider:

- Cohesive energy: Energy required to separate bound atoms. The cohesive energy of a solid is the sum of the cohesive energies of the bonds.
- Ionization energy: Energy required to remove an electron from an atom.

The ionization energy is larger because the Van der Waals interaction is a weaker bond. Given two inert gas atoms, there is no dipole or charge distribution contributing to the interactions between the atoms. In QM, there is no zero point energy, so we have to consider the atoms to not be perfect, but rather vibrate around a mean position. This is a dipole-dipole interaction.

**dipole-dipole** Given two electrons spaced by a distance  $R$  in a 1D lattice, one atom fluxuates by  $x_2$  and the other by  $x_1$ . The Hamiltonian of the unperturbed system is

$$H_o = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2$$

The Coulomb interaction:

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2}$$

Using Taylor expansion (2nd order) for small  $x_1$  and  $x_2$  we get

$$H_1 = -\frac{2e^2}{R^3}x_1x_2$$

Since this has 2 degrees of freedom, we have a 2x2 matrix with 2 eigenvalues diagonalized by the normal mode transform. This results in 2 Canconical Modes:

$$x_s = \frac{1}{\sqrt{2}}(x_1 + x_2) \quad x_a = \frac{1}{\sqrt{2}}(x_1 - x_2)$$

The total Hamiltonian is

$$\begin{aligned} H &= \frac{1}{2m} \left[ \frac{1}{2}(p_s + p_a)^2 \right] + \frac{1}{2m} \left[ \frac{1}{2}(p_s - p_a)^2 \right] - 2\frac{e^2}{R^3} \cdot \frac{1}{2}(x_s^2 - x_a^2) + \frac{1}{2}cx_1^2 + \frac{1}{2}cx_2^2 \\ &= \left[ \frac{p_s}{2m} + \frac{1}{2} \left( c - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[ \frac{p_a}{2m} + \frac{1}{2} \left( c + \frac{2e^2}{R^3} \right) x_a^2 \right] \end{aligned}$$

## Chapter 3: cont'd

The momenta of the harmonic oscillators from last time are also in the ofmr 2 modes:

$$p_s = \frac{1}{\sqrt{2}}(p_1 + p_2) \quad p_a = \frac{1}{\sqrt{2}}(p_1 - p_2)$$

The matrix form

$$\begin{pmatrix} E_o & 0 \\ 0 & E_o \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \hbar\omega \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\begin{vmatrix} E_o - \hbar\omega & \Delta \\ \Delta & E_o - \hbar\omega \end{vmatrix} = 0$$

solving for the eigenstates

$$\frac{1}{\sqrt{2}} \begin{pmatrix} a \\ b \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} a \\ -b \end{pmatrix}$$

The Hamiltonian of the single harmonic oscillator is

$$H_o = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2$$

thus we can compare the frequencies of the harmonic oscillator and the Van der Waals interaction

$$\omega = \sqrt{\frac{c \pm \frac{2e^2}{R^3}}{m}}$$

and we know the *zero-point energy*  $1/2\hbar\omega$  or in this case

$$\frac{1}{2}\hbar\Delta\omega = \frac{1}{2}\hbar[\Delta\omega_s + \Delta\omega_a]$$

From the uncoupled sum and using Taylor expansion

$$\omega = \omega_o \left[ 1 \pm \frac{1}{2} \left( \frac{2e^2}{R^3 c} \right) \pm \frac{1}{8} \left( \frac{2e^2}{R^3 c} \right)^2 + \dots \right]$$

thus we ge the interaction energy

$$\Delta U = \frac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = \frac{\hbar\omega_o}{2} \left[ \frac{e^4}{c^2 R^6} \right] = -\frac{A}{R^6}$$

where the minus sign indicates an attractive force. We would expect the atoms to collapse, but this is not the case due to the Pauli exclusion principle (electrons cannot occupy the same state).

### Pauli exclusion principle

As the atoms get closer, there is an overlap of the wavefunctions. If the wavefunctions are symmetric, the spin states must be anti-symmetric. Therefore anti-symmetric wavefunctions have symmetric spin states. This repulsive force from the Pauli exclusion principle is typically found empirically  $\propto \frac{1}{R^{12}}$ . Therefore the total potential is

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

AKA the Lennard-Jones potential. We could find the equilibrium distance by minimizing the potential  $\frac{dU}{dR} = 0$ . This is fine for inert gases that are spherical, but other molecules are depend on more than

the scalar distance  $R$ . This decays faster than the scale of Coulombs Law  $\propto \frac{1}{R^2}$ . The total energy for a crystal is

$$E = \frac{1}{2}N(4\epsilon) \left[ \sum_j' \left( \frac{\sigma}{P_{ij}R} \right)^{12} - \sum_j' \left( \frac{\sigma}{P_{ij}R} \right)^6 \right]$$

where the prime indicates that the sum is over the nearest neighbors. The fcc lattice

$$\sum_j' \left( \frac{1}{P_{ij}} \right)^{12} = 12.13188; \quad \sum_j' \left( \frac{1}{P_{ij}} \right)^6 = 14.45392$$

for the 12 nearest neighbors. Solving for the minimum energy  $\frac{dU}{dR} = 0$  we get

$$R_o/\sigma = 1.09$$

### Ionic Crystal

The Coulomb interaction:

$$\pm \frac{q^2}{r_{ij}}$$

The short-term interaction

$$\lambda e^{-r_{ij}/\rho}$$

thus the potential is

$$U_{ij} = \lambda e^{-r_{ij}/\rho} \pm \frac{q^2}{r_{ij}}$$

where at one site (one ion)

$$U_i = \sum_j' U_{ij}$$

and the total energy is

$$U = NU_i$$

For N molecules

$$U_{ij} = \begin{cases} \lambda e^{-r_{ij}/\rho} - \frac{q^2}{r_{ij}} & \text{nearest neighbor} \\ \pm \frac{q^2}{r_{ij}} & \text{otherwise} \end{cases}$$

and the total energy is

$$U_{tot} = N \left[ ze^{-R/\rho} - \alpha \frac{q^2}{R} \right] \quad \alpha = \sum_j' \frac{\pm}{p_{ij}}$$

where  $z$  is the number of nearest neighbors, and  $\alpha$  is the Madelung constant. From this we can find the lattice constant by using

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha \rho \frac{q^2}{z \lambda}$$

solving for  $R_o$  and putting into the total energy equation we get

$$U_{tot} = -\frac{N \alpha q^2}{R_o} \left( 1 - \frac{\rho}{R_o} \right)$$

where we have a special term

$$-\frac{N \alpha q^2}{R_o}$$

known as the ‘Madelung Energy’.

## Bonds Bonds and Bonds

From last time:

$$U_{ij} = \begin{cases} \lambda e^{-R/\rho} - \frac{q^2}{R} & \text{nearest neighbor} \\ \pm \frac{q^2}{p_{ij} R} & \text{otherwise} \end{cases}$$

where  $p_{ij}R = r_{ij}$  and the total energy (sum) is

$$U_{tot} = N \left[ z e^{-R/\rho} - \alpha \frac{q^2}{R} \right]$$

where  $z$  is the number of nearest neighbors,  $N$  is the total ions, and  $\alpha$  is the Madelung constant:

$$\alpha = \sum_j' \frac{\pm}{p_{ij}}$$

At the equilibrium separation

$$\frac{dU}{dR} = 0 \rightarrow R_o^2 e^{-R_o/\rho} = \alpha \rho \frac{q^2}{z \lambda}$$

$R_o$  is the equilibrium separation (position). Substituting this back into the total energy we get the empirical formula for the equilibrium energy (ground state):

$$U_{tot} = -\frac{N \alpha q^2}{R_o} \left( 1 - \frac{\rho}{R_o} \right)$$

where the first term outside the parenthesis is the Madelung energy

$$-\frac{N \alpha q^2}{R_o}$$

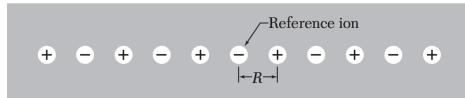


Figure 0.5: Line of ions with alternating charges

**The Evaluation of Madelung Constant** Letting  $R$  denote the distance between the ions, we can write the Madelung constant for the 1D line of ions with alternating charges as.

$$\begin{aligned} \frac{\alpha}{R} &= 2 \left[ \frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} + \dots \right] \\ &= \frac{2}{R} \left[ 1 - \frac{1}{2} + \dots \right] \\ \alpha &= 2 \ln 2 \end{aligned}$$

Remember these numbers

- Bohr radius  $a_o = 0.529A$
- fine structure constant  $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$

For the covalent bond, we have to use QM because the electron distribution is homogenous like a sea of electrons. Sometimes we think of this as a homogenous electron gas. This is a very difficult problem to solve. So we move on to the Hydrogen bond. This is a very weak bond typically at the scale of meV—room temperature is around 25 meV. So the bonds can break easily.

## Chapter 4: Phonons (Lattice Vibrations)

First starting with the 1D case: evenly spaced atoms we can take the minimum energy energy at the atom and take the limit as it approaches zero or

$$\frac{\partial U}{\partial x} = 0$$

the first term is  $V \propto x^2$  so we can approximate the potential as

$$U = \frac{1}{2}U''x^2 = \frac{1}{2}cx^2$$

where  $c$  is the spring constant. So we can imagine that the atoms  $(u_{s-1}, u_s, u_{s+1})$  are connected by springs. For 2 coupled springs in series we end up with 2 eigenmodes. But we look at each pair of atoms and sum up the forces. Using newton's second law we get the force of the  $s$  atom

$$F_s = c(u_{s+1} - u_s) + c(u_{s-1} - u_s) = c[u_{s+1} + u_{s-1} - 2u_s]$$

or as a differential equation

$$\begin{aligned} M \frac{d^2 u_s}{dt^2} &= c[u_{s+1} + u_{s-1} - 2u_s] \\ u &= u(\gamma)e^{-i\omega t} \\ \implies -M\omega^2 u_s &= c[u_{s+1} + u_{s-1} - 2u_s] \end{aligned}$$

this momentum of the crystal is not conserved but the Hamiltonian can still be written as

$$H(\gamma)H(\gamma + T)$$

where we discretize the translational symmetry, so we can write the periodic part of the atom as

$$u_s^k = ue^{-ik\gamma} \quad u(\gamma)=u(\gamma+T)$$

where  $k = 2\pi/L$  is the wavevector. So we can write the  $u_{s-1}$  and  $u_{s+1}$  as a translation of  $u_s$ :

$$\begin{aligned} u_{s-1} &= ue^{-i(s-1)ka} \\ u_{s+1} &= ue^{i(s+1)ka} \\ u_s &= ue^{-iska} \end{aligned}$$

where  $a$  is the lattice spacing. subbing this back in:

$$\begin{aligned} -M\omega^2 &= c[e^{-ika} + e^{ika} - 2] \\ \omega^2 &= 2\frac{c}{M}(1 - \cos(ka)) \end{aligned}$$

using the trig identity for half angles we get

$$\omega^2 = \frac{4c}{M} \sin^2\left(\frac{ka}{2}\right) \quad \text{or} \quad \omega = 2\sqrt{\frac{c}{M}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

where  $\omega = ck$  is the dispersion relation where we have boundaries at  $\pm\pi/a$  and max  $2\sqrt{c/m}$ . The group velocity is

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

for  $k \rightarrow 0$  we get the group velocity

$$v_g = a\sqrt{\frac{c}{M}}$$

we also get from the graph of  $\omega$  is that the slope at the boundaries are zero.

## Chapter 4: cont'd

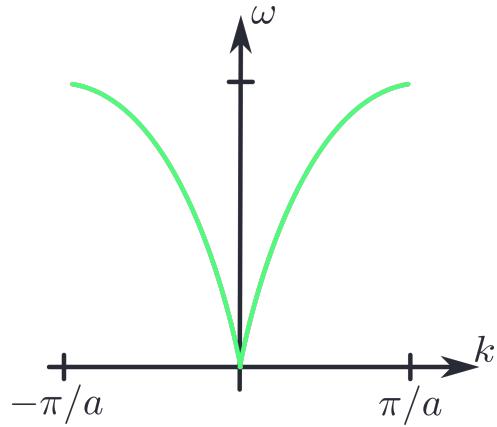


Figure 0.6: Graph of  $\omega$  vs  $k$

Graphing  $\omega$  vs  $k$  we get the graph in Figure 0.6. The slope at the boundaries is zero, and the maximum is  $2\sqrt{c/M}$ . But as  $k \rightarrow 0$  we know that  $\omega = 0$  and the energy is also zero. We can imagine the atoms are moving in phase (oscillating in the same direction) and amplitude. For  $\omega = 2\sqrt{c/M}$  we have the atoms moving out of phase (moving in opposite of their neighbors with equal amplitude). At this point  $k = \pi/a$  the potential is

$$e^{i\pi/a \cdot a} \rightarrow e^{i\pi}$$

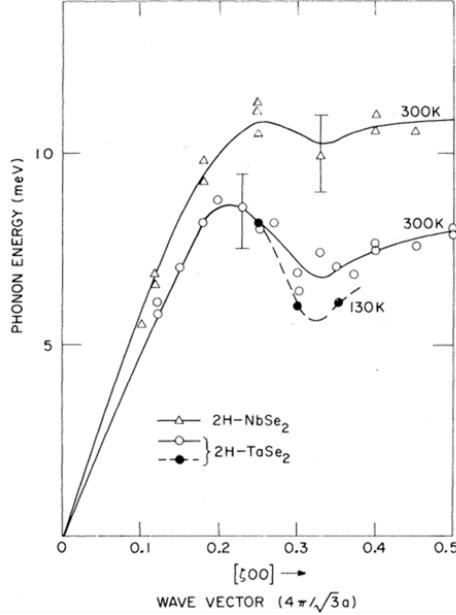


Figure 0.7: Graph of  $\omega$  vs  $k$  for different material and temperature

Figure 0.7 shows the graph of  $\omega$  vs  $k$  for neutron scattering observed in different materials and temperatures. We can see that the lower temperature has a low energy mode.

**Aside:** For phonons in low temperature, we see a double well potential, but for high temperatures, we see negative potential as shown in Figure 0.7.

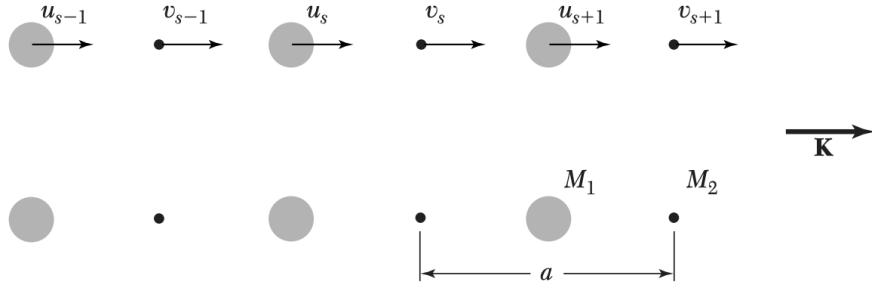


Figure 0.8: Two atom per unit cell

**Two atom per unit cell** (primitive basis) For the 1D case again:  
Using newton's second law

$$\begin{aligned} M_1 \ddot{u}_s &= c[v_s + v_{s-1} - 2u_s] \\ M_2 \ddot{v}_s &= c[u_s + u_{s+1} - 2v_s] \end{aligned}$$

and the periodic nature of the lattice

$$\begin{aligned} u_s &= ue^{iska} e^{-i\omega t} \\ v_s &= ve^{iska} e^{-i\omega t} \end{aligned}$$

from substitution we get

$$\begin{aligned} -M_1 \omega^2 u &= cv[1 + ve^{-ika}] - 2u \\ -M_2 \omega^2 v &= cu[1 + ue^{ika}] - 2v \end{aligned}$$

or in matrix form

$$-\omega^2 \begin{pmatrix} M_1 & 0 \\ 0 & M_2 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = c \begin{pmatrix} -2c & c[1 + e^{-ika}] \\ c[1 + e^{ika}] & -2c \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} \quad (0.1)$$

to find the eigenvalues we solve the determinant of the matrix. We can only do this if the matrix is real (hermitian: complex conjugate is the same as the original). Solving for zero

$$A = \begin{vmatrix} -\omega^2 M_1 + 2c^2 & -c^2(1 + e^{-ika}) \\ -c^2(1 + e^{ika}) & -\omega^2 M_2 + 2c^2 \end{vmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = 0$$

and the determinant of  $A$  is

$$\begin{aligned} \omega^4 M_1 M_2 - 2c^2 \omega^2 (M_1 + M_2) + 4c^4 + c^2 (1 + e^{-ika})(1 + e^{ika}) &= 0 \\ \omega^4 (M_1 M_2 - 2c^2 (M_1 + M_2) + 4c^4 - c^4 [2 + 2 \cos(ka)]) &= 0 \end{aligned}$$

for  $k = 0$  we get

$$M_1 M_2 w^4 - 2c[M_1 + M_2]\omega^2 = 0$$

we get the solutions

$$\begin{aligned} \omega_o &= 0 \\ \omega_1 &= \sqrt{\frac{2c(M_1 + M_2)}{M_1 M_2}} \end{aligned}$$

for  $k = \pi/a$  we get

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

Physically, the  $k = 0$  mode there are two solutions, one where all basis move in the same direction, and the other where each atom moves in the opposing direction. For  $k = \pi/a$  we have a solution where the basis pair move in the opposite direction of its neighbors. For this special case, we know that the Brillouin zone is half the size of the original zone, so the zone folds in half.

**Phonon modes** For the  $k = 0$ , in the  $\omega_o = 0$  case we know that  $\lambda \rightarrow \infty$  and it is called an acoustic phonon, but for  $\omega_1$  this is an optical phonon. This is in the order of meV around the room temperature. For energy of the phonon,

$$E = \hbar\omega = pc \quad \text{and} \quad p = \hbar k$$

Raman scattering is related to the scattering of light from the optical phonon. The wavelength of incoming and outgoing light shift by the energy of the phonon.

**3D Case:**  $N$  atoms per unit cell. We have  $3N$  branches of phonons. 3 acoustic and  $3N - 3$  optical phonon.

**Raman Scattering & Infrared** (THz)  $\sim 100$  meV. For the 3D case, we have 3 acoustic modes and  $3N - 3$  optical modes. For the acoustic mode,

$$k \rightarrow 0, \quad \omega \rightarrow 0$$

and for the optical modes

$$k \rightarrow 0, \quad \omega \rightarrow \infty$$

## Chapter 5: Phonon properties

The heat capacity is in general

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v$$

The proportionality of heat capacity in different materials

- Metal:  $C_v \propto I + QT^3$
- Insulator:  $C_v \propto T^3$

The Energy of an  $N$  particle system is  $E = Nk_B T$ . and the heat capacity is

$$C_v = \frac{\partial E}{\partial T} = \omega k_B$$

The total energy is

$$U_{tot} = \sum k, p \hbar \omega_{k,p} \langle n_{k,p} \rangle$$

where  $\langle n_{k,p} \rangle$  is the Bose-Einstein distribution

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

where there is no chemical potential. At low temperatures the constant goes to

$$\exp\left(\frac{\hbar\omega}{k_B T}\right)$$

or a boltzmann distribution.

$$U_{tot} \sum_{k,p} \frac{\hbar \omega_{k,p}}{\exp\left(\frac{\hbar \omega_{k,p}}{k_B T}\right) - 1}$$

or into an integral

$$\int dk f(\omega) \rightarrow \int d\omega f(\omega) \frac{1}{\frac{d\omega}{dk}}$$

We can compute this numerically from the phonon dispersion relation. For the Heat capacity of a solid, this  $T^3$  term is in the order of 3 meV. We only need to take the acoustic modes into account for finding  $\frac{d\omega}{dk}$  which approximately a constant  $C$ , so

$$\int_0^a d\omega \frac{\hbar \omega^2}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1}$$

where we can simplify using the substitution

$$x = \frac{\hbar \omega}{k_B T}$$

to change the integral from  $k$  space to  $\omega$  space and the integral becomes

$$T^2 \int_0^\infty dx \frac{x}{\exp(x) - 1}$$

where the  $T^2$  term comes from substituting for  $\omega$  twice. So the total energy is

$$U_{tot} = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

where  $D_p(\omega)$  is the density of states. Using the substitution for  $x$  we get

$$U_{tot} = \sum_p \int \omega d\omega D_p(\omega) \frac{x}{e^x - 1}$$

and the heat capacity is

$$C_v = \frac{\partial U_{tot}}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2}$$

The density of states (DOS) is given by

$$D(\omega) = \frac{dN}{d\omega}$$

where  $N$  is the number of states. For a 3D phonon gas, the total allowed states is

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

Which is equivalent to the volume of a sphere for each unit volume. So the DOS is

$$D(\omega) = \frac{dN}{d\omega} = \frac{dN}{dk} \frac{dk}{d\omega} = \frac{V}{2\pi^2} \frac{k^2}{1}$$

and the heat capacity is

$$C_v \propto k_B \sum_p \in d\omega \frac{k^2 V}{2\pi^2} \frac{1}{\frac{d\omega}{dk}} \frac{x^2 e^x}{(e^x - 1)^2}$$

and since  $\omega = vk$  and  $\frac{d\omega}{dk} = v$  we get

$$C_v \propto \sum_p \int_0^{\omega_D} d\omega \frac{V}{1} \frac{\omega^2}{v^3} \frac{x^2 e^x}{(e^x - 1)^2}$$

so we get the number of states

$$N = \int_0^{\omega_D} d\omega D(\omega)$$

where

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

the total energy is

$$U_{tot} = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2T^2 v^3} \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

and substituting for  $x$  we get

$$\propto T^4 \int_0^{x_D} dx x^2 \frac{x}{e^x - 1}$$

where we have four  $x$  terms that are substituted thus the  $T^4$  term. We get Debye's law for the heat capacity

$$U_{tot} \propto T^4 f(x_D) \quad C_v = \frac{\partial U}{\partial T} \propto T^3$$

for low temperature  $T \rightarrow 0$ ,  $x_D \rightarrow \infty$  so the  $f(x_D) \rightarrow 1$  which will give us Debye's law. Some constants:  $\omega_D$  is the Debye frequency and the Debye temperature is

$$\theta_D = \frac{\hbar\omega_D}{k_B}$$

### Einstein Model

$$D(\omega) = N\delta(\omega - \omega_0)$$

so we get a simple expression for the total energy

$$U_{tot} \propto \frac{\hbar\omega_o}{\exp\left(\frac{\hbar\omega_o}{k_B T}\right) - 1}$$

and the heat capacity is

$$C_v = \frac{\partial U}{\partial T} \Big|_{T \rightarrow 0} \propto \frac{1}{T} \frac{\exp\left(\frac{\hbar\omega_o}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega_o}{k_B T}\right) - 1\right)^2} \rightarrow T \exp\left(\frac{\hbar\omega_o}{k_B T}\right)$$

For the einstein model we get a wrong number because we assumed the density of states is a delta functions ,but it reality it is a constant.

## Chapter 6: Free Electron Fermi Gas

Read [Slater Determinant](#): We typically use an approximation of the wavefunction for  $N$  fermions as

$$E\psi_N = \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi_N$$

found using the [Hartree-Fock method](#) where we use the Slater determinant to find the energy of the system. For a system of  $N$  fermions we have a periodic potential and we can approximate this  $N$  fermions to one mean-field. Also related: [Dyson Equation](#). When we treat the group of particles as one *mean-field* we call them *quasiparticles*. The quasiparticle must obey the charge conservation e.g. a bare electron drags a positive cloud which also drags nearby electrons as a quasi electron and the total charge of the dragged cloud is still -1. We desire small mass quasi particles for semiconductors due to a faster acceleration. For the free-electron case we assume that the electrons do not interact with each other thus, we can quantize the single electron states.

**Energy** The quantized energies are related to the quantized standing waves of the particle in a box. The Hamiltonian is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi_n = E_n \psi_n$$

which has a sinusoidal solution of the wavefunction

$$\psi_n = A \sin\left(\frac{2\pi}{\lambda_n} x\right)$$

and the boundary condition determines the wavelength

$$n\lambda_n = 2L$$

and thus the energy of a state is

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \left( \frac{n\pi}{L} \right)^2$$

**Fermi (level) energy** is pretty much the highest occupied state (energy). For the 1D case the wave number can only be satisfied at the states for the standing waves:

$$k_0 = 0, \quad k_2 = \pm \frac{2\pi}{L}, \quad k_4 = \pm \frac{4\pi}{L}, \quad \dots$$

the fermi level at  $N$  is

$$k = \frac{N\pi}{2L} \rightarrow \epsilon_f = \frac{\hbar^2}{2m} \left( \frac{N\pi}{2L} \right)^2$$

For the 3D case, we have a cube with a small box of volume  $(\frac{2\pi}{L})^3$  and for the large number  $10^{23}$  we get a rough estimate of a spherical shell. The fermi energy is

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

where the  $N/2$  comes from the degeneracy of the spin states. This is equivalent to the ratio of the volume of the sphere to the volume element. The fermi momentum is

$$k_f = \left( \frac{3}{8} \sqrt{(2\pi)^3 L^3} \frac{1}{\pi} \right)^{1/3}$$

or

$$K_f = \left( \frac{3\pi^2 N}{V} \right)^{1/3}$$

and the fermi energy is

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

and the electron velocity is

$$v_f = \frac{\hbar k_f}{m} = \frac{\hbar}{m} \left( \frac{3\pi^2 N}{V} \right)^{1/3}$$

much like the phonon example, we can find the density of states for the free electron gas:

$$D(\epsilon) = \frac{dN}{d\epsilon}$$

we can solve the fermi energy equation as a function of energy

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

we also have a relation between  $N$  and  $k_f$  so we can write the volume in  $k$  space:

$$V_k = \frac{4}{3}\pi k^3$$

and since the energy is quantized as

$$E = \frac{\hbar^2 k^2}{2m} \rightarrow k = \frac{\sqrt{2mE}}{\hbar}$$

thus

$$V_k = \frac{4}{3}\pi \frac{(2mE)^{3/2}}{\hbar^3}$$

and since the number of states is

$$\begin{aligned} N &= \frac{V_k}{\left(\frac{2\pi}{L}\right)^3} \cdot 2 \\ &= \frac{V}{3\pi^2} \left( \frac{2mE}{\hbar^2} \right)^{3/2} \end{aligned}$$

thus the density of states is

$$D(\epsilon) = \frac{dN}{d\epsilon} = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}$$

so the DOS is proportional to  $\sqrt{E}$ . Also it is proportional to the mass!

## Chapter 6: Cont'd

**Fermi Energy** We have a 3D free electron gas with a DOS of

$$D(\epsilon) = \square\epsilon^{1/2}$$

For the 2D case we have

$$D(\epsilon) = \text{const}$$

which will look like a Heaviside step function. For the 1D case we have

$$D(\epsilon) = \frac{1}{\sqrt{\epsilon}}$$

where we have the energy dispersion relation

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

for graphene (2D material) what does the DOS look like? We would expect it to look like step function, but the electron dispersion relation is linear:  $\epsilon = ck$  so the DOS is a linear function.

**weird li yang writing:**

$$C_v \propto \alpha T^3 + \beta T$$

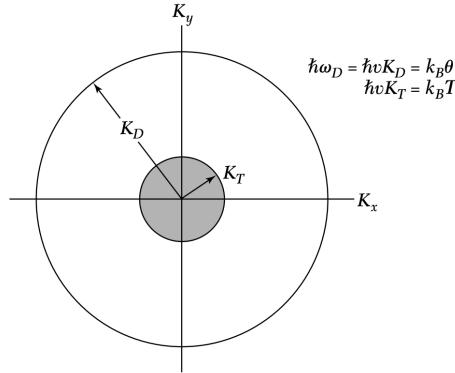


Figure 0.9: Fermi sphere

**Fermi sphere** at roughly 30 K the classical thermal energy is roughly  $k_B T \sim 3$  meV. As the temperature goes up, there is a smearing of the shell at the edges of the fermi sphere. So there are more electrons that can be excited to higher energy states thus  $N \propto k_B T$ . The fermi energy is then roughly  $N k_B T \approx T^2 \propto U$ . And the heat capacity is

$$C_v \propto \frac{\partial U}{\partial T} \propto T$$

**Fermi-Dirac distribution** We have 3 parameters that describe the distribution

$$f(T, \epsilon, \mu) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) + 1}$$

For  $T \rightarrow 0$ , if  $\epsilon > \mu$  then  $f \rightarrow 0$  and if  $\epsilon < \mu$  then  $f \rightarrow 1$ . at very small temperatures, we have a step function. As  $T$  increases, the energy states are more smoothed out.

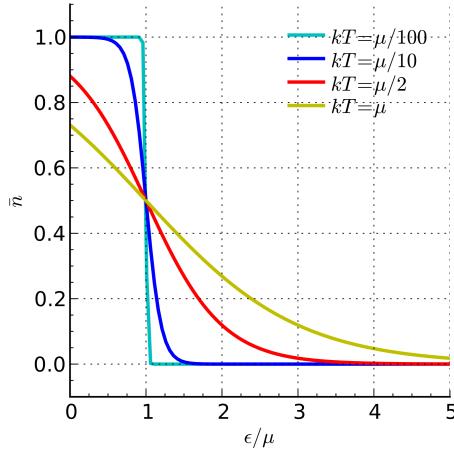


Figure 0.10: Fermi-Dirac distribution

### Energy change

$$\Delta U = U(T) - U(0)$$

for  $U(0)$  we have

$$U(0) = \int_0^{\epsilon_f} d\epsilon D(\epsilon)\epsilon$$

where we are taking the density of energy and multiplying by the energy at each state and summing them up from 0 to  $\epsilon_f$ . For  $U(T)$  we have

$$\begin{aligned} U(T) &= \int_0^{\infty} d\epsilon D(\epsilon)\epsilon f(\epsilon) \\ &= \left( \int_0^{\epsilon_f} + \int_{\epsilon_f}^{\infty} \right) d\epsilon D(\epsilon)\epsilon f(\epsilon) \end{aligned}$$

where we can split this integral into two parts. So we get the change in energy

$$\Delta U = \int_{\epsilon_f}^{\infty} [\epsilon - \epsilon_f]f(\epsilon)D(\epsilon) d\epsilon + \int_0^{\epsilon_f} [\epsilon_f - \epsilon][1 - f(\epsilon)]D(\epsilon) d\epsilon$$

where the first term  $I$  is the part to the right of the chemical potential and the second term  $II$  is the part to the left of the chemical potential. We can then find the chemical potential in reference to the zero energy state.:

$$\begin{aligned} C_v = \frac{d(\Delta U)}{dT} &= \int_{\epsilon_f}^{\infty} d\epsilon (\epsilon - \epsilon_f) \frac{\partial f}{\partial T} D(\epsilon) + \int_0^{\epsilon_f} d\epsilon (\epsilon_f - \epsilon) \left( -\frac{\partial f}{\partial T} \right) D(\epsilon) \\ &= \int_0^{\infty} d\epsilon (\epsilon - \epsilon_f) \frac{\partial f}{\partial T} D(\epsilon) \end{aligned}$$

where we first redefine  $\tau = k_B T$ , and

$$f(\epsilon, \tau, \mu) = \frac{1}{\exp\left(\frac{\epsilon-\mu}{\tau}\right) + 1}$$

so

$$\frac{\partial f}{\partial T} = k_B \frac{\partial f}{\partial \tau} = \frac{\epsilon - \epsilon_f}{\tau^2} \frac{\exp\left(\frac{\epsilon-\mu}{\tau}\right)}{\left(\exp\left(\frac{\epsilon-\mu}{\tau}\right) + 1\right)^2}$$

as  $\mu/\epsilon_f$ . We can define another variable

$$x = \frac{\epsilon - \mu}{\tau}$$

So

$$C_v = k_B^2 T D(\epsilon_f) \int_{-\epsilon_f/\tau}^{\infty} dx x^2 \frac{\exp(x)}{(\exp(x) + 1)^2}$$

and at  $T \rightarrow 0$  we get reduce this to

$$C_v = k_B^2 T D(\epsilon_f) \int_{-\infty}^{\infty} dx x^2 \frac{\exp(x)}{(\exp(x) + 1)^2}$$

and the analytical solution gives us

$$\frac{\pi^2}{3}$$

e.g. for the free electron gas with a DOS

$$D(\epsilon_f) = \frac{3N}{2k_B T_f}$$

the heat capacity is

$$C_v = \frac{1}{2} \pi^2 N k_B \frac{T}{T_f}$$

**Electrical Conductivity** for an electron the force is

$$\begin{aligned} \mathbf{F} &= -e\mathbf{E} = m \frac{d\mathbf{v}}{dt} = \hbar \frac{d\mathbf{k}}{dt} \\ m \frac{d\mathbf{v}}{dt} &= -eE \quad \Delta U = -\frac{eE}{m} \Delta t \end{aligned}$$

From the Drude model, we have a mean free path that explains the motion of the electrons. This  $\Delta t$  is related to teh scattering (where high  $\tau$  means less scattering). And from the Drude model we can define the current density:

$$\mathbf{j} = ne\mathbf{v} = n \frac{e^2 \tau \mathbf{E}}{m}$$

with conductance

$$\sigma = \frac{ne^2 \tau}{m}$$

the overall collision time is

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \dots$$

So applying an electric field will shift the center of the fermi sphere since the electric field will apply a force on the electrons.

## Chapter 6: Cont'd

From the conductance eq, we usually see that well conductive materials have a lighter effective mass.

**Hall Effect:** Consider a 2D material with a longitudinal electric field  $E_x$  and a orthogonal magnetic field  $\mathbf{H} = B_z$ . There will be a resulting voltage drop(electric field) in the transverse direction  $E_y$ : We first define the longitudinal conductance

$$\rho(H) = \frac{E_x}{J_x}$$

and the Hall coefficient is

$$R_H = \frac{E_y}{J_x H}$$

from the Lorentz force we have

$$\frac{d\mathbf{p}}{dt} = q(\mathbf{E} + \frac{\mathbf{p}}{m} \times \mathbf{H}) - \frac{\mathbf{p}}{\tau}$$

where  $\mathbf{p}$  is the momentum. We can assume that this is a steady state:

$$\frac{d\mathbf{p}}{dt} = 0$$

and we can a set of equations for the steady state:

$$\begin{cases} 0 = qE_x - \omega_c p_y - \frac{p_x}{\tau} \\ 0 = qE_y + \omega_c p_x - \frac{p_y}{\tau} \end{cases}$$

where  $\omega_c = \frac{qH}{mc}$  is the cyclotron frequency. Or in terms of the conductance and resistivity:

$$\begin{cases} -\sigma_0 E_x = \omega_c \tau j_y + j_x \\ -\sigma_0 E_y = -\omega_c \tau j_x + j_y \end{cases}$$

and since  $j_y = 0$  we get

$$\begin{aligned} -\sigma_0 E_x &= j_x; & \sigma_0 &= -\frac{j_x}{E_x}, \\ -\sigma_0 E_y &= -\omega_c \tau j_x; & E_y &= \frac{\omega_c \tau}{\sigma_0} j_x \end{aligned}$$

substituting back into the Hall coefficient we get

$$\begin{aligned} R_H &= \frac{E_y}{j_x H} = \frac{\omega_c \tau}{\sigma_0 H} = \frac{q\tau}{mc\sigma_0} \\ \text{using } \sigma_0 &= n \frac{q^2 \tau}{m} \\ R_H &= \frac{1}{ncq} \end{aligned}$$

## Chapter 7: Energy Bands

For a free electron, we know that the energy is quadratic i.e.  $\epsilon \propto k^2$ . We have a boundary condition for each states  $2\pi/L$  and the energy is quantized. Some definitions

- Metal: continuous filled energy bands
- Insulator: an unfilled energy band
- Energy band gap  $E_g$
- Metal:  $E_g \rightarrow 0$
- Semi metal:  $E_g < 0.4$  eV
- Semi conductor:  $E_g \approx 0.1 \rightarrow 4$  eV
- Insulator:  $E_g > 4$  eV

insert book fig 2 chp 7 For the unperturbed case, we have a free electron with energy

$$E_k = \frac{\hbar^2 k^2}{2m} (k_x^2 + k_y^2 + k_z^2), \quad k_x, k_y, k_z = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots$$

and wavefunction

$$\psi_k(\gamma) = e^{i\mathbf{k}\cdot\gamma}$$

we have a plane wave with the Bragg condition

$$(\mathbf{k} + \mathbf{G})^2 = k^2 \implies k = \pm G/2$$

where the  $\mathbf{G}$  vector is the reciprocal lattice vector  $\mathbf{G} = 2\pi/a$ . The most scattered wave is  $k = \pm\pi/a$ , and we get two solutions as a linear combination,

$$\psi = e^{ikx} \pm e^{-ikx}$$

We can substitute for when  $k = \pm\pi/a$  for the standing waves and we get

$$\begin{aligned} \psi(+)&=2\cos\left(\frac{\pi}{a}x\right) \\ \psi(-)&=i2\sin\left(\frac{\pi}{a}x\right) \end{aligned}$$

We can then define the corresponding probability density.

$$\begin{aligned} |\psi(+)|^2 &\propto \cos^2\left(\frac{\pi}{a}x\right) \\ |\psi(-)|^2 &\propto \sin^2\left(\frac{\pi}{a}x\right) \end{aligned}$$

insert book fig 3 chp 7

## Chapter 7: Cont'd

The first order energy difference is

$$\begin{aligned} E_g &= \int_0^1 dx U(x) [|\psi(+)|^2 - |\psi(-)|^2] \\ &= 2 \int_0^1 dx U(x) \cos\left(\frac{2\pi}{a}x\right) \left( \cos^2\left(\frac{2\pi}{a}x\right) - \sin^2\left(\frac{2\pi}{a}x\right) \right) \\ &= U \end{aligned}$$

This is equal to the Fourier component of the crystal potential:

$$U = U_o + U_1 \cos\left(\frac{2\pi}{a}x\right) + U_2 \cos\left(\frac{4\pi}{a}x\right) + \dots$$

**Bloch Theorem** A constraint on the wavefunction as it is a periodic function:

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

where  $u(\mathbf{r} + na) = u(\mathbf{r})$  is the periodic part of the wavefunction.  $k$  is like a quantum number where it represents the crystal momentum.

**Simple proof:** (not accurate, take a look at Ashcroft and Mermin) Given a wavefunction

$$\psi(x + a) = C\psi(x)$$

where  $a$  is the lattice constant and  $C$  is a constant or eigenvalue in the formal case. The *Periodic boundary condition* [Born-Karman] we have a ring with  $N$  lattice points so

$$\begin{aligned} \psi(x + Na) &= \psi(x) \\ C^N \psi(x) &= \psi(x) \implies C^N = 1 \\ \implies C &= e^{i2\pi s/N}; \quad s = 0, 1, 2, \dots, N-1 \\ \implies \psi(x) &= u_k(x) e^{i2\pi s x / Na} \end{aligned}$$

where

$$\frac{2\pi}{a} \frac{s}{N}$$

is the  $k$  vector. So we don't need to solve the whole equation, but rather just the periodic part  $u_k(x)$ . But true materials are not perfect crystals or harmonic potentials, so we have to solve the Schrodinger (wave) equation for the crystal potential.

$$me^2\tau/N1$$

remember this???

**Kronig-Penney Model** We have a periodic finite potential well where the height of the potential is  $U_o$ , and in the region  $0 < x < a$  we have a potential well  $U = 0$  and in the region  $-b < x < 0$  we have a barrier  $U = U_o$  that is periodic. From the wave equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi$$

where  $\epsilon$  is the eigenenergy. For the first region:

$0 < x < a$ ,  $U = 0$  the general solution is the linear combination

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

where the energy is only kinetic:

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

$-b < x < 0$ ,  $U = U_o$  which is constant, which is renormalized::

$$\psi(x) = Ce^{Qx} + De^{-Qx}$$

where there is no  $i$  in the exponent since the plane wave is not oscillatory, but decays.

$$U_o - \epsilon = \frac{\hbar^2 Q^2}{2m}$$

at the boundary  $x = 0$ , the wavefunction and the derivative must be continuous:

$$\begin{aligned} A + B &= C + D \\ ik(A - B) &= Q(C - D) \end{aligned}$$

Using Bloch's theorem, we know that each potential barrier is the same, but with a phase shift:

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

we get the continuity condition:

$$\begin{aligned} Ae^{ika} + Be^{-ika} &= (Ce^{-Qb} + De^{Qb})e^{ik(a+b)} \\ ik[Ae^{ika} - Be^{-ika}] &= Q[Ce^{-Qb} - De^{Qb}]e^{ik(a+b)} \end{aligned}$$

with four equations and four unknowns, we can solve for the energy eigenvalues. To solve for the energy eigenvalues, we can use the determinant of the matrix of the coefficients of the equations.

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ ik & -ik & -Q & Q \\ e^{ika} & e^{-ika} & -e^{-Qb+ik(a+b)} & -e^{Qb+ik(a+b)} \\ ike^{ika} & -ike^{-ika} & -Qe^{-Qb+ik(a+b)} & Qe^{Qb+ik(a+b)} \end{pmatrix}$$

and the solution is

$$\left[ \frac{Q^2 - K^2}{2Qk} \right] \sinh(Qb) \sin(Ka) + \cosh(Qb) \cos(ka) = \cos(k(a+b))$$

we can simplify this equation for  $b \rightarrow 0$ ,  $U_o \rightarrow \infty$ : so

$$\frac{Q^2 \cdot ba}{2} = P$$

where  $Q \gg K$  and  $Qb \ll 1$  from

$$\begin{aligned} U_o - \epsilon &= \frac{\hbar^2 Q^2}{2m} \\ Q &= \sqrt{\frac{2m(U_o - \epsilon)}{\hbar^2}} \end{aligned}$$

thus

$$\frac{P}{Ka} \sin(Ka) + \cos(Ka) = \cos(ka)$$

The only allowed states are between  $-1$  and  $1$  since  $\cos ka$  has a range of  $-1$  to  $1$ . We can also think of this as a band structure where the allowed states are the energy bands and the grey areas are the forbidden states.

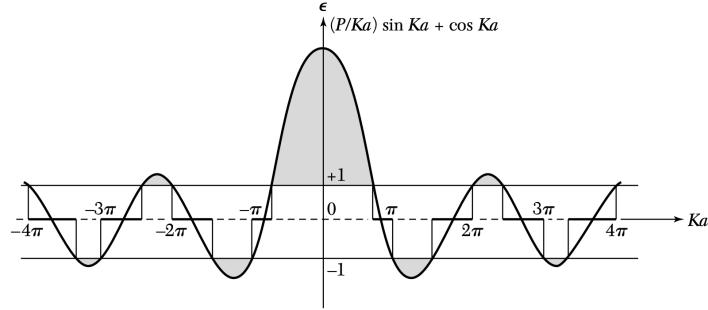


Figure 0.11: The allowed states are where the  $1 > \epsilon > 0$

**1D Case** from the Schrödinger equation for a periodic potential:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi$$

where  $U(x+a) = U(x)$  is the periodic potential which can be expanded in a Fourier series:

$$U(x) = \sum_G U_G e^{iGx}$$

so

$$\left( -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \sum_G U_G e^{iGx} \right) \psi(x) = \epsilon\psi$$

the wavefunction can be expanded in a Fourier series:

$$\psi(x) = \sum_k C_k e^{ikx} \quad k = \frac{2\pi n}{L}$$

so we can substitute this into the Schrödinger equation:

$$\begin{aligned} \left[ -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \sum_G U_G e^{iGx} \right] \sum_k C_k e^{ikx} &= \epsilon \sum_k C_k e^{ikx} \\ \frac{\hbar^2}{2m} \sum_k k^2 C_k e^{ikx} + \sum_{G,k} U_G C_k e^{i(k+G)x} &= \epsilon \sum_k C_k e^{ikx} \end{aligned}$$

## Chapter 7: Cont'd

From the single particle picture. The Schr EQ is

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \psi(x) = \epsilon \psi(x)$$

where the potential is periodic:

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{a})$$

so the Fourier expansion of the solution

$$\psi(x) = \sum_k C_k e^{ikx}; \quad U(x) = \sum_G U_G e^{iGx}$$

and subbing back in to the Schr EQ

$$\sum_k \frac{\hbar^2 k^2}{2m} C_k e^{ikx} + \sum_{G,k} U_G C_k e^{i(k+G)x} = \epsilon \sum_k C_k e^{ikx}$$

And since the reflected wave is  $k' = k + G$ , we can write the Schr EQ as

$$\begin{aligned} \sum_k \left[ \frac{\hbar^2 k^2}{2m} + \sum_G C_{k-G} U_G e^{ikx} \right] &= \epsilon \sum_k C_k e^{ikx} \\ \frac{\hbar^2 k^2}{2m} + \sum_G C_{k-G} U_G &= \epsilon C_k \end{aligned}$$

we define

$$\begin{aligned} \lambda_k &= \frac{\hbar^2 k^2}{2m} \\ \implies (\lambda_k - \epsilon) C_k + \sum_G U_G C_{k-G} &= 0 \end{aligned}$$

which is the *central equation* which can be solved for the energy eigenvalues. If we know the wavefunction in 1D for a fixed  $k$ , the general formula for this wave function

$$\psi_k(x) = \sum_G C_{k-G} e^{i(k-G)x}$$

can satisfy the Bloch theorem i.e.

$$\psi_k(x) = \sum_G C_{k-G} e^{-iGx} e^{ikx} = u_k(x) e^{ikx}$$

where

$$\begin{aligned} u_k(x+a) &= u_k(x) \\ &= \sum_G C_{k-G} e^{-iG(x+a)} \\ \text{using } G \cdot a = 2\pi n &\implies e^{-iGx} = e^{-i2\pi n} = 1 \\ &= \sum_G C_{k-G} e^{-iGx} = u_k(x) \end{aligned}$$

where the wave vector  $k$  describes the crystal momentum. For a large oscillation, the kinetic energy

(curvature) is large and the potential energy is small, so the wavefunction is

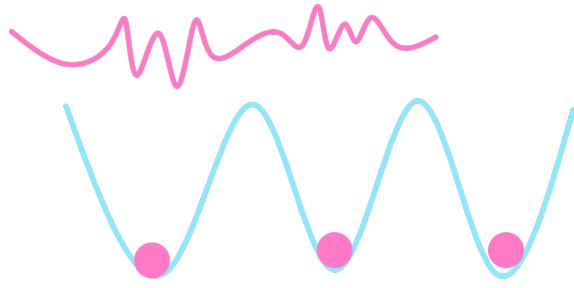


Figure 0.12: For a small potential well, the wavefunction (in pink) has high curvature.

For Silicon the orbital configuration is  $1s^2 2s^2 2p^2 3s^2 3p^2$  and the important valence orbital is the  $3s^2 3p^2$  where we denote  $sp^3$  hybridization. There is a pseudo potential within the core of the atom (Coulomb Potential) and the core electrons smooth out the potential AKA the pseudo potential approach. This is easier than the density functional theory (DFT) which is a

**Example:** Oversimplified case of a purely harmonic potential. THe  $G$  vector has only one component so  $U(x) = U_G e^{iGx}$  where we fix  $U_g = U_{-g} \neq 0$ . For fixed  $k$ ,

$$\begin{aligned} \text{For } k : \quad & (\lambda_k - \epsilon)C_k + U_g C_{k-g} + U_g + C_{k+g} = 0 \\ & k - g; \quad (\lambda_{k-g} - \epsilon)C_{k-g} + U_g C_{k-2g} + U_g + C_k = 0 \\ & \vdots \\ & k + g : \end{aligned}$$

from  $k - 2g$  to  $k + 2g$ . The matrix is

$$\left( \begin{array}{ccccccc} \ddots & & & & & & \\ \dots & \lambda_{k-2g} - \epsilon & U_g & 0 & 0 & 0 & \dots & e^{i(k-2g)x} \\ & U & \lambda_{k-g} - \epsilon & U & 0 & 0 & \dots & e^{i(k-g)x} \\ & 0 & U & \lambda_k - \epsilon & U & 0 & \dots & e^{ikx} \\ & & & & & & & \ddots \end{array} \right)$$

**Kronig-Penney Model in Reciprocal Space** Defining the potential barriers as a delta function, the new potential is

$$\begin{aligned} U(x) &= A \cdot a \sum_s \delta(x - sa) = \sum_G U_G \cos(Gx) \\ &= 2 \sum_{G>0} U_G \cos(Gx) \end{aligned}$$

where  $A$  is a constant,  $s$  is an integer, and  $a$  is the lattice spacing. The Fourier transform of  $U_G$  is

$$U_G = \int_0^1 dx U(x) \cos(Gx) = A$$

Using the reciprocal lattice vector  $G = 2\pi n/a$ , we can write the central equation

$$(\lambda_k - \epsilon)C_k + A \sum_n C_{k-2\pi n/a} = 0$$

to solve this, we define a function

$$f(k) = \sum_n C_{k-2\pi n/a} \implies f(k) = f(k - 2\pi m/a)$$

so

$$C_k = -\frac{\frac{2mA}{\hbar^2} f(k)}{k^2 - \frac{2m\epsilon}{\hbar^2}} \quad \lambda_k = \frac{\hbar^2 k^2}{2m}$$

and the shifted constant is

$$\begin{aligned} C_{k-2\pi n/a} &= -\frac{\frac{2mA}{\hbar^2} f(k)}{(k - 2\pi n/a)^2 - \frac{2m\epsilon}{\hbar^2}} \\ \implies f(k) &= -\sum_n \frac{\frac{2mA}{\hbar^2} f(k)}{(k - 2\pi n/a)^2 - \frac{2m\epsilon}{\hbar^2}} \end{aligned}$$

we can cancel the  $f(k)$  and move the terms:

$$\implies \frac{\hbar^2}{2mA} = -\sum_n \frac{1}{(k - 2\pi n/a)^2 - \frac{2m\epsilon}{\hbar^2}}$$

from the Kronig-Penney model, we defined the wave vector

$$K^2 = \frac{2m\epsilon}{\hbar^2}$$

so

$$\implies = -\sum_n \frac{1}{(k - 2\pi n/a)^2 - K^2} = I$$

using the very cool and interesting identity

$$\cot(x) = \sum_n \frac{1}{\pi n + x}$$

and the algebraic identity

$$-\sum_n \frac{1}{A^2 - B^2} = \sum_n \frac{1}{A+B} \pm \sum_n \frac{1}{A-B}$$

so

$$\begin{aligned} I &\implies \frac{a^2 \sin(Ka)}{4Ka[\cos(ka) - \cos(Ka)]} \\ \implies \frac{mAa^2}{2\hbar^2} \cdot \frac{1}{Ka} \sin(Ka) + \cos(Ka) &= \cos(ka) \end{aligned}$$

From the central equation:

$$(\lambda_k - \epsilon)C_k + \sum_G U_G C_{k-G} = 0$$

where

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

where at the zone boundary  $k = \pm\pi/a$ , there is a strong resonance and the potential attenuates dispersion. The reciprocal lattice vector is  $G = 2\pi n/a$  and we have a dispersion relation at the point  $U(\pm G/2)$  or in other words

$$U = U_{G/2} = U_{-G/2}$$

so we need to find the wave function at the zone boundary: A linear combination of the first boundary conditions

$$\psi_k = C_{G/2} e^{iGx/2} + C_{-G/2} e^{-iGx/2}$$

this gives the central equation

$$\begin{cases} (\lambda - \epsilon)C_{G/2} + UC_{-G/2} = 0 \\ (\lambda - \epsilon)C_{-G/2} + UC_{G/2} = 0 \end{cases}$$

where we can solve this eigenvalue problem by finding where the determinant is zero:

$$\begin{vmatrix} \lambda - \epsilon & U \\ U & \lambda - \epsilon \end{vmatrix} = 0$$

The two solutions are

$$\begin{aligned} \epsilon = \lambda \pm U &= \frac{\hbar^2}{2m} (G/2)^2 \pm U \\ &\implies \epsilon_G \sim 2U \end{aligned}$$

so the wavefunction is

$$\psi = e^{iGx/2} + e^{-iGx/2} = \begin{cases} \cos(Gx/2) \\ \sin(Gx/2) \end{cases}$$

the derivative of energy (slope) roughly relates to the velocity, and the curvature is proportional to the mass:

$$\frac{\partial^2 (\frac{\hbar^2 k^2}{2m})}{\partial k^2} \propto \frac{1}{m}$$

so around  $G/2, -G/2$  the wavefunction is

$$\implies \psi(x) = C_k e^{ikx} + C_{k-g} e^{i(k-g)x}$$

and we get a pair of central equations:

$$\begin{cases} (\lambda_k - \epsilon)C_k + UC_{k-G} = 0 \\ (\lambda_{k-g} - \epsilon)C_{k-g} + UC_k = 0 \end{cases}$$

and we solve the eigenvalues by finding the determinant resulting in the solutions:

$$\epsilon = \frac{1}{2}(\lambda_{k-g} + \lambda_k) \pm \left[ \frac{1}{4}(\lambda_{k-g} - \lambda_k)^2 + U^2 \right]^{1/2}$$

we define the value

$$K = k - \frac{G}{2} \quad |k| \ll 1$$

so the dispersion relation is

$$\begin{aligned}\epsilon_k &= \frac{\hbar^2}{2m}(G^2/4 + K^2) \pm \left[ 4\lambda\left(\frac{\hbar^2 K^2}{2m}\right) + U^2 \right]^{1/2} \\ &= \frac{\hbar^2}{2m}(G^2/4 + K^2) \pm \left[ 1 + \frac{\lambda}{U^2} \frac{\hbar^2 K^2}{2m} \right]^{1/2} \\ &= C \pm \frac{\hbar^2 K^2}{2m} \left[ 1 + \frac{2\lambda}{U} \right] \\ &= \frac{\hbar^2 K^2}{2m^*}\end{aligned}$$

where

$$m^* = \frac{mU}{\lambda}$$

is the effective mass. So if the curvature is large, the effective mass is approaches zero. We want the curvature to be smooth so the kinetic energy is large. Holes in semiconductors have a effective mass.

**Filling the Bands** Due to the Pauli exclusion principle, we can only occupy a finite space within a band of energy. Each electron will occupy

$$n = \frac{2\pi/a}{2\pi/N} = N$$

$N$  is the number of unit cells... But there is spin degeneracy, so the electrons will actually occupy

$$n = 2N$$

So one band can hold 2 electrons from a unit cell. Silicon (fcc hexagonal holds 4 atoms )has 2 atoms(2 Primitive cells) of valence 4, so we have 8 valence electrons filling the 4 bands in full hence an insulator. For alkali metals, the band is only half filled, and thus a metal:

- Even number of electrons: insulator
- Odd number of electrons: metal

Gallium Arsenide (GaAs) is a semiconductor with a band gap of 1.4 eV. It is highly mobile structure, and for example Gallium Nitride which has a band gap of 3.4 eV is used in blue LED's, as it can carry higher voltage with less current(less heat). But its not used very much because it is hard to grow. Compounds are harder to grow than elements, so it is more expensive than using Silicon.

## Chapter 8: Semiconductor Crystals

Orders of Magnitude:

- $\rho \sim 10^{14} \Omega \text{ cm}$ : Insulator resistivity
- $\rho \approx 10^{-2} \sim 10^9 \text{ ohm} * \text{cm}$ : Semiconductor resistivity
- $v_g = \frac{\partial E}{\partial k}$  is the group velocity
- The intrinsic carrier concentration is dependent on

$$\frac{E_g}{k_B T}$$

or the number of carriers

$$n_e \propto e^{\frac{-E_g}{k_B T}}$$

so for a gap energy of  $E_g = 0.5 \text{ eV}$  at room temperature  $k_B T \approx 0.03 \text{ eV}$

- $10^{-19} \sim 10^{-20} \text{ e/cm}^3$  is the roughly the number of carriers in a semiconductor.

**Doping** Doping silicon with phosphorus (V)— or n doping— introduces an extra electron while doping with boron (III)— or p doping— introduces a hole.

**Defect level** Finding this level where the effective mass is almost infinite thus zero curvature. For Phosphorus doped silicon, the defect level is close to the conduction band because the extra electron is weakly bound to the phosphorus atom(donor level). The electron is freely moving in the conduction band which relates to the bound state of the hydrogen atom. The rydberg energy is roughly

$$\Delta E \propto \frac{m}{\epsilon^2}$$

for the hydrogen atom this energy is roughly 10 eV, and for silicon the effective mass is

$$m_e^* \approx 0.1 m_e$$

and the dielectric constant is roughly

$$\epsilon \approx 10$$

so

$$\Delta E \approx \frac{1}{1000} E_{\text{Ryd}} \approx 10 \text{ meV}$$

which is much smaller than the boltzmann factor at room temperature 25 meV. This allows for self-doping where the electron can be thermally excited to the conduction band. For a (III) doped silicon, the defect level is closer to the lower band and the electron jumps up to the level—or hole jumps down—otherwise known as shallow doping (acceptor level). If the state is closer to the middle of the band gap, it is called deep.

**Hole** The group velocity for the electron in the conduction band is the slope or

$$\frac{\partial E}{\partial k} < 0$$

and for the hole the slope is positive on the left:

$$\text{hole} > 0$$

so the hole has a negative sign in the energy  $-E_h$  so the lower hole will move upward like a bubble in a liquid.

**Motion of electron under electric field** The equation is

$$v_g = \frac{\partial \omega}{\partial k} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \omega(\mathbf{k}) \quad E(k) = \hbar \omega k$$

and phase velocity

$$v_p = \frac{\omega}{k}$$

so a small change in energy is

$$\delta\epsilon = \frac{d\epsilon}{dk} \delta k$$

$$V_g = \frac{1}{\hbar} \frac{d\epsilon}{dk}$$

so

$$\begin{aligned} \delta\epsilon &= -eEV_g\delta t \\ &= \hbar v_g \delta k \\ \implies \hbar \frac{dk}{d\epsilon} &= -eE \\ \implies \frac{d\hbar k}{dt} &= -eE = F = -eE - \frac{e}{c} \mathbf{c} \times \mathbf{B} \end{aligned}$$

where  $\hbar k$  is the crystal momentum.

## Chapter 14: Plasmons, Polaritons, and Polaron

### E&M Stuff

In E&M, we extensively study two fields: the electric field  $\mathbf{E}$  and the magnetic field  $\mathbf{B}$ . We also have a vector

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$$

where  $\mathbf{P}$  is the polarization vector, and  $\mathbf{D}$  is the displacement vector. In a static field, we see that the divergence of the electric field

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$$

is equivalent to the ratio of the charge density  $\rho$  and the permittivity of free space  $\epsilon_0$ . We also know that the curl

$$\nabla \times \mathbf{E} = 0$$

is zero as the electric field can be expressed as the gradient of a scalar(Hemholtz) potential. Looking at the displacement vector,

$$\nabla \cdot \mathbf{D} = 4\pi\rho_f$$

where in CGS units we define

$$\mathbf{D} = \epsilon\mathbf{E}$$

where the dielectric function  $\epsilon(\omega, \mathbf{K})$  has a dependence on frequency and wave vector which makes it a difficult problem to solve.

**Plasmon** The total charge density

$$\rho = \rho_{\text{ext}} + \rho_{\text{ind}}$$

is the sum of the external charge density and the induced charge density. In CGS units, the divergence of the two fields are

$$\begin{aligned}\nabla \cdot \mathbf{D} &= \rho_{\text{ext}} \\ \nabla \cdot \mathbf{E} &= 4\pi(\rho_{\text{ext}} + \rho_{\text{ind}}) \\ &= 4\pi\rho\end{aligned}$$

We define the following

$$D(\mathbf{K}) = \epsilon(\mathbf{K})\mathbf{E}(\mathbf{K})$$

so the divergence of the electric field and displacement vector are

$$\nabla \cdot \mathbf{E} = \nabla \cdot \left[ \sum_K \mathbf{E}(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}} \right] = 4\pi \sum_K \rho(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}}$$

and

$$\nabla \cdot \mathbf{D} = \nabla \cdot \left[ \sum_K \epsilon(\mathbf{K}) \mathbf{E}(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}} \right] = 4\pi \sum_K \rho_{\text{ext}}(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}}$$

diving the two equations we find

$$\epsilon(\mathbf{K}) = \frac{\rho_{\text{ext}}(\mathbf{K})}{\rho(\mathbf{K})} = 1 - \frac{\rho_{\text{ind}}}{\rho(\mathbf{K})}$$

**Free Electron** In 1D, the EOM of an electron in an electric field is

$$m \frac{d^2x}{dt^2} = -eE$$

where time dependence is harmonic i.e.

$$\begin{aligned} x &= x_0 e^{-i\omega t} \\ \implies -\omega^2 mx_0 &= -eE; \quad x_0 = \frac{eE}{m\omega^2} \end{aligned}$$

The polarization, or dipole moment per unit volume of the electron, is

$$P = -nex_0 = \frac{ne^2 E}{m\omega^2}$$

where  $n$  is the electron density. So the dielectric function is

$$\epsilon(\omega) = \frac{D}{E} = \frac{E + 4\pi P}{E} = 1 - \frac{4\pi ne^2}{m\omega^2}$$

We define the plasma frequency as

$$\omega_p^2 = \frac{4\pi ne^2}{m}$$

so

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

**Example** In the background the dielectric constant  $\epsilon(\infty)$  then

$$\epsilon(\omega) = \epsilon(\infty) \left[ 1 - \frac{\bar{\omega}_p^2}{\omega^2} \right]$$

where

$$\bar{\omega}_p^2 = \frac{4\pi ne^2}{m\epsilon(\infty)}$$

## Electromagnetic wave

From the Poynting vector

$$\mathbf{S} = \mathbf{E} \times \mathbf{B}$$

### Aside: 3 Types of Differential Equations

- The wave equation

$$A \nabla^2 f = \frac{\partial^2 f}{\partial t^2}$$

- The diffusion equation

$$D \nabla^2 f = \frac{\partial f}{\partial t}$$

- The Poisson equation

$$\nabla^2 f = A$$

For EM waves, the wave equation is

$$\frac{d^2D}{dt^2} = c^2 \nabla^2 \mathbf{E}$$

where we have a solution

$$E \propto e^{i\omega t} e^{i\mathbf{K} \cdot \mathbf{r}} \quad \text{and} \quad \mathbf{D} = \epsilon \mathbf{E}$$

so the wave equation tells us the dispersion relation

$$\omega^2 \epsilon(\omega, \mathbf{K}) = c^2 K^2$$

This tells us some interesting things

- $\epsilon$  is real,  $\epsilon > 0$ , and for real  $K$  and  $\omega$  the wave propagates transversely with phase velocity

$$v_p = \frac{c}{\sqrt{\epsilon}}$$

- If  $\epsilon$  is real and  $\epsilon < 0$ , then  $K$  is imaginary and the wave is damped.

- If  $\epsilon$  is complex and  $\omega$  is real,  $\mathbf{K}$  is complex and is damped.

From the dispersion relation

$$\epsilon(\omega, \mathbf{K}) = 1 - \frac{\omega_p^2}{\omega^2}$$

if  $\omega < \omega_p$  there is total reflection, and if  $\omega > \omega_p$  the material is transparent.

**Metal** In a metal with positive charge density, we apply an electric field to slightly displace the electrons and cause them to oscillate. The EOM is

$$nm \frac{d^2x}{dt^2} = -neE$$

This displaces the surface charge density  $\sigma = \pm neu$  or a capacitor. Using a gaussian pillbox at the two surfaces of the capacitor, we know that

$$E \cdot S = \frac{\sigma \cdot s}{\epsilon_0} = \frac{\sigma}{\epsilon_0}$$

and from Gauss's law

$$E = 4\pi n u e$$

so the wave equation is

$$\begin{aligned} nm \frac{d^2u}{dt^2} &= -neE = -4\pi ne^2 u \\ \implies \frac{d^2u}{dt^2} + \omega_p^2 u &= 0 \end{aligned}$$

where the frequency is

$$\omega_p = \sqrt{\frac{4\pi ne^2}{m}}$$

We can approximately find that for  $10^{23}$  electrons per cubic centimeter (Avogadro's number) we get a frequency of roughly  $10^{16}$  Hz, and the energy is roughly

$$\hbar \omega_p \approx \frac{10^{-34} \cdot 10^{16}}{10^{-19}} = 1 \text{ eV}$$

Experimentally we find that the plasmon energy is roughly 10 eV since the frequency is  $10^{16}$  Hz.

When  $\mathbf{K}$  goes to zero, we look at the optical modes for the dielectric function, when  $\omega$  goes to zero i.e.  $\epsilon(0, \mathbf{K})$ , we find that the applied field is screened by the electrons.

$$\begin{aligned}\epsilon(K) &= \frac{\Delta\rho}{\rho} = 1 - \frac{\rho_{\text{ind}}}{\rho} \\ &= \frac{\varphi_{\text{ext}}}{\varphi}\end{aligned}$$

where  $\varphi$  is the potential. The electron response has a perturbed density

$$\rho(x) = -n_0 e + \rho_{\text{ind}}(\mathbf{K}) \sin(\mathbf{K} \cdot \mathbf{x})$$

And we use the Poisson equation for the total charge density

$$\nabla^2 \varphi = -4\pi\rho$$

but this depends on  $\mathbf{r}$  so to solve this in terms of  $\mathbf{K}$  we use the Fourier transform

$$\begin{aligned}\int \psi(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{x}} d\mathbf{K} \\ \implies K^2 \psi(\mathbf{K}) = 4\pi\rho(\mathbf{K})\end{aligned}$$

**Chemical Potential** From the 3D fermi energy

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

we can find the chemical potential

$$\mu = \epsilon_F^0 = \frac{\hbar^2}{2m} (3\pi^2 n_0)^{2/3}$$

is perturbed by the potential  $-e\varphi(x) \rightarrow n$  so

$$\mu = \epsilon_F^0 - e\varphi(x) = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} - e\varphi(x)$$

and we can solve for  $e\varphi(x)$  and use Taylor expansion to find

$$\begin{aligned}e\varphi(x) &= \frac{d\epsilon_F}{dn_0}[n(x) - n_0] \quad \frac{d\epsilon_F}{dn_0} = \frac{2\epsilon_F}{3n_0} \\ \implies n(x) - n_0 &= \frac{3}{2}n_0 \frac{e\varphi(x)}{\epsilon_F}\end{aligned}$$

which is equivalent to the induced charge density

$$\begin{aligned}\rho_{\text{ind}} &= -\frac{3}{2}n_0 \frac{e^2}{\epsilon_F} \varphi(x) \\ \implies \rho_{\text{ind}}(\mathbf{K}) &= -\frac{3}{2}n_0 \frac{e^2}{\epsilon_F} \varphi(\mathbf{K})\end{aligned}$$

and using

$$k^2 \rho(\mathbf{K}) = 4\pi\rho(\mathbf{K})$$

we get

$$\rho_{\text{ind}}(\mathbf{K}) = -\frac{6\pi n_0 e^2}{\epsilon_F K^2} \rho(\mathbf{K})$$

and the dielectric function is

$$\epsilon(\mathbf{K}) = 1 - \frac{\rho_{\text{ind}}}{\rho} = 1 + \frac{6\pi n_0 e^2}{\epsilon_F K^2}$$

Defining

$$\begin{aligned} k_s^2 &= \frac{6\pi n_0 e^2}{\epsilon_F} \\ &= 4 \left( \frac{3}{\pi} \right)^{1/3} \frac{n_0^{1/3}}{a_0} \end{aligned}$$

so

$$\epsilon(\mathbf{K}) = 1 + \frac{k_s^2}{K^2}$$

which is the Thomas-Fermi screening. This also means we have a screening length  $1/k_s$ .

**Screened Coulomb Potential** For a point charge the Poisson equation is a delta function

$$\nabla^2 \varphi = -4\pi q \delta(\mathbf{r}) \implies \varphi_0 = \frac{q}{r}$$

taking the Fourier transform of both sides

$$\begin{aligned} \varphi_0(\mathbf{r}) &= \frac{1}{(2\pi)^3} \int d\mathbf{K} \varphi_0(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}} \\ \delta(\mathbf{r}) &= \frac{1}{(2\pi)^3} \int d\mathbf{K} e^{i\mathbf{K}\cdot\mathbf{r}} \end{aligned}$$

So each fourier component is independent and we find

$$\varphi(\mathbf{K}) = \frac{4\pi q}{K^2}$$

since

$$\begin{aligned} \epsilon(\mathbf{K}) &= \frac{\varphi_{\text{ext}}}{\varphi} = 1 + \frac{k_s^2}{K^2} \\ \implies \varphi(K) &= \frac{4\pi q}{K^2} \frac{K^2}{K^2 + k_s^2} = \frac{4\pi q}{K^2 + k_s^2} \end{aligned}$$

And we find the screened potential by taking the Fourier transform

$$\begin{aligned} \varphi(r) &= \frac{1}{(2\pi)^3} \int d\mathbf{K} \frac{4\pi q}{K^2 + k_s^2} e^{i\mathbf{K}\cdot\mathbf{r}} \\ &= \frac{q}{r} e^{-k_s r} \end{aligned}$$

from the residue theorem. We can see that we have two decaying terms where the exponential term decays much faster, or the short regime. So we have the two cases

$$\epsilon(\omega, 0) = 1 - \frac{\omega_p^2}{\omega^2} \quad \epsilon(0, K) = 1 + \frac{k_s^2}{K^2}$$

**Metal-Insulator Transition** We'd expect that doping a metal with more impurities would decrease the resistivity gradually. However, we find that the resistivity drops suddenly at a critical concentration. As  $k_s$  increases we move the bound state up in energy, and at a critical point, the bound states overlap with the other wells and the system becomes a metal. A bare Coulomb potential always has a bound state. For a delta function potential, there is only one bound state.

## Phonon in metal

The T-F(Thomas-Fermi) screening of the dielectric function

$$\epsilon(\mathbf{K}) = 1 + \frac{k_s^2}{K^2}$$

approximates for an electron where at small  $\lambda$  the constant is 1 or a vacuum. The plasma contribution from the ions gives us

$$\epsilon(\mathbf{K}, \omega) = 1 + \frac{k_s^2}{K^2} - \frac{4\pi n e^2}{M \omega^2} \quad \omega_p^2 = \frac{4\pi n e^2}{M}$$

For the long wavelength limit, we look at a short range in  $K$  or

$$k, \omega \ll 1$$

so we can neglect the 1 term in the dielectric function, and looking at the dielectric function at zero tells us the phonon information (the excitation state of the lattice):

$$\omega^2 = \frac{4\pi n e^2}{M k_s^2} K^2$$

Replacing  $k_s$  with the fermi energy  $\epsilon_F$  we get

$$\omega^2 = \frac{4\pi n e^2}{M} \frac{\epsilon_F}{6\pi n e^2} K^2$$

and using the fermi velocity  $\epsilon_F = \frac{1}{2} m V_F^2$

$$\begin{aligned} &= \frac{m}{3M} V_F^2 K^2 \\ \omega &= \left( \frac{m}{3M} \right)^{1/2} V_F K \\ \implies V &= \frac{\omega}{K} = \left( \frac{m}{3M} \right)^{1/2} V_F \end{aligned}$$

where  $v$  is the sound velocity of the phonon in the metal. This describes how long wavelength phonons propagate in the metal. We can think of the plasmon and phonon to be a coupled system which can be represented as a matrix equation

$$\begin{pmatrix} E_1 & \Delta \\ \Delta & E_2 \end{pmatrix} \begin{pmatrix} \text{plasmon} \\ \text{phonon} \end{pmatrix} = 0$$

which has two solutions

$$\begin{pmatrix} \text{plasmon} \\ 0 \end{pmatrix} \quad \begin{pmatrix} 0 \\ \text{phonon} \end{pmatrix}$$

And the plasmon has optical modes and the phonon has acoustic modes (longitudinal) which is similar to the two dispersion relations as shown in the figure below.

## Polaritons

From the wave equation

$$\frac{d^2 D}{dt^2} = c^2 \nabla^2 \mathbf{E}$$

and we know that the wavelike nature of E&M waves so

$$\begin{aligned} E, D &\sim e^{i\omega t} e^{i\mathbf{E} \cdot \mathbf{r}} \\ D &= E + 4\pi P \\ D &= \epsilon E \end{aligned}$$

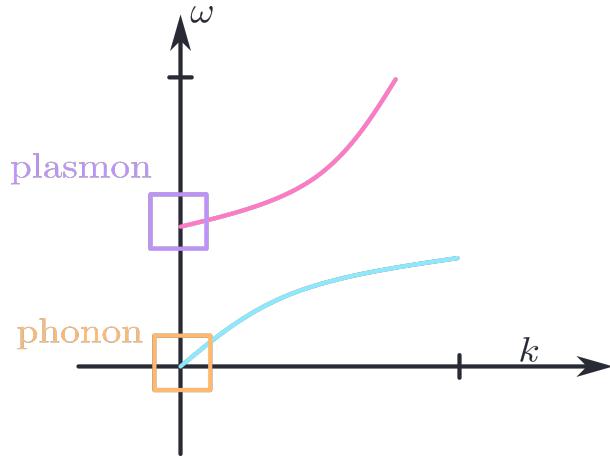


Figure 0.13: Phonon and Plasmon Dispersion Relations

so

$$\omega^2 [E + 4\pi P] = c^2 k^2 E$$

And from Newtons laws, we know that the displacement of the positive ions are given by

$$M \frac{d^2 u}{dt^2} = -\frac{\partial V}{\partial u}$$

With two equations and two unknowns, we have a matrix equation where

$$\begin{pmatrix} E \\ P \end{pmatrix} \Rightarrow \begin{vmatrix} \omega^2 - c^2 k^2 & 4\pi\omega^2 \\ \frac{Nq^2}{M} & \omega^2 - \omega_T^2 \end{vmatrix} = 0$$

which gives the equation

$$-\omega^2 P + \omega_T^2 P = \frac{Nq^2}{M} E$$

And the two solutions are at  $\omega \rightarrow 0, k \rightarrow 0$  thus

$$\omega = 0, \quad \omega^2 = \omega_T^2 + \frac{4\pi N q^2}{M}$$

For light in EM we have the relation  $\omega = ck$  which is a photon like branch in the dispersion relation in Figure 0.13. So the polariton relates to the separate top branch.

### Lydane-Sachs-Teller Relation (LST)

$$\frac{\omega_L^2}{\omega_T^2} = \frac{\epsilon(\omega=0)}{\epsilon(\infty)}$$

where  $\epsilon(0)$  has the ion and electron part, and  $\epsilon(\infty)$  or at very high frequency the electron part dominates as the heavy ions are not able to respond to the high frequency. For 4 atoms in a 3D unit cell so we have  $3N = 12$  phonon modes, so 9 optical modes and 3 acoustic modes. LO (longitudinal optical) lie below the TO (transverse optical) phonons

**Electron + phonon = Polaron** In a crystal lattice, we have a mobility of the electron

$$j = \frac{ne^2\tau}{m} E$$

(Read about adiabatic approximation) In materials, the mobility is much less than the free electron. The lattice structure distorts the motion of the electron which gives rise to the polaron. Photocatalytic water splitting tries to use light to split water into hydrogen.

**Optical Absorption** A photon of energy  $\hbar\omega$  and momentum  $\hbar k$  ( $\omega = ck$ ) absorbed in the electron band will excite an electron to move up into the conduction band. For a 1eV band gap, the wavelength is roughly

$$\lambda = \frac{hc}{E} \approx 1000 \text{ nm}$$

so the wave vector is  $k = \frac{2\pi}{\lambda}$  in comparison to the lattice spacing  $\frac{2\pi}{a}$  where  $a \approx 0.1 \text{ nm}$  we can see that the lattice spacing is much larger than the wave vector.

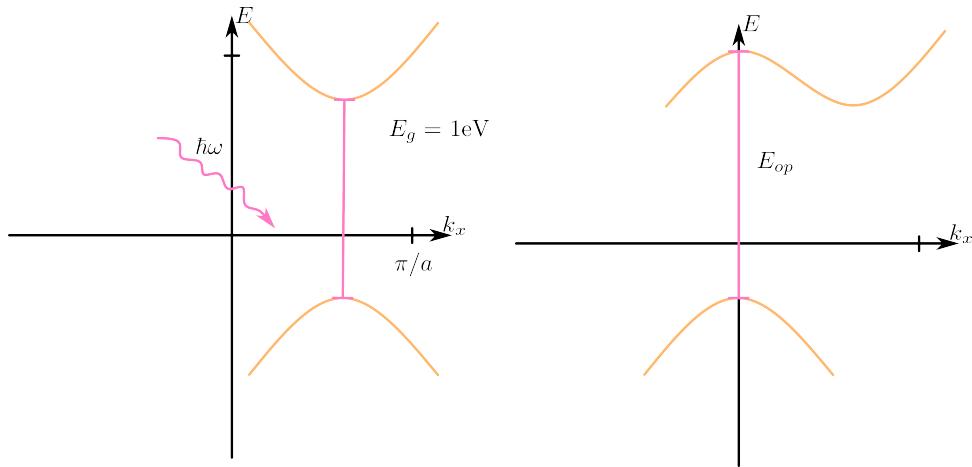


Figure 0.14: The left shows a direct band gap. The right shows indirect band gap.

**LED** A current will inject holes in the bottom band and electrons in the top band, and the recombination of the two will emit a photon. For the indirect band gap, the holes build up near the top of the valence band, and the phonon carries the momentum as the system recombines. The phonon will vibrate and heat up the system. The phonon of roughly 10 meV is small in comparison to the photon.

- photon takes energy
- phonon takes momentum

**Dirac Notation** The valence state  $|v\rangle$  and the conduction state  $|c\rangle$  we can represent the displacement of the two states with

$$\langle v | \mathbf{r} \text{ dipole} | c \rangle$$

The absorption spectrum has several peaks, but we can approximate the absorption spectrum with a smoothed Gaussian distribution. Each transition relates to the individual peaks, so we can take the sum or

$$\sum |\langle v | \mathbf{r} \text{ dipole} | c \rangle|^2$$

The absorption will be proportional to the density of states and the strength of the dipole oscillator strength. If the valence and conduction states have the same parity, the product (whether even or odd) will be even. So  $\mathbf{r}$  is odd and we get a zero. We usually look at the valence band as a p orbital(odd) and the conduction band as an s orbital(even).

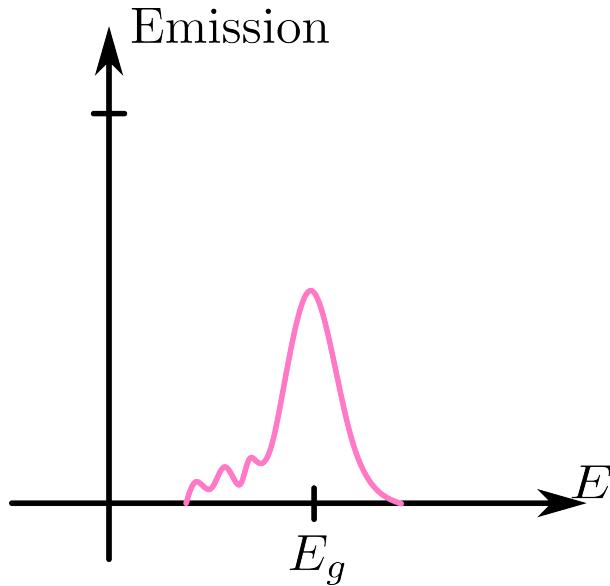


Figure 0.15: The emission spectrum at low temperature.

**Emission Spectrum at Low Temperature** We can see small peaks from the phonon excitation from experimental data (Stokes Shift). The electron hole pair have a bound state which has a binding

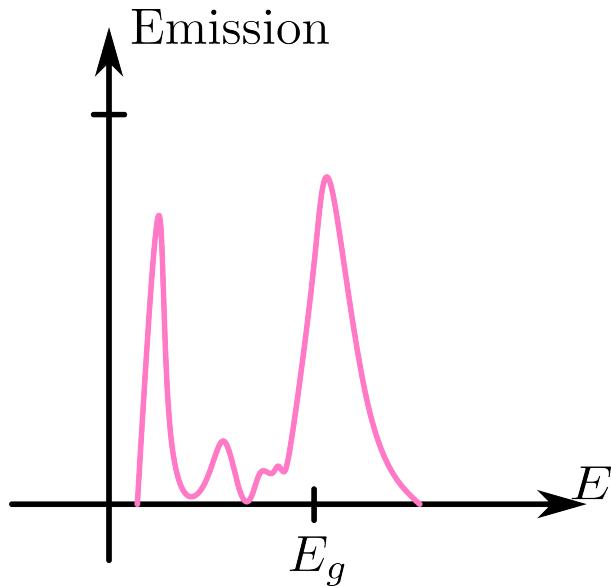


Figure 0.16: The emission spectrum at low temperature has a large peak at low energy.

energy of roughly 10 meV ( the gap between the first peak and the gap energy).

**Hydrogen Model** The Rydberg energy for a hydrogen atom is

$$\frac{m_0 e^4}{8\epsilon_0^2 \hbar^2} = 13.6 \text{ eV} = 1 \text{ Ry}$$

In a material the mass and dielectric constant change, i.e., the effective mass and dielectric constant of a material. For silicon  $\epsilon_0 \approx 10$  and the effective mass is

$$m_e^* \approx 0.1 m_e$$

or from the curvature of the energy band

$$m \propto \frac{1}{\frac{d^2\epsilon}{dk^2}}$$

For silicon, we have a reduced mass for the electron hole pair

$$\frac{1}{m_0} = \frac{1}{m_e} + \frac{1}{m_h}$$

but the dispersion is anisotropic... the top down view of the valence band is oval shaped. The approximation for the mass went from taking the average to a cyclotron mass:

$$\frac{m_x + m_y}{2} \rightarrow m = \sqrt{m_x m_y}$$

**Wavefunction** For the wavefunction of the electron hole pair  $\psi(x_e, x_h)$  we could have an s-orbital with a size of radius 100 nm. This is kind of related to the binding energy 10 meV to the hydrogen atom Rydberg energy of 13.6 eV, so the binding energy is much smaller thus the larger size.

**Exciton** To get an exciton (electron hole pair) we need to have a lot of pairs that contribute to the effective mass.

## Quantum Mechanics in Materials

Fun Lecture

Simulation + Novel Materials = New Quantum Properties, Materials and Applications

- Novel Materials: Carbon Nanotube, Bucky Ball...
- Quantum Excitation: Nature is boring, and we can only observe things that are ‘excited’.
- High pressure: Metal-Insulator Transition
- Similar Electron and hole group velocity: Exciton (electron hole pair)
- DFT (Density functional theory): Underestimates band gap
- GW approximation improves on the theoretical to experimental band gap by asserting the screening effect which reduces the coulomb interaction.
- Exciton Insulators: Condensation of excitons
- Exciton have an attractive force which leads to a red shift (lowering) of the band gap.
- Qdots: Smaller sizes become more blue shifted because of the quantum confinement effect:
- Nanowires with Silicon.
- Experiment usually gets smaller exciton binding energy because of a substrate

## Chapter X: Magnetism

**Mermin Chapter 32 ~ pg. 680** For  $T = 0$  We have many different types of magnetism:

- Paramagnetism: Random unaligned spins, but the net magnetization is in one direction (PM)
- Ferromagnetism: All spins aligned in the same direction (FM)
- Antiferromagnetism: Neighboring spins are anti-aligned: Néel Vector (AFM)

**Real Materials** Real materials prefer a magnetic moment in the plane of the material, but is there a ground state? For a 2D material the magnetic moment lies in the  $XY$  plane e.g.  $CrCl_3$  or meron. At finite temperatures, there are spin defects(spins that are not aligned) or vertex defects and increase as the temperature increases.

**Interaction between Spin** Using the magnetic moment, we can calculate the interaction between two spins. The dipole-dipole interaction

$$U = \frac{1}{r^3} [\mathbf{m}_1 \cdot \mathbf{m}_2 - 3(\mathbf{m}_1 \cdot \hat{\mathbf{r}})(\mathbf{m}_2 \cdot \hat{\mathbf{r}})]$$

$$\mathbf{m}_1 = \frac{e\hbar}{mc} \quad \mathbf{r} \approx 1 \text{ \AA}$$

where this potential is roughly 0.1 meV and is much smaller than the room temperature energy of 25 meV.

**1D Chain** We can not have a long range order in a 1D chain using the Ising model, so we can not have a ferromagnetic state. At 1D the Curie Temperature is  $T_c = 0$ , so we do not have a stable state.

**2D Ising Model** We can analytically solve the 2D Ising model as Onsager did using transfer matrix methods.

### Hamiltonian

$$H = \sum i, j J \mathbf{S}_i \cdot \mathbf{S}_j$$

For when  $J > 0$  we have an AFM state, and when  $J < 0$  we have a FM state. The energy difference of the two states of spins are

$$\langle \uparrow\uparrow | H | \uparrow\uparrow \rangle - \langle \uparrow\downarrow | H | \uparrow\downarrow \rangle = E_1 - E_2 \sim J$$

From the wavefunction of the states

$$\Psi = \psi(\mathbf{r}) \cdot \chi(\mathbf{S})$$

we know the fermion wf is antisymmetric (Pauli Exclusion Principle), so the wavefunction must overlap in the local space, i.e.  $J$  is short-range (exchange interaction). We call this because we change the spin of the electron which results in a change in the energy states.

**Example:** A two electron system. The Hamiltonian is

$$H\Psi = -\frac{\hbar^2}{2m} [\nabla_1^2 + \nabla_2^2] \Psi + V(\mathbf{r}_1, \mathbf{r}_2) \Psi$$

$$= E\Psi$$

where the total wavefunction is

$$\Psi = \psi(\mathbf{r})\phi_s$$

The total spin is either 0 or 1, and the  $z$  component of the spin is either 0 or  $\pm 1$ :

$S$	$S_z$	$\chi$
0	0	$\frac{1}{\sqrt{2}}[ \uparrow\downarrow\rangle -  \downarrow\uparrow\rangle]$
1	1	$ \uparrow\uparrow\rangle$
1	0	$\frac{1}{\sqrt{2}}[ \uparrow\downarrow\rangle +  \downarrow\uparrow\rangle]$
1	-1	$ \downarrow\downarrow\rangle$

Where the singlet state is antisymmetric (minus sign) and the triplet state is symmetric. For the model with two hydrogen atoms, neglecting the electron-electron interaction, we have

$$(h_1 + h_2)\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

where the Hamiltonian is

$$h_i = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}_i - \mathbf{R}_2|}$$

This implies the symmetric solution

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)$$

where  $\psi_0$  is an eigenstate of  $h_i$ . The antisymmetric solution

$$\psi_t(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_0(\mathbf{r}_1)\psi_1(\mathbf{r}_2) - \psi_1(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]$$

Slater Determinant:

$$\begin{pmatrix} \psi_1(r_1) & \psi_2 & \psi_3 \\ \psi_1(r_2) & \psi_2 & \psi_3 \end{pmatrix} =$$

The symmetric state is the ground state because it has a lower energy. So the two states are

$$\begin{aligned} \psi_0 &= \phi_1(\mathbf{r}_1) + \phi_2(\mathbf{r}_2) \\ \psi_1 &= \phi_1(\mathbf{r}_1) - \phi_2(\mathbf{r}_2) \end{aligned}$$

The singlet state is

$$\begin{aligned} \psi_s(\mathbf{r}_1, \mathbf{r}_2) &= \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) \\ &\quad + \phi_1(\mathbf{r}_1)\phi_1(\mathbf{r}_2) + \phi_2(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \end{aligned}$$

where the last two terms are roughly zero (Heitler-London Approximation), and the Triplet state

$$\psi_t(\mathbf{r}_1, \mathbf{r}_2) = 2[\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2) - \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)]$$

**H-L Approximation** So the energy difference of the singlet and triplet state is

$$\begin{aligned} E_s - E_t &= \frac{\langle \psi_s | \hat{H} | \psi_s \rangle}{\langle \psi_s | \psi_s \rangle} - \frac{\langle \psi_t | \hat{H} | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle} \\ &\propto \int d\mathbf{r}_1 d\mathbf{r}_2 [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)][\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)] \\ &\left[ \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_2|} \right] \end{aligned}$$

This is the exchange interaction, and not the Coulomb interaction, and is what reduces the attractive forces between the electrons.

**Heisenberg Model** The Hamiltonian

$$H^{\text{spin}} = \frac{1}{4}(E_s + 3E_t) - (E_s - E_t)\mathbf{S}_1 \cdot \mathbf{S}_2$$

where the eigenvalue of the triplet state is  $E_t$ :

$$H^{\text{spin}} |\uparrow\uparrow\rangle = E_t |\uparrow\uparrow\rangle$$

This also gives us the exchange interaction between the two spins

$$H^{\text{spin}} = -(E_s - E_t)\mathbf{S}_1 \cdot \mathbf{S}_2 = -J\mathbf{S}_1 \cdot \mathbf{S}_2$$

where  $J$  is the exchange interaction. In a hexagonal lattice we have a Hamiltonian

$$H = - \sum_{ij} J \mathbf{S}_i \cdot \mathbf{S}_j$$

where we have 3 nearest neighbors and 6 next nearest neighbors for  $J$ . In all  $\hat{\mathbf{z}}$  we can describe the ferromagnetic states (FM).

**Example:** CrI<sub>3</sub> (Hexagonal Structure) we find that the exchange interaction is

$$J_1 = 2.12, \quad J_2 = 0.35, \quad J_3 = 0.05$$

which decreases exponentially. For the other similar materials,

$$\begin{aligned} \text{CrBr}_3 : J_1 &= 1.35, \quad J_2 = 0.14 \\ \text{CrCl}_3 : J_1 &= 0.8, \quad J_2 = 0.07 \end{aligned}$$

This decrease in  $J$  comes from the spin-orbital coupling, or the mass of the element leads to a stronger exchange interaction. Which one would have a higher Curie Temperature? The stronger interaction or  $J$  would require a higher Curie Temperature  $T_c$  to change from a FM to a PM state.

**Temperature Dependence** To get the temperature dependence, we use a monte carlo method to simulate random spins assigned to a lattice.

- As the Temperature gets close to Curie temperature but not quite there  $T < T_c$ , we will see small islands of opposite spin states which come up and disappear quickly (quench to zero).
- As the Temperature is similar  $T \sim T_c$  we see large islands with a fractal structure.

$$\langle M \rangle = \mu(T - T_c)^\delta$$

From the experiment vs. the theoretical results

Material	$T_c$ Exp(K)	Theory
$\text{CrCl}_3$	17	13
$\text{CrBr}_3$	27	24
$\text{CrI}_3$	45	43

For 2D materials, we see a negative linear slope at  $T < T_c$  which has no explanation...

**Direct Exchange** For perfectly aligned spins of the same orbital. A small orbital (d or f orbitals) may lead to a possible magnetic field. From the variational principle

- The s orbital is spherical as it is symmetric and has the least energy
- The p orbital is dumbbell shaped for the orthogonal relationship
- The d orbital is clover shaped

The two small orbitals 3d and 4f are typically very magnetic.

**Superexchange** Between two small d/f orbitals we have a large s/p orbital (e.g. Oxygen) that mediates the exchange.

**Indirect Exchange** An exchange between electrons where the charge distributions don't overlap, but the exterior field has a random distribution of spin.

**Layers** In experiment for CrI<sub>3</sub> in two layers we see that the layers are antiferromagnetic, but theory predicts that the layers are ferromagnetic... which is from the stacking method of the layers, i.e. AA. Unintuitively, this is a higher energy configuration compared to AB. This may be due to the room temperature keeping the layers in a higher energy state.

## Intro to Density Functional Theory

Software that use DFT [wiki](#). John Bardeen is a very important figure in solid state physics for the development of the field effect transistor and the BCS theory of superconductivity.

### Widely Used Software

- VASP (Paid)
- Quantum Espresso (Free & Recommended)
- ABINIT (Free)

**Some Math From Kohn and Sham’s “Self-Consistent Equations Including Exchange and Correlation Effects”** Given an ions  $M_i$  and electrons  $m_i$  the Hamiltonian is

$$H = \sum_i \frac{\mathbf{p}_i^2}{2M_i} + \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i < j} \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i < i'} \frac{e^2}{|\mathbf{r}_2 - \mathbf{r}_j|} + \sum_{i,j} \frac{-z_i e^2}{|\mathbf{R}_i - \mathbf{r}_j|}$$

And the adiabatic approximation  $\Rightarrow$  many-electron  $N$  with ground-state properties:

1. The ground state energy is

$$E_v[\rho] = \langle v(\mathbf{r})\rho(\mathbf{r}) \rangle + F[\rho]$$

where the bracket is a functional and  $v$  is the external potential.  $F[\rho]$  is a universal functional of  $\rho$ .

2.  $E_v[\rho]$  is a minimum for the correct physical density where  $\rho(\mathbf{r})$  safisfies

$$N = \int \rho(\mathbf{r}) d\mathbf{r}$$

3.  $\rho(\mathbf{r})$  and  $E_v[\rho]$  can in principle be exactly obtained from the solution of an associated one-electron problem with an effective potential  $V_{\text{eff}}$ .

**Hohenberg-Kohn “Inhomogeneous Electron Gas”** And electron has a Hamiltonian

$$\begin{aligned} H &= \sum_i \frac{\Phi_i^2}{2m} + \sum_i V(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ &= T + V + U \end{aligned}$$

They state:

1. Two external potentials,  $V, V' \Rightarrow H, H'$  that is

$$H |\Psi\rangle = E |\Psi\rangle, \quad H' |\Psi'\rangle = E' |\Psi'\rangle$$

where the first is the ground state, and the second is an excited state.

$$\begin{aligned} E' &= \langle \Psi' | H' | \Psi' \rangle \leq \langle \Psi | H' | \Psi \rangle \\ \text{and } H' &= T + V' + U \\ \Rightarrow \langle \Psi | H' | \Psi \rangle &= \langle \Psi | H + V' - V | \Psi \rangle \\ &= E + \langle \Psi | V' - V | \Psi \rangle \\ &= E + \int [V'(\mathbf{r}) - v(\mathbf{r})]\rho(\mathbf{r}) d\mathbf{r} \\ \Rightarrow E' &< E + \int [V' - v]\rho d\mathbf{r} \end{aligned}$$

and vice versa

$$E = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H | \Psi' \rangle$$

$$E < E' + \int [V(\mathbf{r}) - V'(\mathbf{r})] \rho'(\mathbf{r}) d\mathbf{r}$$

But if the density is the same, i.e.,  $\rho = \rho'$

$$E + E' < E + E'$$

which means there can only be one ground state.

**Kohn-Shannon** The equation from the seminal 1965 paper

$$E_v[\rho] = \int V(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + T_s[\rho] + \frac{1}{2} e^2 \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

where the kinetic energy in QM is in the form of a laplacian

$$T_s[\rho] = -\frac{\hbar^2}{2m} \sum_{i=1} \int \rho_i^* \nabla^2 \varphi_i d\mathbf{r}$$

there also is a correction term known as the exchange-correlation function added to the universal functional:

$$E_v[\rho] = \dots + E_{xc}[\rho]$$

Using the Euler-Lagrange method we get the Kohn-Sham equation:

$$\left[ \frac{p^2}{2m} + V(\mathbf{r}) + U_F(\mathbf{r}) + V_{ex}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = E_i \varphi_i$$

The Hartree potential is

$$V_H(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad \rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2$$

and the exchange potential is

$$V_{xc} = \frac{\delta E_{ex}[\rho]}{\delta \rho(\mathbf{r})}$$

but the exact form of  $V_{xc}$  is unknown. So we use a local density approximation (LDA) where

$$E_{xc}[\rho] \sim E_{xc}[\mathbf{r}] \quad \text{or} \quad \int \rho(\mathbf{r}) E_{xc}(\mathbf{r}) d\mathbf{r}$$

There is another approximate form: the Generalized Gradient Approximation (GGA) is

$$E_{xc}[\rho] = E_x[\rho(\mathbf{r})] \doteq E_x[\rho(\mathbf{r}), \frac{d\rho(\mathbf{r})}{d\mathbf{r}}]$$

The GGA approximation shows an exponential decay in the potential, but the LDA encapsulates the quantum well of the potential (morse potential like shape).

**Free Gas** From the uniform electron gas, we can represent the functional of the exchange potential as

$$V_{xc} = -\frac{3}{2} \frac{e^2}{\pi} (3\pi^2)^{1/3} \rho^{1/3} [\alpha(\rho)]$$

where  $[\alpha(\rho)]$  is calculated via quantum monte carlo (QMC) methods.

- DFT underestimates the band gap  $E_g^{\text{DFT}} < E_g^{\text{Exp}}$
- The ground state energy is similar to the experimental value.

1. For the HCP structure ABAB... the atoms in the B layer are equidistant from the atoms in the lower basal plane. The distance between an atom in the A layer and the atom in the B layer is equivalent to the distance between the atoms in the basal plane  $a$ . Also the height of the B layer is  $c/2$ . We can draw a right triangle with the hypotenuse being the distance between the atoms  $a$  and two sides of length  $c/2$  and  $x$  as shown in Figure 17.

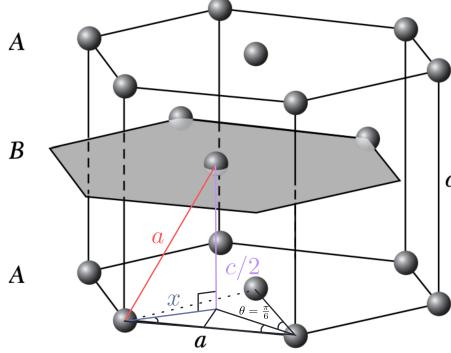


Figure 17: HCP structure (From Kittel)

To find  $x$  we can project the B atom onto the basal plane and use trig to find that

$$x \cos \frac{\pi}{6} = \frac{a}{2} \rightarrow x = \frac{a}{\sqrt{3}}$$

So using the Pythagorean theorem we can find the distance between the atoms in the A and B layers

$$\begin{aligned} a^2 &= \left(\frac{c}{2}\right)^2 + x^2 \\ a^2 &= \frac{c^2}{4} + \left(\frac{a}{\sqrt{3}}\right)^2 \\ \frac{2}{3}a^2 &= \frac{c^2}{4} \\ \frac{c}{a} &= \sqrt{\frac{8}{3}} \approx 1.633 \end{aligned}$$

2. (a) Given

$$\mathbf{a}_1 = (\sqrt{3}a/2)\hat{x} + (a/2)\hat{y}; \quad \mathbf{a}_2 = -(\sqrt{3}a/2)\hat{x} + (a/2)\hat{y}; \quad \mathbf{a}_3 = c\hat{z}$$

the volume of the primitive cell is equivalent to the volume of the parallelepiped:

$$\begin{aligned} V_c &= \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \\ &= \mathbf{a}_1 \cdot \det \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\sqrt{3}a/2 & a/2 & 0 \\ 0 & 0 & c \end{vmatrix} \\ &= \left( \frac{\sqrt{3}a}{2}\hat{x} + \frac{a}{2}\hat{y} \right) \cdot \left( \frac{ac}{2}\hat{x} + \frac{\sqrt{3}ac}{2}\hat{y} \right) \\ &= \frac{\sqrt{3}a^2c}{4} + \frac{\sqrt{3}a^2c}{4} \\ &= \frac{\sqrt{3}a^2c}{2} \end{aligned}$$

(b) The first reciprocal lattice vector is

$$\begin{aligned}\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V_c} \\ &= 2\pi \frac{\left(\frac{ac}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}ac}{2}\hat{\mathbf{y}}\right)}{\frac{\sqrt{3}a^2c}{2}} \\ &= 2\pi \frac{\hat{\mathbf{x}} + \sqrt{3}\hat{\mathbf{y}}}{\sqrt{3}a} \\ &= \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}}\hat{\mathbf{x}} + \hat{\mathbf{y}} \right)\end{aligned}$$

The other reciprocal lattice vectors can be found similarly:

$$\mathbf{a}_3 \times \mathbf{a}_1 = \det \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 0 & 0 & c \\ \sqrt{3}a/2 & a/2 & 0 \end{vmatrix} = -\frac{ac}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}ac}{2}\hat{\mathbf{y}}$$

so

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V_c} = \frac{2\pi}{a} \left( -\frac{1}{\sqrt{3}}\hat{\mathbf{x}} + \hat{\mathbf{y}} \right)$$

and

$$\mathbf{a}_1 \times \mathbf{a}_2 = \det \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ \sqrt{3}a/2 & a/2 & 0 \\ -\sqrt{3}a/2 & a/2 & 0 \end{vmatrix} = (\sqrt{3}a^2/4 + \sqrt{3}a^2/4)\hat{\mathbf{z}} = \frac{\sqrt{3}a^2}{2}\hat{\mathbf{z}}$$

so

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V_c} = \frac{2\pi}{c}\hat{\mathbf{z}}$$

(c) A sketch of the 2D Brillouin zone is a hexagon as shown in Figure 18.

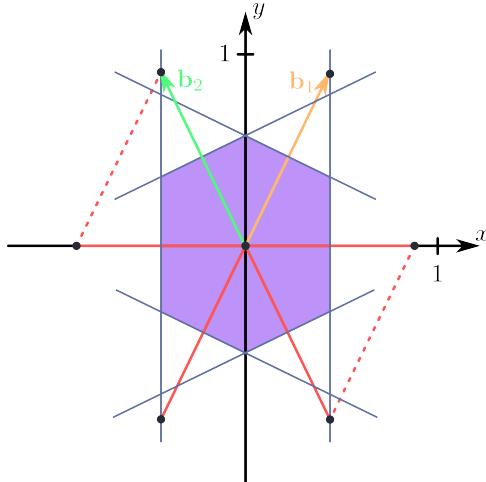


Figure 18: 2D Brillouin zone on  $xy$  plane

3. (a) The total potential energy is

$$U(R) = N \left( \frac{A}{R^n} - \frac{\alpha q^2}{R} \right)$$

where the Madelung constant for a 1D chain of ions is  $\alpha = 2 \ln 2$ , and we replace the usual repulsive potential  $\lambda \exp(-R/p)$  with  $A/R^n$ . Taking the derivative with respect to  $R$  and finding the equilibrium separation at a critical point:

$$\begin{aligned}\frac{dU}{dR} &= N \left( -\frac{nA}{R^{n+1}} + \frac{\alpha q^2}{R^2} \right) = 0 \\ \frac{NA}{R^{n+1}} &= \frac{\alpha q^2}{R^2} \\ \frac{R^{n+1}}{R^2} &= \frac{nA}{\alpha q^2} \\ R_o^{n-1} &= \frac{nA}{\alpha q^2} \\ A &= \frac{\alpha q^2 R_o^{n-1}}{n}\end{aligned}$$

substituting back into the potential energy:

$$\begin{aligned}U(R_o) &= N \left( \frac{\alpha q^2 R_o^{n-1}}{n R_o^n} - \frac{\alpha q^2}{R_o} \right) \\ &= N \left( \frac{\alpha q^2}{n R_o} - \frac{\alpha q^2}{R_o} \right) \\ &= \frac{N \alpha q^2}{R_o} \left( \frac{1}{n} - 1 \right) \\ U(R_o) &= -\frac{2Nq^2 \ln 2}{R_o} \left( 1 - \frac{1}{n} \right)\end{aligned}$$

(b) Approximating the potential around  $x$  using Taylor expansion  $f(x+h) = f(x) + f'(x)h + \frac{1}{2}f''(x)h^2$ :

$$\begin{aligned}U(R_o(1-\delta)) &= U(R_o + (-R_o\delta)) \\ &= U(R_o) - [U'(R_o)](R_o\delta) + \frac{1}{2}[U''(R_o)](R_o\delta)^2 + \dots\end{aligned}$$

and since  $\frac{dU}{dR} = 0$  at  $R_o$ , the second term is zero. And the second order derivative gives

$$\begin{aligned}\frac{d^2U}{dR^2} &= N \left( \frac{n(n+1)A}{R^{n+2}} - \frac{2\alpha q^2}{R^3} \right) \Big|_{R=R_o} \\ \text{using } R_o^{n-1} &= \frac{nA}{\alpha q^2} \\ &= N \left( \frac{n(n+1)A}{\frac{nA}{\alpha q^2} R_o^3} - \frac{2\alpha q^2}{R_o^3} \right) \\ &= N \left( \frac{(n+1)\alpha q^2}{R_o^3} - \frac{2\alpha q^2}{R_o^3} \right) \\ &= \frac{N\alpha q^2}{R_o^3} ((n+1) - 2) \\ \frac{d^2U}{dR^2} &= \frac{N\alpha q^2}{R_o^3} (n-1)\end{aligned}$$

so potential is approximately

$$U(R_o(1-\delta)) \approx U(R_o) + \frac{1}{2} \frac{N\alpha q^2}{R_o^3} (n-1)(R_o\delta)^2$$

so the leading coefficient is (ignoring the  $\frac{1}{2}\delta^2$  part)

$$C = \frac{N\alpha q^2}{R_o^3} (n - 1) R_o^2$$

To cancel the  $N$  we can use that fact that compressing to the unit length makes the separation between ions  $2NR_o = 1$ , so  $N = 1/(2R_o)$ , so

$$C = \frac{1}{2R_o} \frac{\alpha q^2}{R_o^3} (n - 1) R_o^2 = \frac{\alpha q^2}{2R_o^2} (n - 1)$$

and using the Madelung constant  $\alpha = 2 \ln 2$ , the leading term is finally

$$C = \frac{(n - 1)q^2 \ln 2}{R_o^2}$$

so the work done is

$$\begin{aligned} W &= \Delta U = U((R_o\delta)) - U(R_o) \\ &\approx U(R_o) + \frac{1}{2}C\delta^2 - U(R_o) \\ W &\approx \frac{1}{2}C^2\delta^2 \end{aligned}$$

where the leading term is indeed in the order of  $\frac{1}{2}C\delta^2$ .

**Problem 1.** Given

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

where the nearest neighbors is displaced by  $\pm p$  which is small so using the Taylor expansion

$$\begin{aligned} u_{s+a} &\approx u_s + a \frac{\partial u}{\partial x} + \frac{1}{2} a^2 \frac{\partial^2 u}{\partial x^2} \\ u_{s-a} &\approx u_s - a \frac{\partial u}{\partial x} + \frac{1}{2} a^2 \frac{\partial^2 u}{\partial x^2} \end{aligned}$$

so

$$C(u_{s+1} + u_{s-1} - 2u_s) \approx C \left( \cancel{u_s} + a \cancel{\frac{\partial u}{\partial x}} + \frac{1}{2} a^2 \frac{\partial^2 u}{\partial x^2} + \cancel{u_s} - a \cancel{\frac{\partial u}{\partial x}} + \frac{1}{2} a^2 \frac{\partial^2 u}{\partial x^2} - 2u_s \right) = Ca^2 \frac{\partial^2 u}{\partial x^2}$$

and

$$\begin{aligned} M \frac{d^2 u_s}{dt^2} &= Ca^2 \frac{\partial^2 u}{\partial x^2} \\ \frac{d^2 u_s}{dt^2} &= \frac{Ca^2}{M} \frac{\partial^2 u}{\partial x^2} \end{aligned}$$

since the original differential equation can have solutions with time dependence  $e^{i\omega t}$

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

and the displacements are translationally symmetric so

$$u_s = ue^{iska} \quad u_{s+1} = ue^{i(s+1)ka} = ue^{iska} e^{ika} \quad u_{s-1} = ue^{i(s-1)ka} = ue^{iska} e^{-ika}$$

so

$$\begin{aligned} -M\omega^2 ue^{iska} &= Cue^{iska} (e^{ika} + e^{-ika} - 2) \\ -M\omega^2 &= C(e^{ika} + e^{-ika} - 2) \end{aligned}$$

where we have the trigonometric identity

$$e^{ika} + e^{-ika} = 2 \cosh(ika) = 2 \cos(ka)$$

so

$$\begin{aligned} -M\omega^2 &= C(2 \cos(ka) - 2) \\ \omega^2 &= \frac{2C}{M}(1 - \cos(ka)) \end{aligned}$$

and from the half angle identity

$$1 - \cos(ka) = 2 \sin^2\left(\frac{ka}{2}\right)$$

so

$$\omega = \sqrt{\frac{4C}{M}} \sin\left(\frac{ka}{2}\right)$$

we can also find the group velocity

$$v = \frac{d\omega}{dk} = \sqrt{\frac{4C}{M}} \cos\left(\frac{ka}{2}\right) \frac{a}{2} = \sqrt{\frac{Ca^2}{M}} \cos\left(\frac{ka}{2}\right)$$

and when  $ka \ll 1$  or  $\approx 0$ , cosine is 1 so the group velocity is

$$v = \sqrt{\frac{Ca^2}{M}} \quad \text{or} \quad v^2 = \frac{Ca^2}{M}$$

so we get the wave equation

$$\frac{d^2 u}{dt^2} = v^2 \frac{d^2 u}{dx^2}$$

**Problem 2.** There will be two equations for alternate force constants where the nearest neighbor for atom  $u_s$  are  $u'_s$  and  $u'_{s-1}$ , and for atom  $u'_s$ , the nearest neighbors are  $u_s$  and  $u_{s+1}$ . So the equations of motion are

$$\begin{aligned} M \frac{d^2 u}{dt^2} &= C(u'_s - u_s) + C'(u'_{s-1} - u_s) \\ M \frac{d^2 u'}{dt^2} &= C'(u_{s+1} - u'_s) + C(u_s - u'_s) \end{aligned}$$

where  $C' = 10C$ . The shifted parts are

$$\begin{aligned} u'_{s-1} &= ue^{iska} e^{-ika} = ue^{iska} e^{-ika} \\ u_{s+1} &= ue^{iska} e^{ika} = ue^{iska} e^{ika} \end{aligned}$$

and from the previous problem  $e^{iska}$  will cancel out (but not  $u$  or  $u'$ ) so

$$\begin{aligned} -M\omega^2 u &= C(u' - u) + C'(u'e^{-ika} - u) \\ -M\omega^2 u' &= C'(ue^{ika} - u') + C(u - u') \end{aligned}$$

rearranging the terms for the first EQ:

$$\begin{aligned} M\omega^2 u &= -C(u' - u) - C'(u'e^{-ika} - u) \\ &= (C + C')u + (-C - C'e^{-ika})u' \\ 0 &= (C + C' - M\omega^2)u + (-C - C'e^{-ika})u' \end{aligned}$$

and for the second EQ:

$$\begin{aligned} M\omega^2 u' &= -C'(ue^{ika} - u') - C(u - u') \\ &= (-C - C'e^{ika})u + (C + C')u' \\ 0 &= (-C - C'e^{ika})u + (C + C' - M\omega^2)u' \end{aligned}$$

so we have the matrix equation

$$\begin{pmatrix} C + C' - M\omega^2 & -C - C'e^{-ika} \\ -C - C'e^{ika} & C + C' - M\omega^2 \end{pmatrix} \begin{pmatrix} u \\ u' \end{pmatrix} = 0$$

we can solve for the eigenvalues of the matrix by finding the determinant:

For  $K = 0$ , the matrix is

$$\begin{pmatrix} C + C' - M\omega^2 & -C - C' \\ -C - C' & C + C' - M\omega^2 \end{pmatrix}$$

and we have a special case where  $u = u'$  or

$$0 = (C + C' - M\omega^2)u + (-C - C')u = -M\omega^2 \implies \omega^2 = 0$$

and the other case where the determinant is zero

$$\begin{aligned} 0 &= (C + C' - M\omega^2)^2 - (-C - C')^2 \\ \text{using } (a + b + c)^2 &= a^2 + b^2 + c^2 + 2ab + 2bc + 2ac \\ &= C^2 + C'^2 + M^2\omega^4 + 2CC' - 2C'M\omega^2 - 2CM\omega^2 \\ &\quad - (C^2 + C'^2 + 2CC') \\ &= M^2\omega^4 - 2C'M\omega^2 - 2CM\omega^2 \\ &= M\omega^2 - 2(C' + C) \end{aligned}$$

and plugging in  $C' = 10C$

$$0 = M\omega^2 - 2(11C) \implies \omega^2 = 22C/M$$

For  $K = \pi/a$  and separation  $a = \pi/2$

$$e^{ika} = e^{i\frac{\pi}{a}\frac{a}{2}} = e^{i\pi} = -1 \quad e^{-ika} = -1$$

so the matrix is

$$\begin{pmatrix} C + C' - M\omega^2 & -C + C' \\ C - C' & C + C' - M\omega^2 \end{pmatrix} \begin{pmatrix} u \\ u' \end{pmatrix} = 0$$

so for the special case where  $u = u'$ :

$$\begin{aligned} 0 &= (C + C' - M\omega^2) + (-C + C') \\ &= 2C' - M\omega^2 \implies \omega^2 = 20C/M \end{aligned}$$

and the other case where the determinant is zero

$$\begin{aligned} 0 &= (11C - M\omega^2)^2 - (9C)^2 \\ &= 121C^2 - 22CM\omega^2 + M^2\omega^4 - 81C^2 \\ &= M^2\omega^4 - 22CM\omega^2 + 40C^2 \\ &= (M\omega^2)^2 - 22C(M\omega^2) + 40C^2 \end{aligned}$$

solving this quadratic equation where  $a = 1, b = -22C, c = 40C^2$

$$\begin{aligned} M\omega^2 &= \frac{22C \pm \sqrt{(-22C)^2 - 4(40C^2)}}{2} = \frac{22C \pm \sqrt{484C^2 - 160C^2}}{2} \\ &= \frac{22C \pm \sqrt{324C^2}}{2} = \frac{22C \pm 18C}{2} = 20C, 2C \end{aligned}$$

so

$$\omega^2 = \frac{20C}{M}, \frac{2C}{M}$$

thus the dispersion relations are

$$\begin{aligned} K = 0 : \quad \omega &= 0, \sqrt{\frac{22C}{M}} \\ K = \pi/a : \quad \omega &= \sqrt{\frac{20C}{M}}, \sqrt{\frac{2C}{M}} \end{aligned}$$

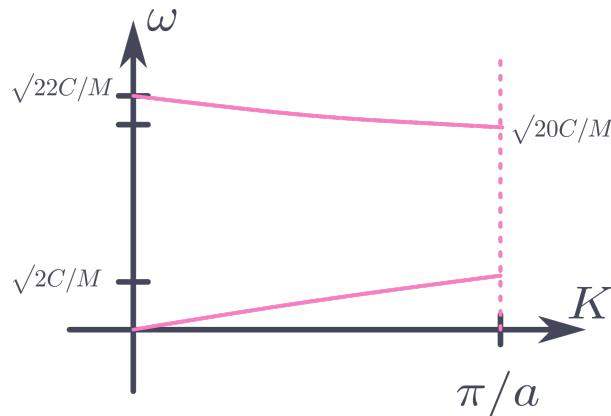


Figure 19: Dispersion relation for  $K = 0, \pi/a$

**Problem 3.** Given

$$m\left(\frac{dv}{dt} + \frac{v}{\tau}\right) = -eE$$

for time varying  $E$  and  $v$

$$E = E_0 e^{-i\omega t} \quad v = v_0 e^{-i\omega t}; \quad \frac{dv}{dt} = -i\omega v$$

so solving for  $v$

$$\begin{aligned} m\left(-i\omega v + \frac{v}{\tau}\right) &= -eE \\ v &= \frac{-eE}{m\left(-i\omega + \frac{1}{\tau}\right)}\left(\frac{\tau}{\tau}\right) \\ &= \frac{-eE}{m} \frac{\tau}{-i\omega\tau + 1} \end{aligned}$$

from Ohm's Law

$$\begin{aligned} j &= \sigma E = nqv \quad \text{or} \quad \sigma = \frac{-nev}{E} \\ \text{where } \sigma(0) &= \frac{ne^2\tau}{m} \end{aligned}$$

where the charge is  $q = -e$ . Substituting  $v$  from the previous equation

$$\begin{aligned} \sigma &= \frac{-ne}{E} \frac{-eE}{m} \frac{\tau}{-i\omega\tau + 1} \\ &= \frac{ne^2\tau}{m} \frac{1}{-i\omega\tau + 1} \left( \frac{1 + i\omega\tau}{1 + i\omega\tau} \right) \\ \sigma(\omega) &= \sigma(0) \frac{1 + i\omega\tau}{1 + (\omega\tau)^2} \end{aligned}$$

where we multiply by the complex conjugate in the second step.

**Problem 1.** (a) From Kittel, for a periodic delta-function potential we get the simplified equation

$$\frac{P}{Ka} \sin(Ka) + \cos(Ka) = \cos(ka)$$

where  $\cos(ka) = 1$  at  $k = 0$ . Taking the Taylor series approximations for small  $Ka$ :

$$\begin{aligned}\sin(Ka) &= Ka \dots \\ \cos(Ka) &= 1 - \frac{1}{2}(Ka)^2 + \dots\end{aligned}$$

but if we approximate only to the first order, we get

$$\frac{P}{Ka} Ka + 1 = 1 \implies P = 0$$

which doesn't tell us any information to find the band gap

$$\epsilon = \frac{\hbar^2 K^2}{2m}$$

so we take the second order approximation for the cosine term:

$$\begin{aligned}\frac{P}{Ka} Ka + 1 - \frac{1}{2}(Ka)^2 &= 1 \\ \implies K^2 &= \frac{2P}{a^2}\end{aligned}$$

so the band gap is

$$\epsilon \approx \frac{\hbar^2 P}{ma^2}$$

(b) For  $k = \pi/a$ ,  $\cos ka = -1$  and the equation becomes

$$\frac{P}{Ka} \sin(Ka) + \cos(Ka) = -1$$

and from Figure 20 we can approximate the Taylor series around  $Ka = \pi + h$ :

$$f(x+h) \approx f(x) + hf'(x) + \frac{1}{2}h^2f''(x)$$

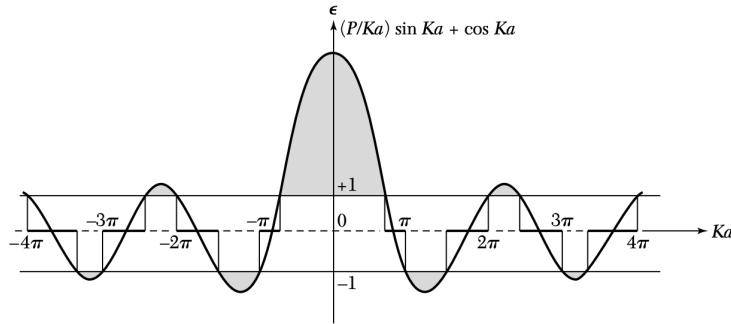


Figure 20: From Kittel

so we have

$$\begin{aligned}\sin(Ka) &\approx \sin \pi + h \cos \pi = -h \\ \cos(Ka) &\approx \cos \pi + h(-\sin \pi) + \frac{1}{2}h^2(-\cos \pi) = -1 + \frac{1}{2}h^2\end{aligned}$$

and thus

$$\begin{aligned} \frac{P}{\pi}(-h) + \left(-1 + \frac{1}{2}h^2\right) &= -1 \\ \implies h &= \frac{2P}{\pi} \end{aligned}$$

where

$$\begin{aligned} (Ka)^2 &= (\pi + h)^2 = \pi^2 + 2\pi h + h^2 \\ \implies K^2 &= \frac{\pi^2 + 2\pi h}{a^2} = \frac{\pi^2 + 4P}{a^2} \end{aligned}$$

so the band gap is

$$\epsilon \approx \frac{\hbar^2 K^2}{2ma^2} = \frac{\hbar^2}{2ma^2} \frac{\pi^2 + 4P}{a^2}$$

**Problem 2** Using the central equation

$$(\lambda_k - \epsilon)C(k) + \sum_G U_G C(k - G) = 0$$

where the energy gap occurs at

$$k = \pm \frac{\pi}{a} \hat{x} + \pm \frac{\pi}{a} \hat{y}$$

and from the Bragg condition  $(\mathbf{k} + \mathbf{G})^2 = k^2$  the reciprocal lattice vector is

$$G = \frac{2\pi}{a} \hat{x} + \frac{2\pi}{a} \hat{y}$$

using the relation  $k - G = -\frac{\pi}{a}$  we have two equations to solve for the energy gap:

$$\begin{aligned} (\lambda - \epsilon)C\left(\frac{\pi}{a}, \frac{\pi}{a}\right) + U_G C\left(-\frac{\pi}{a}, -\frac{\pi}{a}\right) &= 0 \\ (\lambda - \epsilon)C\left(-\frac{\pi}{a}, -\frac{\pi}{a}\right) + U_G C\left(\frac{\pi}{a}, \frac{\pi}{a}\right) &= 0 \end{aligned}$$

which can be written as a matrix equation

$$\begin{pmatrix} \lambda - \epsilon & U_G \\ U_G & \lambda - \epsilon \end{pmatrix} \begin{pmatrix} C\left(\frac{\pi}{a}, \frac{\pi}{a}\right) \\ C\left(-\frac{\pi}{a}, -\frac{\pi}{a}\right) \end{pmatrix} = 0$$

so the determinant of the matrix is

$$\begin{aligned} (\lambda - \epsilon)^2 - U_G^2 &= 0 \\ \implies \epsilon &= \lambda \pm U_G \end{aligned}$$

and thus the two roots tells us that the energy gap is  $E_g = 2|U_G|$ . From the Fourier transform of the potential:

$$\begin{aligned} U &= \sum_G U_G e^{i\mathbf{G} \cdot \mathbf{r}} \\ U(x, y) &= \sum_G U_G \cos(G_x x) \cos(G_y y) \end{aligned}$$

so the fourier coefficients of the potential is

$$\begin{aligned} U_G &= \iint_0^a U(x, y) \cos(G_x x) \cos(G_y y) dx dy \\ &= \iint_0^a U(x, y) \cos\left(\frac{2\pi x}{a}\right) \cos\left(\frac{2\pi y}{a}\right) dx dy \\ &= 4U \frac{4}{a^2} \iint_0^a \cos^2\left(\frac{2\pi x}{a}\right) \cos^2\left(\frac{2\pi y}{a}\right) dx dy \end{aligned}$$

where

$$\int_0^a \cos^2\left(\frac{2\pi x}{a}\right) dx = \frac{a}{2}$$

so

$$U_G = -4U \frac{4}{a^2} \left(\frac{a}{2} \frac{a}{2}\right) = -4U$$

and the magnitude of the band gap is

$$E_g = 2|U_G| = 8U$$

**Problem 1.** For a Fermi Gas in 3D we assume a sphere in  $k$ -space with radius  $k_F$  and volume  $\frac{4}{3}\pi k_F^3$ . For each volume element we have 3D potential well with a plane wave solution  $k^3 = \left(\frac{2\pi}{L}\right)^3$ . So the total number of states in the sphere is

$$\begin{aligned} N &= 2 \cdot \frac{\frac{4}{3}\pi k_F^3}{(2\pi/L)^3} = \frac{8\pi k_F^3}{3\pi^2/L^3} = \frac{8}{3}k_F^3 \frac{V}{(2\pi)^3} = \frac{V}{3\pi^2}k_F^3 \\ &\implies k_F = \left(\frac{3\pi^2}{V}N\right)^{1/3} \end{aligned}$$

where  $V = L^3$  is the volume of the box in  $k$ -space and the factor of 2 comes from the spin degeneracy. From Kittel we know that the Fermi surface has an energy

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

so we can find the average energy by integrating over all states

$$\begin{aligned} U_0 &= \int_0^N \epsilon_F dN \\ &= \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{V}\right)^{2/3} \int_0^N N^{2/3} dN \\ &= \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{V}\right)^{2/3} \frac{3}{5} N^{5/3} \\ &= \frac{\hbar^2}{2m} \left(\frac{3\pi^2}{V}N\right)^{2/3} \frac{3}{5} N^{3/3} \\ U_0 &= \frac{3}{5} \epsilon_F N \end{aligned}$$

**Problem 2.** The number of electrons per unit area is given by the integral (From Kittle)

$$n = \int_0^\infty D(\epsilon) f(\epsilon) d\epsilon$$

where the Fermi Dirac Function tells us the average number of fermions in a state

$$f(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$

where  $\beta = \frac{1}{k_B T}$ , and since the 2D density of states  $D(\epsilon) = \frac{m}{\pi\hbar^2}$  is constant

$$n = \frac{m}{\pi\hbar^2} \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon$$

To compute the integral we rewrite the integral as

$$\int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \left( \frac{e^{-\beta(\epsilon-\mu)}}{e^{-\beta(\epsilon-\mu)}} \right) d\epsilon = \int_0^\infty \frac{e^{-\beta(\epsilon-\mu)}}{e^{-\beta(\epsilon-\mu)} + 1} d\epsilon$$

and make the substitution  $x = e^{-\beta(\epsilon-\mu)}$  so that  $dx = -\beta e^{-\beta(\epsilon-\mu)} d\epsilon$ :

$$\begin{aligned} n &= -\frac{m}{\pi\hbar^2} \frac{1}{\beta} \int_{\epsilon=0}^\infty \frac{1}{x+1} dx \\ &= -\frac{m}{\pi\hbar^2} \frac{1}{\beta} \ln(x+1) \Big|_{\epsilon=0}^\infty \\ \frac{n\pi\hbar^2}{m} \beta &= -\ln(e^{-\beta(\epsilon-\mu)} + 1) \Big|_0^\infty \\ &= -[\ln(0+1) - \ln(e^{\mu\beta} + 1)] \\ &= \ln(e^{\mu\beta} + 1) \end{aligned}$$

Finally to solve for  $\mu$  we take the exponential of both sides

$$\begin{aligned} e^{n\pi\hbar^2\beta/m} &= e^{\mu\beta} + 1 \\ \implies e^{\mu\beta} &= e^{n\pi\hbar^2\beta/m} - 1 \\ \mu &= \frac{1}{\beta} \ln(\exp(n\pi\hbar^2\beta/m) - 1) \\ \text{or } \mu(T) &= k_B T \ln[\exp(\pi n \hbar^2 / m k_B T) - 1] \end{aligned}$$

**Problem 3.** (a) The corner electron has a wave vector  $\mathbf{k}_b = (\frac{\pi}{a}, \frac{\pi}{a})$  and the side face electron has a

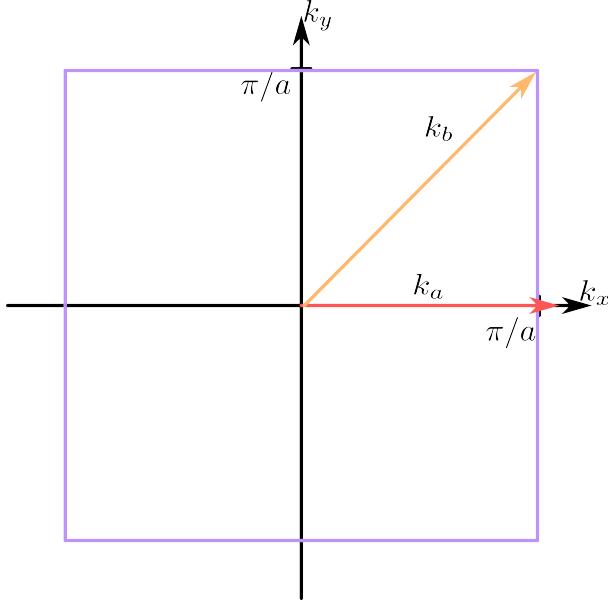


Figure 21: Square Lattice with free electron at corner ( $k_b$ ) and at the midpoint of a side face ( $k_a$ ).

wave vector  $\mathbf{k}_a = (\frac{\pi}{a}, 0)$ . The energy of the electron in the lattice is given by

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

so the ratio of the two electrons are

$$\frac{\epsilon_b}{\epsilon_a} = \frac{k_b^2}{k_a^2}$$

and since the square of the magnitudes of the wave vectors are

$$k_b^2 = \frac{\pi^2}{a^2} + \frac{\pi^2}{a^2} = \frac{2\pi^2}{a^2} \quad \text{and} \quad k_a^2 = \frac{\pi^2}{a^2}$$

the ratio of the energies is

$$\frac{\epsilon_b}{\epsilon_a} = \frac{2\pi^2/a^2}{\pi^2/a^2} = 2$$

(b) For three dimensions the wave vectors are

$$\begin{aligned} \mathbf{k}_b &= \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right) \quad \text{and} \quad \mathbf{k}_a = \left(\frac{\pi}{a}, 0, 0\right) \\ \implies k_b^2 &= \frac{3\pi^2}{a^2} \quad \text{and} \quad k_a^2 = \frac{\pi^2}{a^2} \end{aligned}$$

so the electron at the corner has a kinetic energy larger than the electron at the side face by a factor of

$$\frac{\epsilon_b}{\epsilon_a} = 3$$

(c) For divalent metals—two valence electrons per atom—the fermi surface extends out of the first Brillouin zone and into the second. The spill over of the valence electrons and neglect filling up the high energy corner states causes the conductivity of divalent metals to be higher than that of monovalent metals.

**Problem 1.** (a) In the vacuum  $\varphi_0(x, z) = A \cos(kx)e^{kz}$ , and the electric field is the negative gradient of the electrostatic potential, so

$$\begin{aligned}\mathbf{E}_0 &= -\nabla\varphi_0 = \left(-\frac{\partial\varphi_0}{\partial x}, -\frac{\partial\varphi_0}{\partial z}\right) \\ &= (kA \sin(kx)e^{kz}, kA \cos(kx)e^{kz})\end{aligned}$$

and the tangential component of the electric field  $\mathbf{E}_{x0} = Ak \sin(kx)e^{kz}$  satisfies the boundary condition  $\mathbf{E}_{xi} = kA \sin(kx)e^{-kz} = \mathbf{E}_{x0}$  for  $z < 0$ .

(b) The normal (or  $z$ ) component of the Displacement field at the boundary is given as

$$D_{zi} = \epsilon(\omega)E_{zi} = \epsilon(\omega)kA \cos(kx)e^0 = \epsilon(\omega)kA \cos(kx)$$

for a vacuum we have

$$D_{z0} = E_{z0} = -\frac{\partial\varphi_0}{\partial z} = -kA \cos(kx)e^0 = -kA \cos(kx)$$

So for

$$\epsilon(\omega)kA \cos(kx) = -kA \cos(kx) \implies \epsilon(\omega) = -1$$

And the dielectric function for a plasma is

$$\begin{aligned}\epsilon(\omega) &= 1 - \frac{\omega_p^2}{\omega^2} \\ -1 &= 1 - \frac{\omega_p^2}{\omega^2} \implies \omega^2 = \frac{1}{2}\omega_p^2\end{aligned}$$

**Problem 2.** Metal 1 on the positive side of the interface can be treated as the plasma from Problem 1, and vice versa for Metal 2, so the dielectric functions are

$$\begin{aligned}\epsilon_1(\omega) &= 1 - \frac{\omega_{p1}^2}{\omega^2} \\ \epsilon_2(\omega) &= 1 - \frac{\omega_{p2}^2}{\omega^2}\end{aligned}$$

And the boundary conditions require the Displacement field to be continuous across the interface:

$$\begin{aligned}D_{z01} &= D_{z02} \\ \epsilon_1(\omega) \left[ -\frac{\partial\varphi_{01}}{\partial z} \right] &= \epsilon_2(\omega) \left[ -\frac{\partial\varphi_{02}}{\partial z} \right] \\ \epsilon_1(\omega) \left[ -\frac{\partial}{\partial z} (A \cos(kx)e^{-kz}) \right] &= \epsilon_2(\omega) \left[ -\frac{\partial}{\partial z} (A \cos(kx)e^{kz}) \right] \\ \epsilon_1(\omega) &= -\epsilon_2(\omega)\end{aligned}$$

So the frequency associated with the interface is

$$\begin{aligned}1 - \frac{\omega_{p1}^2}{\omega^2} &= -\left(1 - \frac{\omega_{p2}^2}{\omega^2}\right) \\ 2 &= \frac{\omega_{p2}^2 + \omega_{p1}^2}{\omega^2} \\ \implies \omega &= \left[\frac{1}{2}(\omega_{p1}^2 + \omega_{p2}^2)\right]^{1/2}\end{aligned}$$

**Problem 3.** (a) Starting with the electromagnetic wave equation (53) from Kittel becomes

$$c^2 K^2 E^2 = \omega^2(E + 4\pi P) \rightarrow c^2 K^2 E^2 = \omega^2(\epsilon(\infty)E + 4\pi P)$$

or

$$E(\omega^2 \epsilon(\infty) - c^2 K^2) + P(4\pi \omega^2) = 0$$

and (54) remains

$$\begin{aligned} -\omega^2 P + \omega_T^2 P &= (Nq^2/M)E \\ \text{or } E(Nq^2/M) + P(\omega^2 - \omega_T^2) &= 0 \end{aligned}$$

The two equations have a solution when the determinant of the matrix is zero:

$$\begin{vmatrix} \omega^2 \epsilon(\infty) - c^2 K^2 & 4\pi \omega^2 \\ Nq^2/M & \omega^2 - \omega_T^2 \end{vmatrix} = 0$$

so

$$\begin{aligned} [\omega^2 \epsilon(\infty) - c^2 K^2][\omega^2 - \omega_T^2] - 4\pi \omega^2 \frac{Nq^2}{M} &= 0 \\ \omega^2 [\omega^2 \epsilon(\infty) - \omega_T^2 \epsilon(\infty) - c^2 K^2] + c^2 K^2 \omega_T^2 - 4\pi \omega^2 \frac{Nq^2}{M} &= 0 \end{aligned}$$

at  $K = 0$  we have a two roots for  $\omega^2$ :

$$\begin{aligned} \omega^2 \left[ \omega^2 \epsilon(\infty) - \omega_T^2 \epsilon(\infty) - 4\pi \frac{Nq^2}{M} \right] &= 0 \\ \implies \omega^2 &= \omega_T^2 + \frac{4\pi Nq^2}{M \epsilon(\infty)} \end{aligned}$$

(b) For low  $\omega$  we can neglect the  $\omega^4$  and  $\omega^2 c^2 k^2$  which leaves us with

$$\begin{aligned} -\omega^2 [\omega_T^2 \epsilon(\infty) + 4\pi Nq^2/M] + c^2 k^2 \omega_T^2 &= 0 \\ \implies \omega^2 &= \frac{c^2 k^2 \omega_T^2}{\omega_T^2 \epsilon(\infty) + 4\pi Nq^2/M} \\ &= \frac{c^2 k^2}{\epsilon(\infty) + 4\pi Nq^2/M \omega_T^2} \end{aligned}$$

where we know the dielectric function at  $\omega = 0$  is from Kittel is

$$\epsilon(0) = \epsilon(\infty) + \frac{4\pi Nq^2}{M \omega_T^2} \quad (59)$$

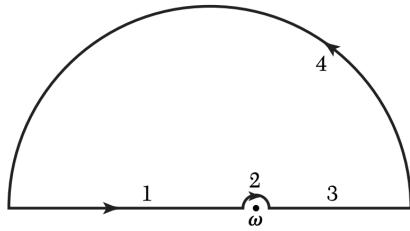
so

$$\omega^2 = \frac{c^2 k^2}{\epsilon(0)} \implies \omega = \frac{ck}{\sqrt{\epsilon(0)}}$$

**Problem 1.** (a) The displacement is given by

$$x(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \alpha(\omega) e^{i\omega t} d\omega$$

where the integral over the contour (the upper semicircle in the figure from Kittel) is zero since  $\alpha(\omega)$  is analytic in the upper plane. (b)



**Figure 2** Contour for the Cauchy principal value integral.

$$x(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{\omega_0^2 - \omega^2 - i\omega\rho} d\omega$$

Since the integral vanishes over the infinite semicircle, the Cauchy integral at the lower half-plane, and with the residues at

$$\pm \frac{1}{2} \left( \omega_0^2 - \frac{1}{4}\rho^2 \right)^{1/2} e^{-\rho t/2} e^{\mp i(\omega_0^2 - \frac{1}{4}\rho^2)^{1/2}t}$$

the displacement is the imaginary part of the sum of the residues:

$$x(t) = \left( \omega_0^2 - \frac{1}{4}\rho^2 \right)^{1/2} e^{-\rho t/2} \sin \left( [\omega_0^2 - \frac{1}{4}\rho^2]^{1/2} t \right)$$

**2** (a) Ferromagnetic Insulators:

- EuO, Crystal Structure: SC, Curie Temp: 69 K (Kittel)
- EuS, Crystal Structure: SC, Curie Temp: 16 K (<https://doi.org/10.1002/smll.200500294>)
- CrBr<sub>3</sub>, Crystal Structure: Hexagonal, Curie Temp: 37 K (<https://doi.org/10.1016/j.physleta.2023.128980>)

(b) Ferromagnetic Metals: (All from Kittel Ch 12 Table 1)

- Fe, Crystal Structure: BCC, Curie Temp: 1043 K
- Co, Crystal Structure: HCP, Curie Temp: 1388 K
- Ni, Crystal Structure: FCC, Curie Temp: 627 K

(c) Antiferromagnetic Insulators:

- MnO, Crystal Structure: FCC, Neel Temp: 116 K (Kittel)
- MnS, Crystal Structure: FCC, Neel Temp: 160 K (Kittel)
- MnTe, Crystal Structure: Hexagonal, Neel Temp: 307 K (Kittel)

(d) Antiferromagnetic Metals:

- Cr, CS: BCC, NT: 308 K (Kittel)
- VO<sub>2</sub>, CS: Monoclinic, NT: 340 K (<https://doi.org/10.1063/5.0027674>)
- MnAs, CS: Hexagonal, NT: 480 K (DOI: 10.1103/PhysRevLett.111.047001)