

# Quantum Condensed Matter

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**Abstract**

Abstract of this course

# 1 Optical Properties

## 1.1 Insulators

The model we used here is Lorentz or dipole oscillator model.

Oscillation of charges around their average position.

Model atoms as nucleus and electron cloud and an applied E-field will lead to displacement of electron cloud.

### 1.1.1 Lorentz Model

Electrons now behave as damped harmonic oscillator.

$$m\ddot{u} + m\gamma\dot{u} + m\omega_T^2 u = qE \quad (1)$$

Natural frequency  $\omega_T$  is determined by force constant and mass.

$\gamma$  is damping rate.

Flow: for a certain frequency  $\omega_T$ , we can obtain

- dipole moment per atom,  $p_\omega$
- Polarisation (dipole moment per unit volume),  $P_\omega$
- Susceptibility,  $\chi_\omega$
- Permittivity,  $\epsilon_\omega$
- Reflectivity between media of different permittivities, power reflection coefficient .etc.

At low frequencies, we study the permittivity of material

$$\epsilon(\omega \approx 0) = 1 + n_v \frac{q^2}{m\epsilon_0\omega_T^2} \quad (2)$$

This explains the different static permittivity of different materials.

**Example: Atomic absorption**

?? [Something about line width](#)

### 1.1.2 Link to quantum mechanics

## 1.2 Metals

Inner electrons closely bounded, contribute to permittivity according to Lorentz oscillator metals. Outer electrons have cut loss from ions, now free to roam around entire metal. Natural frequency  $\omega_T \approx 0$

## 1.3 Drude Model

We used Drude Model to study the conductivity of metals

### 1.3.1 Frequency-dependent Connectivity

- Both current density  $\mathbf{j} = nq\dot{\mathbf{u}}$ , and polarisation  $\vec{\mathbf{P}} = nq\vec{\mathbf{u}}$ .
- For conduction electrons  $\dot{\mathbf{P}}_c = \mathbf{j}$ .
- The polarisation is comprised of core electrons and conduction:
- $\dot{\mathbf{P}} = \mathbf{j} + \epsilon_0\chi_\infty\dot{\mathbf{E}}$
- From this differential equation we have  $\mathbf{j}_\omega = -i\omega\epsilon_0\mathbf{E}_\omega(\chi_\omega - \chi_\infty)$
- Imaginary part of the permittivity can be derived from here

### 1.3.2 Relaxation-time approximation

We denote relaxation time as  $\tau$ , the probability of collision during  $\delta t$  is  $\delta t/\tau$ . Now consider the change in **momentum** change after  $\delta t$ , by considering electrons collided and not collided during that  $\delta t$ :  
The current  $J$  due to electrons of number density  $n$ , mass  $m$  of average (drift velocity)  $\mathbf{v}$  and momentum  $\mathbf{p}$  is given as:

$$\mathbf{j} = -ne\mathbf{v} = -\frac{ne}{m}\mathbf{p} \quad (3)$$

Note that  $\mathbf{J}$  is proportional to  $\mathbf{v}$  and  $\mathbf{p}$ .

The evolution of  $\mathbf{p}$  in time  $\delta t$  under the action of external force  $\mathbf{f}$ , e.g.  $\mathbf{f} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$

**Collided electrons** has a fraction  $\delta t/\tau$  and momentum is acquired is  $\approx \mathbf{f}(t)\delta t$ , as a result, the contribution to the average momentum is of order  $(\delta t)^2$  :**negligible**

**Non-collided electrons:**

$$\mathbf{p}(t + \delta t) = (1 - \delta t/\tau)(\mathbf{p}(t) + \mathbf{f}(t)\delta t + O(\delta t)^2) \quad (4)$$

### 1.3.3 Validity of Drude Model

## 1.4 Sommerfeld Model

Both Lorentz and Drude theories fails dramatically describing thermodynamic properties. Now we apply equipartition theorem to the dipole model, expect contribution of  $k_B$  to heat capacity of each oscillator, and  $3/2k_B$  per atom. Also we consider quantum static effects.

### 1.4.1 Density of states

1. Fermi sphere
2. Note spin degeneracy
3.  $g(E) \equiv$  number of states per unit energy per unit volume.
4. Note that  $C_v$  due to electrons is usually much smaller than lattice specific heat capacity.
5. This is seen in the liquid helium mixture of  $^3\text{He}$  and  $^4\text{He}$  **Example: Specific heat of mixture of  $^3\text{He}$  and  $^4\text{He}$**

We see that at low temp limit,  $C_v$  is linear to  $T$

### 1.4.2 Screening and the Tomas-Fermi approximation

1. Screening: placing positive charges in metal will result in electrons moving around to screen its potential resulting in zero electric field. Compare to dielectric material with electrons are not free to move and have potential reduced by  $\epsilon$
2. A balance is reached between minimising potential and kinetic energy, screening over a short but finite range.
3. In order to study the effect of introducing external potential. We study response of a free electron in a perturbing potential. Free electron in **METAL**, without external potential, gives potential in the metal to be:

$$\nabla^2 V_0(r) = -\frac{\rho_0(r)}{\epsilon} \quad (5)$$

indicating that potential is linked to charge distribution. In plasma or Jellium model.  $\rho_0 = 0$

4. In the presence of perturbing potential  $V_{ext}$ , change density will redistribute and we have a perturbing potential in the metal, its correction is :

$$\nabla^2 \delta V_0(r) = -\frac{\delta \rho_0(r)}{\epsilon} \quad (6)$$

d

**Slowly varying potential** The approximation is: Slowly varying potential, and only shifts the free electron.

**Constant chemical potential** keeping the electrons states filled up to a constant energy  $\mu$  requires we adjust local Fermi energy  $E_F(\mathbf{r})$ :

$$\mu = E_F(\mathbf{r}) - eV_{tot}(\mathbf{r}) \quad (7)$$

**Local density approximation** Small shift in the Fermi energy  $\delta E_F(\mathbf{r})$  will give rise to a change in number density,  $n$ : Recall the then relationship:

$$\int^{E_F} g_v(E) dE = n \quad (8)$$

we obtain:

$$\delta n = e g_V(E_F)(\delta V + V_{ext}) \quad (9)$$

**Linearised Thomas Fermi** now we know the small change in  $\rho$ , as  $\rho = en$  We obtain:

$$\nabla^2 \delta V(\mathbf{r}) = \frac{e^2 g_V(E_F)}{\epsilon_0} (\delta V + V_{ext}) \quad (10)$$

**Density Response** Solve the Equation above, by Fourier Transformation, we obtain:

$$\delta V(\mathbf{q}) = -\frac{q_{TF}^2}{q^2 + q_{TF}^2} V_{ext}(\mathbf{q}) \quad (11)$$

Here  $q_{TF}$  is the *Thomas-Fermi Wave vector* The number density, as now we know  $\delta V$ ,

**Dielectric permittivity** the dielectric permittivity  $\epsilon_{TF}(q)$

$$\epsilon_{TF}(q) = 1 + \frac{q_{TF}^2}{q^2} \quad (12)$$

**Screening** *At small  $q$ , long distance,  $\epsilon_{TF}$*

## 2 Electrons and phonons in periodic solids

In this section, we discuss the type of bonds: "Van der Waal", ionic, covalent. Crystal structure This is like a section that dedicated to material science

### 2.0.1 Binding of crystals

#### Inert gas

1. Filled electron shells and large ionisation energies.
2. Interaction between neutral atoms is weak, and leading attractive force is van der Waals interaction, which gives potential proportional to  $1/R^6$ .
3. Lennard-Jones potential:

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] = \epsilon\left[\left(\frac{R_{min}}{r}\right)^{12} - 2\left(\frac{R_{min}}{r}\right)^6\right] \quad (13)$$

#### Ionic Crystals

1. Electrostatic energy for a regular lattice:

$$U_{electrostatic} = -\frac{1}{2} \frac{\alpha_M q^2}{4\pi\epsilon_0 R} \quad (14)$$

where  $\alpha_M$  is a dimensionless constant that depend only on the crystal structure

### 2.1 Complex materials

### 2.2 Description of periodic materials

#### 2.2.1 Index system for lattice

#### 2.2.2 Reciprocal Lattice and Diffraction

#### 2.2.3 Diffraction Condition

The spacing

$$2d \sin \theta = n\lambda \quad (15)$$

### 2.3 Lattice dynamics and phonons

#### 1D monatomic chain

#### 1D diatomic chain

#### 1D different spring constant

#### 1D different mass

**3D crystal** In 3D crystal, there are always 3 acoustic modes and  $3(m-1)$  optical modes where  $m$  is the number of atoms per unit cell.

## 2.4 Density of states

## 2.5 Heat Capacity

When studying heat capacities, we discuss optical branch (Einstein Model) and acoustic model (Debye model)

### 2.5.1 Debye Model

2.8 Lattice specific heat Phonons obey Bose-Einstein statistics, but their number is not conserved and so the chemical potential is zero, leading to the Planck distribution

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

The internal energy is

$$U = \int d\omega D(\omega) n(\omega) \hbar\omega$$

For the Einstein model

$$U_E = \frac{N\hbar\omega_o}{e^{\hbar\omega_o/k_B T} - 1}$$

and the heat capacity is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = Nk_B \left( \frac{\hbar\omega_o}{k_B T} \right)^2 \frac{e^{\hbar\omega_o/k_B T}}{(e^{\hbar\omega_o/k_B T} - 1)^2}$$

At low temperatures, this grows as  $\exp -\hbar\omega_o/k_B T$  and is very small, but it saturates at a value of  $Nk_B$  (the Dulong and Petit law) above the characteristic temperature  $\theta_E = \hbar\omega_o/k_B$ .<sup>6</sup>

At low temperature, the contribution of optical modes is small, and the Debye spectrum is appropriate. This gives

$$U_D = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Defining the Debye temperature  $\theta_D = \hbar\omega_D/k_B T$  and using  $\omega_D^3 = 6\pi^2 v^3 N/V$  from above, we obtain  $\theta_D = (6\pi^2 N/V)^{1/3} \hbar b/k_B$ .

By writing  $x = \hbar\omega/k_B T$  and including a factor of 3 for different modes, we obtain for the internal energy

$$U_D = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} = 9Nk_B T \frac{T}{\theta_D} \int_0^{\theta_D/T} dx \frac{x^3}{e^x - 1}$$

and by differentiating the middle expression with respect to temperature, the heat capacity (see Fig. 2.29) is

$$C_V = 9Nk_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

where the Debye temperature is  $\theta_D = \hbar\omega/k_B$ . We have multiplied by 3 to account for the three acoustic branches.

### 2.5.2 Heat capacity due to lattice vibration and electrons

Two major contribution to heat capacity: electrons and lattice vibrations. Electron heat capacity is linear to  $T$  ??? while lattice vibration heat capacity is  $\propto T^3$

### 2.5.3 Compare Einstein and Debye models

Why we are comparing these two models???

## 2.6 Thermal Conductivity of insulators

1. The thermal conductivity,  $\kappa$  is defined by  $\mathbf{J}_q = -\kappa \nabla T$ , where  $\mathbf{J}_q$  is the flux of heat (energy per unit area per unit time).
2. Kinetic theory gives  $\kappa = \frac{1}{3} C_V \ell v = \frac{1}{3} C_V v^2 \tau$ , where  $C_V$  is the phonon specific heat per unit volume,  $v$  is the phonon velocity,  $\ell = v\tau$  is the mean free path and  $\tau$  is the scattering time.
3. Debye theory predicts that  $C_V \propto T^3$  **at low**  $T$  and that it is constant at high  $T$  (While in reality, at high temperature, thermal conductivity is dominated by scattering).
4.  $v$ , the velocity of sound, is almost constant, but  $\tau$  depends on several scattering mechanisms.
5. Scattering Mechanisms include normal, Umklapp, points defects sample boundaries and crystal dislocations.
6. At high temperature  $\kappa$  falls rapidly due to rapid fall in  $\tau$ , the scattering time.

## 3 Electrons in periodic potential

By solving Hamiltonian's equation, we conclude Bloch's theorem: Eigenstates of the 1D Hamiltonian can be chosen to be a plane wave multiplied by a function with the periodicity of the Bravais lattice. We consider first a formal treatment in terms of a complete set of basis functions, namely the set of all plane-wave states which satisfy the periodic boundary conditions. The results from this treatment can be used to obtain Bloch's theorem, which is one of the cornerstones of electronic structure in solids. Next, we will approach Bloch's theorem from a more abstract but also more elegant direction, which uses the translational symmetry of the lattice directly.

### 3.1 Shrodinger equation ina periodic table

### 3.2 Bloch theorem from discrete translational symmetry

Another way to think about Bloch theorem, consider what happens to eigenstate of Hamiltonian.

The underlying reason is that if an operator is unchanged under a change of coordinate sstem, then applying a symmetry opertatioin on the eigenstate of such operator produces another eigenstate of the operatore, with teh sam eigenvalue of teh original one.

For two commuting operators  $H$  and  $T$ , we can always choose simulatneous eienstates of both  $H$  and  $T$

Two forms of Bloch theorem:

$$\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q} \cdot \mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}} e^{-i\mathbf{G} \cdot \mathbf{r}} = e^{i\mathbf{q} \cdot \mathbf{r}} u_{j,\mathbf{q}}(\mathbf{r})$$

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{\mathbf{k}}^{(n)}(\mathbf{r})$$