

## Chapter 14: Plasmons, Polaritons, and Polarons

### 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

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

so the divergence of the electric field and displacement vector are

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

and

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

dividing 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

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

where time dependence is harmonic i.e.

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

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

$$P = -n e x_0 = \frac{n e^2 E}{m \omega^2}$$

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

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

We define the plasma frequency as

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

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

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

## 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

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

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

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

This displaces the surface charge density  $\sigma = \pm ne u$  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

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

so the wave equation is

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

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

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

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):

$$\omega^2 = \frac{4\pi ne^2}{Mk_s^2} K^2$$

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

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

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

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

where we  $v$  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

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

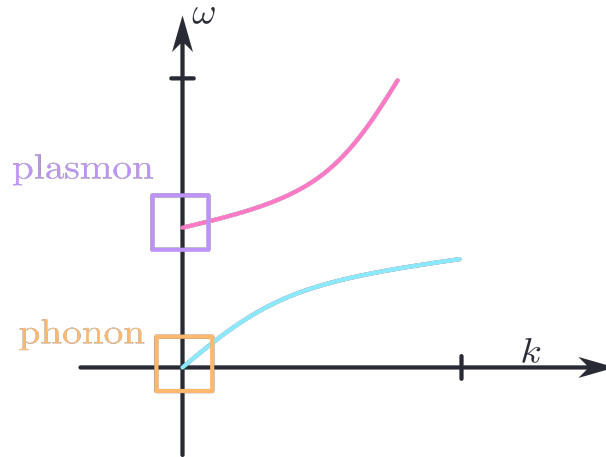


Figure 0.1: Phonon and Plasmon Dispersion Relations

so

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

And from Newton's 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

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

For light in EM we have the relation  $\omega = ck$  which is a photon like branch in the dispersion relation in Figure 0.1. 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.

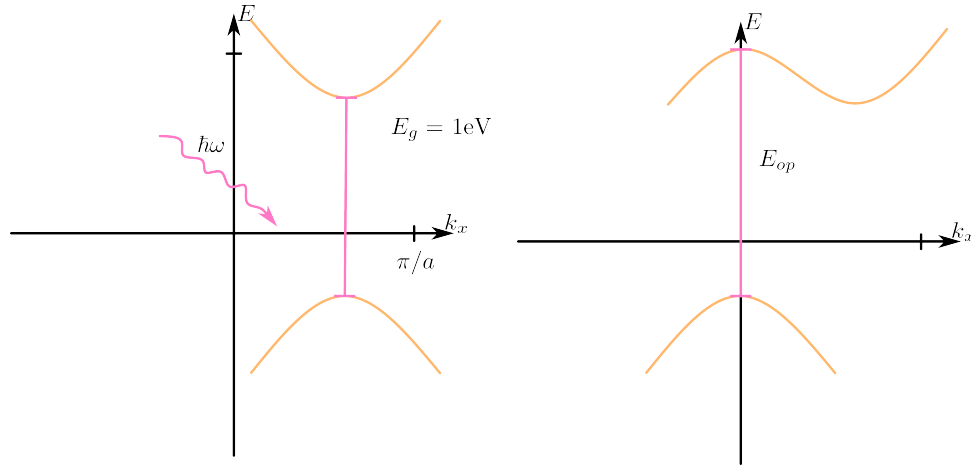


Figure 0.2: The left shows a direct band gap. The right shows indirect band gap.

**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).



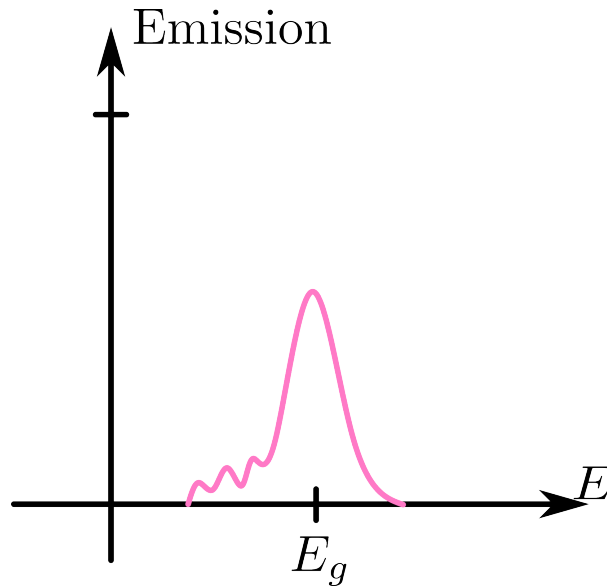


Figure 0.3: The emission spectrum at low temperature.

**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

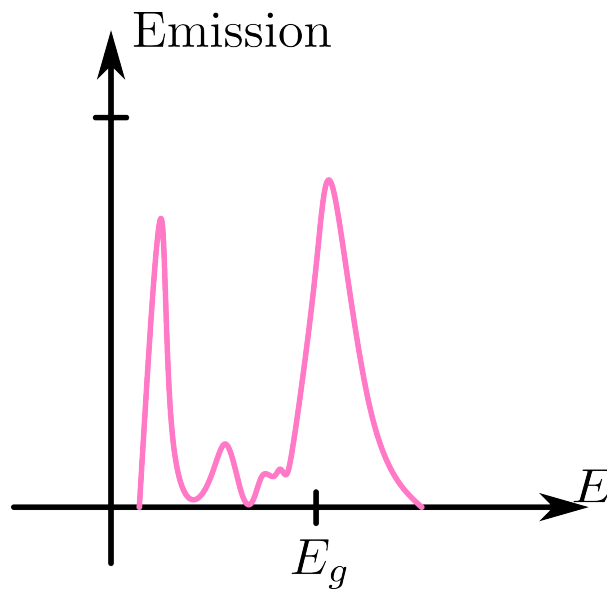


Figure 0.4: The emission spectrum at low temperature has a large peak at low energy.

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 to 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

$$E_s - E_t = \frac{\langle \psi_s | \hat{H} | \psi_s \rangle}{\langle \psi_s | \psi_s \rangle} - \frac{\langle \psi_t | \hat{H} | \psi_t \rangle}{\langle \psi_t | \psi_t \rangle}$$

$$\propto \int d\mathbf{r}_1 d\mathbf{r}_2 [\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)][\phi_2(\mathbf{r}_1)\phi_1(\mathbf{r}_2)]$$

$$\left[ \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{e^2}{|\mathbf{r}_2 - \mathbf{R}_1|} \right]$$

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:**  $\text{CrI}_3$  (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,

$$\text{CrBr}_3 : J_1 = 1.35, \quad J_2 = 0.14$$

$$\text{CrCl}_3 : J_1 = 0.8, \quad J_2 = 0.07$$

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

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

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

1. The ground state energy is

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

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  $\rho(\mathbf{r})$  satisfies

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

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

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

They state:

1. Two external potentials,  $V, V' \implies H, H'$  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.

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



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.