3.024 Electrical, Optical, and Magnetic Properties of Materials Spring 2012
Recitation 8 Notes

Overview

1. Electronic Band Diagram Review
2. Spin Review
3. Density of States
4. Fermi-Dirac Distribution

1. Electronic Band Diagram Review

Considering 1D crystals with periodic potentials of the form:

$$V(x) = \sum_G V_G e^{iGx}$$

Here $G = \frac{2\pi n}{a} = gn$ where n is an integer, a is the crystal lattice constant, and g is the reciprocal space lattice constant.

The Schrodinger equation for these systems has a general solution of the form:

$$u(x) = \sum_k C_k e^{ikx}$$

Upon substitution of this solution into Schrodinger's equation, the following Central Equation is found:

$$\left(\frac{\hbar^2}{2m}k^2 - E\right)C_k + \sum_G V_G C_{k-G} = 0$$

This is an eigenvalue/eigenvector equation where the eigenvalues are given by E and the eigenvectors by the coefficients C_k.

By rewriting the above expression as a matrix equation, one can computationally solve for the energy eigenvalues for given values of k and produce a band diagram.

$$\begin{bmatrix} \vdots & \vdots & \vdots & \vdots & \vdots & \\ \ddots\ \frac{\hbar^2}{2m}(k-2g)^2 - E & V_g & V_{2g} & V_{3g} & V_{4g} & \iddots \\ \cdots & \frac{\hbar^2}{2m}(k-g)^2 - E & V_g & V_{2g} & V_{3g} & \cdots \\ \cdots\ V_{-g} & V_{-g} & \frac{\hbar^2}{2m}k^2 - E & V_g & V_{2g} & \cdots \\ \cdots\ V_{-2g} & V_{-2g} & V_{-g} & \frac{\hbar^2}{2m}(k+g)^2 - E & V_g & \cdots \\ \cdots\ V_{-3g} & V_{-3g} & V_{-2g} & V_{-g} & \frac{\hbar^2}{2m}(k+2g)^2 - E & \ddots \\ \iddots\ V_{-4g} & \vdots & \vdots & \vdots & \vdots & \end{bmatrix} \begin{bmatrix} \vdots \\ C_{k-2g} \\ C_{k-g} \\ C_k \\ C_{k+g} \\ C_{k-2g} \\ \vdots \end{bmatrix} = 0$$

The steps to solving this equation for just the energy eigenvalues is as follows:

1. Set values of V_G equal to values of coefficients of the periodic potential of interest.
2. Truncate the infinite matrix to an $N \times N$ matrix approximation suitable for the number of energy bands that is required for the problem to be investigated. If N is odd, set the center term to the C_k matrix coefficient. If N is even, an asymmetry will be introduced in the top band depending on whether the C_k matrix coefficient is placed to the left diagonal of the matrix center or the right diagonal of the matrix center. This asymmetry can be avoided by only using odd matrices or by solving both even matrices and superimposing the highest band energy solutions.
3. Set k equal to a value in the first Brillioun zone and use a numerical method to evaluate the eigenvalues. Since the Central Matrix equation is Hermitian, these eigenvalues will all be real. In order from least to greatest they represent the bottom N energies in the band diagram at the chosen value of k.
4. Plot the N energies obtained in step 3 at the chosen value of k.
5. Repeat steps 3-4 until enough values of k have been plotted within the first Brillioun zone to produce the band diagram for the first N bands.

Once the energy eigenvalues are known, one can in principle then attempt to find the C_k coefficients of the wave function. However, unless one is really interested in the exact form of the wave function solution, this is usually unnecessary as the energy band diagram tells us the general physics of the electron in the crystal lattice.

2. Spin Review

In addition to classical observables such as energy *E*, momentum *p*, angular momentum *l*, etc. electrons and other wave-particles have a property known as spin. Originally named spin because of the correspondence to classical angular momentum, there exists no real classical explanation of the property as all attempts to use classical theory to predict the measured values of the spin of particles has resulted in incorrect values, only invoking quantum relativistic mechanics can one accurately predict the value of spin for a given wave-particle which is beyond the scope of this course. The best practical way to think of spin is as an intrinsic property of the particle such as mass or charge.

Regardless, spin is extremely important in calculating the electromagnetic properties of materials. This is because electrons exhibit a spin of $\pm\frac{1}{2}$ which makes them Fermions. Fermions obey Fermi-Dirac statistics and the Pauli exclusion principle which means no two Fermions can occupy the same quantum state due to their total wave function being antisymmetric. This means for example that in the hydrogen atom, a given electron has 4 degrees of freedom that when determined define which orbitals it will occupy. 3 of these degrees of freedom are of course the energy represented by quantum number *n*, orbital angular momentum *l*, and magnetic angular momentum *m*. Coupled with the spin quantum number *s* a given set of the first 3 quantum numbers can only have 2 states of the spin quantum number and thus each orbital can have up to 2 electrons each with spin $+\frac{1}{2}$ and $-\frac{1}{2}$.

Other particles have different integer or half-integer values of spin. Integer value spin particles obey Bose-Einstein statistics rather than Fermi-Dirac statistics and can have any number of such particles in a given state by virtue of their total wave function being symmetric.

Examples of Fermions and Bosons are listed below with their spin magnitudes:

Spin Magnitude	Wave-Particle Type	Example Wave-Particles
0	Boson	Alpha Particles, Higgs Boson (If it exists)
$\frac{1}{2}$	Fermion	Electron, Charm Quark, Tau Lepton
1	Boson	Photon, Gluon
$\frac{3}{2}$	Fermion	$^{55}_{26}$Fe Nucleus
2	Boson	Graviton (If it exists)

Since electrons are spin ½ if there are *N* total energy states that can be occupied in a given band, then 2*N* electrons can fill those states as a consequence of their Fermion behavior.

3. Density of States

The density of states $g(E)$ represents the number of states per unit energy and volume in a given system. To calculate the general density of states, first one calculates the total number of states *N* as a function of energy *E* and then normalizes by the generalized volume L^d of the system in the dimension *d* of the system. Then, this volumetric density of states *n* is normalized by the energy by taking the derivative with respect to *E* to obtain the final expression for $g(E)$.

E.g. Density of States in 2D

Consider a piece of Graphene with total area L^2. The crystal lattice is 2D, thus its dimension is $d = 2$. What is the density of states in such a system?

First we calculate the total number of states *N* in terms of the reciprocal space vector *k* and dimension *L*.

$$N = 2\frac{\text{Area of entire Brillouin Zone}}{\text{Area between atoms}} = 2\frac{\pi k^2}{\left(\frac{2\pi}{L}\right)^2} = \frac{k^2L^2}{2\pi}$$

Here the factor of 2 is a result of the electrons being Fermions.
Next we normalize by the total area L^2.

$$n = \frac{N}{A} = \frac{k^2 L^2}{2\pi L^2} = \frac{k^2}{2\pi}$$

We now use the relation of k to E to express n as a function of E.

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

Finally, using $g(E) = \frac{dn}{dE}$.

$$g(E) = \frac{m}{\hbar^2 \pi}$$

Amazing, for a 2D system, the density of states is a constant. This means that the charge carrier density for a given band for T = 0 K is just proportional to the difference in energy of maximum value in the band and the minimum value of the band.

4. Fermi-Dirac Distribution

The probability of finding an electron at a given energy value at a given temperature T is given by the Fermi-Dirac distribution function:

$$f(E) = \frac{1}{e^{\frac{(E-\mu)}{k_B T}} + 1}$$

Here k_B is Boltzmann's constant and is equal to $1.381 \times 10^{-23} \frac{\text{J}}{\text{K}}$ or $8.617 \times 10^{-5} \frac{\text{eV}}{\text{K}}$.
μ here is the chemical potential of the electron which corresponds to the Fermi energy ε_F.
If μ occurs in the conduction band, the material will be a metal.
If μ occurs between the conduction band and valence band, the material will be an insulator if the band gap is wide enough that at high temperatures the Fermi-Dirac distribution still does not overlaps into the conduction band.
If μ occurs between the conduction band and valence band, the material will be a semiconductor if the band gap is small enough that at room temperatures the Fermi-Dirac distribution overlaps into the conduction band.
To calculate the Fermi energy, we set density per volume of charge carriers equal to the known value and solve for ε_F.
E.g. 2D Fermi-Energy
We previously found the 2D density of states per unit volume

$$n = \frac{k^2}{2\pi}$$

If this corresponds to the Fermi level, then we find:

$$\frac{{k_F}^2}{2\pi} = n \;\&\; \varepsilon_F = \frac{\hbar^2 {k_F}^2}{2m} \rightarrow \; \varepsilon_F = \frac{\hbar^2 \pi n}{m}$$

Here k_F is the Fermi wave number and ε_F the Fermi energy in 2D.

Other variables of use include the Fermi temperature T_F and Fermi momentum p_F and Fermi velocity v_F.

$$\text{T}_\text{F} = \frac{\varepsilon_\text{F}}{k_B} = \frac{\hbar^2 {k_F}^2}{2mk_B}$$

$$p_F = \sqrt{2m\varepsilon_\text{F}} = \hbar k_\text{F} = m v_\text{F}$$

Note that these variables have no real physical meaning other than expressing the Fermi energy in terms of other quantities for qualitative comparison or simplification of certain equations.

The number of charge carriers in a band can be calculated using the Fermi-Dirac distribution as follows:

$$n = \int_0^\infty f(E)g(E)dE$$

Here E_t and E_b are the top and bottom energy of the band respectively. The density of states is determined by the energy levels in the band and the dimensionality of the material as derived before, and the Fermi-Dirac distribution is taken at a given temperature T.
Similarly, we can calculate the total potential energy *U* as follows:

$$U = \int_0^\infty f(E)g(E)EdE$$

In the valence band, this corresponds to the following integral.

$$U = \int_0^{\varepsilon_F} \frac{1}{e^{\frac{(E-\mu)}{k_BT}} + 1} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{E^{\frac{1}{2}}}{2\pi^2} EdE$$

E.g. Heat Capacity
The electronic contribution to the heat capacity can be calculated using the above expression for *U* and the relationship:

$$C_{el} = \frac{d\Delta U}{dT}$$

$$C_{el} = \frac{d}{dT}\int_0^\infty f(E)g(E)(E-\varepsilon_F)dE = \int_0^\infty \frac{df(E)}{dT} g(E)(E-\varepsilon_F)dE$$

Since only the Fermi-Dirac distribution depends upon *T*. One can show that the term $\frac{df(E)}{dT}$ is only large near the Fermi energy and to good approximation we can take $g(E)$ outside of the integral evaluating it at the Fermi energy.

$$C_{el} \cong g(\varepsilon_F)\int_0^\infty \frac{df(E)}{dT} EdE$$

$$\frac{df(E)}{dT} = \frac{d}{du}\left(\frac{1}{u}\right)\frac{du}{dv}\frac{dv}{dw}\frac{dw}{dT} = \frac{u^{-2}e^v(E-\varepsilon_F)}{k_BT^2}$$

Where

$$u = e^v + 1 \;\&\; v = (E-\varepsilon_F)w \;\&\; w = \frac{1}{k_BT}$$

$$\frac{df(E)}{dT} = \frac{e^{\frac{(E-\varepsilon_F)}{k_BT}}(E-\varepsilon_F)}{\left(e^{\frac{(E-\varepsilon_F)}{k_BT}}+1\right)^2 k_BT^2}$$

$$C_{el} \cong g(\varepsilon_F)\int_0^\infty \frac{e^{\frac{(E-\varepsilon_F)}{k_BT}}(E-\varepsilon_F)^2}{\left(e^{\frac{(E-\varepsilon_F)}{k_BT}}+1\right)^2 k_BT^2} dE$$

$$\text{Let } y = \frac{(E-\varepsilon_F)}{k_BT} \rightarrow dy = \frac{dE}{k_BT}$$

$$C_{el} \cong k_B^2 T g(\varepsilon_F)\int_{-\frac{\varepsilon_F}{k_BT}}^\infty \frac{e^y y^2}{(e^y+1)^2} dy$$

$$C_{el} \cong k_B^2 T g(\varepsilon_\mathrm{F}) \int_{-\infty}^{\infty} \frac{e^y y^2}{(e^y+1)^2} dy \cong k_B^2 T g(\varepsilon_\mathrm{F}) \frac{\pi^2}{3}$$

The density of states evaluated at the Fermi energy is just a constant for a given dimensional material, thus this shows the electronic contribution to the heat capacity is proportional to *T*.

$$g(\varepsilon_\mathrm{F}) = \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{\varepsilon_\mathrm{F}^{\frac{1}{2}}}{2\pi^2} \text{ but we can replace } n = \frac{\left(\frac{2m\varepsilon_\mathrm{F}}{\hbar^2}\right)^{\frac{3}{2}}}{3\pi^2} \rightarrow \frac{3n}{\varepsilon_\mathrm{F}} = \frac{\left(\frac{2m\varepsilon_\mathrm{F}}{\hbar^2}\right)^{\frac{1}{2}}}{\pi^2}$$

$$g(\varepsilon_\mathrm{F}) = \frac{3n}{2\varepsilon_\mathrm{F}} = \frac{3n}{2k_B \mathrm{T_F}}$$

$$\therefore C_{el} \cong k_B^2 T \frac{3n}{2k_B \mathrm{T_F}} \frac{\pi^2}{3} = \frac{\pi^2}{2} n k_B \frac{T}{\mathrm{T_F}}$$

This is very different from the classical ideal gas where

$$c_V = \frac{3}{2} n k_B$$

which was independent of temperature.

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