3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

Homework # 6, solution

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Homework is due on Thursday November 1st, 5pm

1 Thermodynamics of the free electron gas in 3D

1.1 Physics at T=0K

Let's consider a parallepiped of sides L_x, L_y and L_z, with free electrons inside it. In the free electron gas model, those electrons do not interact with each other, and so we can consider them one by one such that the many-body Schrodinger equation involving N electrons can be simplified into N independant Schrodinger equations for each electron. This simplification is the general framework for the **band theory of solids**. In the case of the free electron model, we go even further in the simplification by taking the effective periodic potential felt by an electron, namely $V(\vec{r})$, to be zero. So the Schrodinger equation for one electron is simply:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi(\vec{r}) = E\psi(\vec{r})$$

Along with the Schrodinger equation, we need some boundary conditions to fully define our problem. In this case we will take the standard Born-Von Karman boundary conditions. So we impose that $\psi(\vec{r}+L_x\vec{e}_x) = \psi(\vec{r})$, $\psi(\vec{r}+L_y\vec{e}_y) = \psi(\vec{r})$ and $\psi(\vec{r} + L_z\vec{e}_z) = \psi(\vec{r})$. Using this model, we have already solved for the eigenenergies and corresponding eigenfunctions. The answer is:

$$E(\vec{k}) = \frac{\hbar^2\vec{k}^2}{2m} \text{ with } \vec{k} = \frac{2\pi}{L_x}n_x\vec{e}_x + \frac{2\pi}{L_y}n_y\vec{e}_y + \frac{2\pi}{L_z}n_z\vec{e}_z$$

where n_x, n_y and n_z are integers. The energy levels are **discretized but** the spacing between those levels is so small that we can actually consider $\vec{k}$ to vary continuously. The corresponding eigenfunction is:

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}}e^{i\vec{k}\vec{r}}$$

is a plane wave and V is the volume of the solid $V = L_xL_yL_z$. This wavefunction is normalized over the volume of the solid. In order to find the ground state of the system, we then need to fill up each of the eigenstates $E(\vec{k})$ with 2 electrons with opposite spin until we reach the Fermi energy E_F.

1) Give an expression for the total energy of the system as a sum over all the occupied $\vec{k}$ states. Use the standard relation that we saw in recitation,

to transform this discrete sum into an integral over the continuous variable $\vec{k}$. **There is no need to calculate the total energy at this point**. We have now two equivalent expressions for the total energy of a free electron gas.

solution:
The total energy of the free electron gas is simply the sum over all the occupied $\vec{k}$ states of **twice** the energy of that $\vec{k}$ state (because of the spin degeneracy). The $\vec{k}$ states are occupied up to the Fermi wavevector $\vec{k}_F$. So we have:

$$E = E_{tot} = 2\sum_{||\vec{k}||\leq||\vec{k}_F||} E(\vec{k}) \text{ over occupied } \vec{k} \text{ states}$$

This discrete formula for the total energy can be easily transformed into an integral formula through the standard substitution that i showed you in recitation: $\sum_{\vec{k}} = \frac{V}{(2\pi)^3}\int d\vec{k}$. So we also have:

$$E = E_{tot} = 2\frac{V}{(2\pi)^3}\int_{||\vec{k}||\leq||\vec{k}_F||} E(\vec{k})d\vec{k} \text{ over occupied } \vec{k} \text{ states}$$

2) If we count all the occupied states up to the Fermi energy (remembering that each $\vec{k}$ state can accomodate 2 electrons because of the spin degeneracy), then we find the total number of electrons. Express this number N as a sum over all the occupied $\vec{k}$ states? Give the equivalent formula using an integral over the continuous variable $\vec{k}$. Calculate this number and give an answer in terms of the Fermi wavevector k_F and another in terms of the Fermi energy E_F.

solution:
The total number of electron is simply obtained by summing the number of occupied states from $||\vec{k}|| = 0$ to $||\vec{k}|| = ||\vec{k}_F||$:

$$N = 2\sum_{||\vec{k}||\leq||\vec{k}_F||} 1$$

The equivalent formula using the continuous variable $\vec{k}$ is simply:

$$N = 2\frac{V}{(2\pi)^3}\int_{||\vec{k}||\leq||\vec{k}_F||} 1d\vec{k}$$

We see that this second formula tell us that the total number of electron is simply equal to twice the volume of the Fermi sphere of radius $k_F = ||\vec{k}_F||$. So we find right-away that:

$$N = 2\frac{V}{(2\pi)^3}\frac{4}{3}\pi k_F^3 = \frac{V}{3\pi^2}k_F^3$$

The Fermi energy expressed with the Fermi wavevector is simply: $E_F = \frac{\hbar^2 k_F^2}{2m}$. So we see that the total number of electron expressed as a function of the Fermi energy is:

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

3) Calculate the total energy of the system and give your answer in terms of k_F, V and fundamental constants like π, $\hbar$ and m. Use the result for N in question 2) to express the total energy as NE_F with a numerical prefactor in front that you must find.

solution:

Given the integral expression for the total energy obtained in question 1), and the spherical symmetry of the function $E(\vec{k})$, i will use the spherical coordinates in $\vec{k}$ space to calculate the integral:

$$E = 2\frac{V}{(2\pi)^3}\int_0^{k_F} 4\pi k^2 \frac{\hbar^2 k^2}{2m}dk = \frac{V\hbar^2}{10\pi^2 m}k_F^5$$

Given that the total number of electron can be written as $N = \frac{V}{3\pi^2}k_F^3$, we see that the total energy can be rewritten as:

$$E = \tfrac{3}{5}NE_F$$

4) In order to give you some orders of magnitude for the different physical quantities defined in the free electron gas model, express the following quantities exclusively in terms of the electron density $n = \frac{N}{V}$:

- The Fermi energy E_F

- The Fermi wavevector $k_F = \sqrt{\frac{2mE_F}{\hbar^2}}$

- The Fermi temperature $T_F = \frac{E_F}{k_B}$

- The Fermi velocity $v_F = \frac{\hbar k_F}{m}$

Now calculate numerically each of those values for the following metals: Au ($n \approx 5.9 * 10^{28}\ m^{-3}$), Na ($n \approx 2.54 * 10^{28}\ m^{-3}$) and Al ($n \approx 18.07 * 10^{28}\ m^{-3}$)

solution:

Using the relationship we established between the total number of electron and the Fermi wavevector, we can easily inverse it and find:

$$k_F = (3\pi^2 n)^{1/3}$$

Plugging in this value for k_F in the definition of the Fermi energy we find:

$$E_F = \tfrac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

The Fermi temperature is obviously given by $T_F = \frac{E_F}{k_B}$, so we find:

$$T_F = \tfrac{\hbar^2}{2mk_B}(3\pi^2 n)^{2/3}$$

and the Fermi velocity is $v_F = \frac{p_F}{m} = \frac{\hbar k_F}{m}$, so we end up with:

$$v_F = \tfrac{\hbar}{m}(3\pi^2 n)^{1/3}$$

The numerical values for the three different metals Au, Na and Al are the following:

- k_F is about $1.20 * 10^{10}\ m^{-1}$ for Au, $9.09 * 10^9\ m^{-1}$ for Na and $1.75 * 10^{10}\ m^{-1}$ for Al

- E_F is about 5.50 eV for Au, 3.15 eV for Na and 11.65 eV for Al

- T_F is about 64000 K for Au, 36500 K for Na and 135300 K for Al

- v_F/c is about 0.0046 for Au, 0.0035 for Na and 0.0067 for Al

1.2   Physics at room temperature

In the free electron gas model, electrons are independant particles, meaning that they do not interact with each other. Since they are independant particles, the calculation of thermodynamic quantities becomes easy. We will see how to generalize the zero temperature mathematical expressions for some physical quantities of interest when one deals with finite temperatures.

1) What is the total density of states $D(E)$ for a free electron gas?

solution:
The density of states is given by the following formula:

$$D(E) = 2\frac{V}{(2\pi)^3} \int \delta(E - E(\vec{k}))d\vec{k} = 2\frac{V}{(2\pi)^3} \int_{E(\vec{k})=E} \frac{dS}{||\vec{\nabla}E(\vec{k})||}$$

The gradient of $E(\vec{k})$ is simply $\frac{\hbar^2\vec{k}}{m}$ and so the norm is $\frac{\hbar^2 k}{m}$. The isosurface $E(\vec{k}) = E$ is simply a sphere of radius $k(E) = \sqrt{\frac{2mE}{\hbar^2}}$. The value of $||\vec{\nabla}E(\vec{k})||$ over this surface being a constant for a given E, the integral gives us simply the surface of the sphere: $4\pi k(E)^2$. When one puts all the term together, one finds:

$$D(E) = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{E}$$

2) Using the density of states, express the total number of electrons as an integral over the energy range $[0, E_F]$. Calculate this number (again!) and express your answer in terms of the Fermi energy.

solution:
We saw in recitation that given the physical meaning of the density of states, the total number of electrons can be evaluated by the following integral:

$$N = \int_{E_{min}}^{E_F} D(E)dE$$

here the minimum energy occupied is simply $E_{min} = E(\vec{0}) = 0$. Using the expression for the total density of states given in question 1), we can calculate this integral and find:

$$N = \int_0^{E_F} \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{3/2}\sqrt{E}dE = \frac{V}{3\pi^2}(\frac{2mE_F}{\hbar^2})^{3/2}$$

This expression is exactly what we found in the first part of the homework so this way of calculating the total number of electron is absolutely correct.

3) At finite temperature, the probability to occupy a state of energy E is no longer 1 for $E < E_F$ and 0 for $E > E_F$ but rather the Fermi factor ,$f(E,T)$, whose value is:

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

We see that this function goes to 1 for $E < \mu$ and 0 for $E > \mu$ when T goes to zero (μ is the chemical potential). So we immediately realize that $\lim_{T\to 0}\mu = E_F$. Give an expression for the total number of electrons N (this number is of course the same at any temperature because we don't loose any

electron) as an integral over the energy range $[0, +\infty]$ involving the density of states and the Fermi factor.

solution:
The total number of electron is given by the extension of the formula in question 2) to finite temperature. The minimum energy is still 0 but because of the Fermi factor the maximum energy is now $+\infty$. The integral formula is then:

$$N = \int_0^{+\infty} D(E)f(E,T)dE$$

4) The integral formula for the total number of electrons at any temperature obtained in question 3) is actually a way to determine the chemical potential μ as a function of N and T. At room temperature we can calculate the Taylor expansion of the chemical potential around the zero temperature limit and find:

$$\mu(T) = E_F\left\{1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2\right\}$$

Calculate the correction to E_F at room temperature (300K) for Gold. What do you think of this correction on the range of temperatures going from 0K to the melting temperature?

solution:
Using the above formula, with $T = 300$ K and the value of the Fermi energy for Gold found before (5.53 eV), we see that the correction at 300K is ridiculus: about 0.000018! Even at the melting temperature of gold ($T_m = 1338$ K), we have a correction of 0.000358! We conclude that for a free electron metal, the chemical potential is always equal to its value at 0K even around the melting temperature.

5) In the same way we calculated the total number of electrons at finite temperature, we can also express the total energy of the system at finite temperature. Give an expression for this total energy as an integral over the energy range $[0, +\infty]$ involving the Fermi factor $f(E,T)$, the density of states $D(E)$, and the energy E. If one carries out a Taylor expansion of the total energy around the zero temperature limit, one can find the following result:

$$E_{\text{tot}}(T) = E_{\text{tot}}(T = 0K)\left\{1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2\right\}$$

From the expression for $E_{\text{tot}}(T = 0K)$ obtained in question 3) of the first section and the above expression, show that the heat capacity per unit volume has a linear dependance on the temperature T? Calculate the prefactor in this linear relationship for Gold, Sodium and Aluminum and compare with the experimental results: 62 $Pa.K^{-2}$ for Gold, 58 $Pa.K^{-2}$ for Sodium and 135 $Pa.K^{-2}$ for Aluminum.

solution:
The total energy at finite temperature can be calculated as follows:

$$E = \int_0^{+\infty} D(E)f(E,T)EdE$$

In the low temperature limit, this total energy is given by the following expression:

$$E_{\text{tot}}(T) = E_{\text{tot}}(T = 0K)\left\{1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2\right\}$$

The heat capacity per unit volume is given by the following thermodynamic formula:

$$c_V(T) = \frac{1}{V}\frac{\partial E_{\text{tot}}(T)}{\partial T}\Big|_{N,V}$$

In our case we find the following result for $c_V(T)$:

$$c_V(T) = \frac{\pi^2}{2}n\frac{k_B^2}{E_F}T$$

where use has been made of the formula $E_{\text{tot}}(0K) = \frac{3}{5}NE_F$. The linear coefficiant is then given by:

$$\gamma = \frac{\pi^2}{2}n\frac{k_B^2}{E_F}$$

Plugging in the values for n and E_F found previously, we end up with:

- $\gamma = 62.6 \; Pa.K^{-2}$ for Au

- $\gamma = 47.3 \; Pa.K^{-2}$ for Na

- $\gamma = 91.1 \; Pa.K^{-2}$ for Al

We can see that despite the roughness of the free electron gas model, the correct order of magnitude for γ is found. Sometimes, like in the case of Gold, we even have quantitative agreement. But one should be carreful and not say that Gold can be described as a free elctron gas model. Other physical properties derived from this model might be in disagreement with experiment even for Gold. All those numbers tell us, is that the physical idea to see the conduction electrons as almost free is pertinent.

2 The nearly free electron model

We have seen in class, when we analyzed the Schrodinger equation and expressed it in a basis of plane waves, that the "master equation" is a matrix equation where one has some diagonal kinetic energy terms like $\frac{\hbar^2(\vec{k}+\vec{G})^2}{2m}$ and off-diagonal terms like $V_{\vec{G}}$ (**See equation (2.23) in the Singleton Book**). The coefficiants $V_{\vec{G}}$ are nothing else than the Fourier coefficiants of the periodic potential when one expands it as a Fourier series like:

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}}e^{i\vec{G}\vec{r}}$$

In this little problem, we are interested to see what happens at the Brillouin Zone boundary **in a 1D system**, i.e for a k vector close to $k = \frac{\pi}{a}$, when one goes from a free electron $V(x) = 0$ to a very weak potential where $V(x) = 2V\cos(\frac{2\pi}{a}x)$ with $0 < V \ll 1$.

1) Write down the "master equation" (as a matrix equation) for a free electron gas where $V(x) = 0$. In this equation the "vector" looks like that:

$$
\begin{pmatrix}
\vdots \\
c_{k-4\frac{\pi}{a}} \\
c_{k-2\frac{\pi}{a}} \\
c_k \\
c_{k+2\frac{\pi}{a}} \\
c_{k+4\frac{\pi}{a}} \\
\vdots
\end{pmatrix}
$$

solution:

The master equation looks like the following:

$$
\begin{pmatrix}
\ddots & & & & \\
V_{-g} & E(k-g)-E & V_g & V_{2g} & \cdots \\
\cdots & V_{-g} & E(k)-E & V_g & \cdots \\
& V_{-2g} & V_{-g} & E(k+g)-E & V_g \\
& & & & \ddots
\end{pmatrix}
\begin{pmatrix}
\vdots \\
c_{k-g} \\
c_k \\
c_{k+g} \\
\vdots
\end{pmatrix}
= 0
$$

where $g = \frac{2\pi}{a}$ and $E(k) = \frac{\hbar^2 k^2}{2m}$. For the free electron this equation is such that all the V_{ng} are zero. Then the eigenenergies are the following dispersions: $E(k+ng)$.

2) Close to the Brillouin Zone boundary $k = \frac{\pi}{a}$, can you see in the hamilto-nian matrix found in question 1), two kinetic energy terms that have the same value? In this case we say that the point $k = \frac{\pi}{a}$ is **2-fold degenerate**. If you simplify the infinite hamiltonian matrix to a 2×2 matrix with only those two kinetic energy terms, what will be the two band dispersions around $k = \frac{\pi}{a}$? Plot those two bands around $k = \frac{\pi}{a}$.

solution:

Close to the Brillouin Zone boundary $k = \frac{\pi}{a}$, we see that the following two dispersions are close in kinetic energy: $E(k)$ and E_{k-g}. The simplified "master equation" becomes a 2×2 matrix equation.

$$
\begin{pmatrix}
E(k-g)-E & 0 \\
0 & E(k)-E
\end{pmatrix}
\begin{pmatrix}
c_{k-g} \\
c_k
\end{pmatrix} = 0
$$

The solutions are trivially given by: $E(k) = \frac{\hbar^2 k^2}{2m}$ and $E(k-g) = \frac{\hbar^2 (k-g)^2}{2m}$. Those two solutions join at $k = \frac{\pi}{a}$.

3) Re-write the "master equation" but this time for the potential discussed above $V(r) = 2V\cos(\frac{2\pi}{a}x)$. In this infinite matrix equation, we will focus on k vectors around the Brillouin Zone boundary $k = \frac{\pi}{a}$. Because at $k = \frac{\pi}{a}$ the energy level in the case of the free electron model is 2-fold degenerate, all we need to keep in the hamiltonian matrix to study what happens around $k = \frac{\pi}{a}$ is the two lines with an almost equivalent kinetic energy. Simplify the "master equation" for the weak potential to a 2×2 matrix equation.

solution:

Re-writting the "master equation" and keeping the V_g and V_{-g} terms, we find:

$$\begin{pmatrix} E(k-g) - E & V_g \\ V_{-g} & E(k) - E \end{pmatrix} \begin{pmatrix} c_{k-g} \\ c_k \end{pmatrix} = 0$$

Here we see from the expression of the potential $V(r) = 2V \cos(\frac{2\pi}{a} x) = V e^{igr} + V e^{-igr}$ that $V_g = V_{-g} = V$ and all the other terms are zero.

4) Find the energy eigenvalues (which corresponds to two bands around $k = \frac{\pi}{a}$) for this simplified 2×2 hamiltonian matrix. Plot those two band dispersions around $k = \frac{\pi}{a}$. What is different with respect to the free electron model? What is the value of the "energy gap" at $k = \frac{\pi}{a}$ between the two bands? What is the slope of the two bands at $k = \frac{\pi}{a}$?

solution:
The eigenvalue equation in question 3) gives us that:

$$E_{\pm}(k) = \tfrac{1}{2} \left\{ E(k) + E(k-g) \pm \sqrt{(E(k) - E(k-g))^2 + 4V^2} \right\}$$

A plot of those energy dispersion with k close to the Brillouin Zone boundary is shown on figure 1.
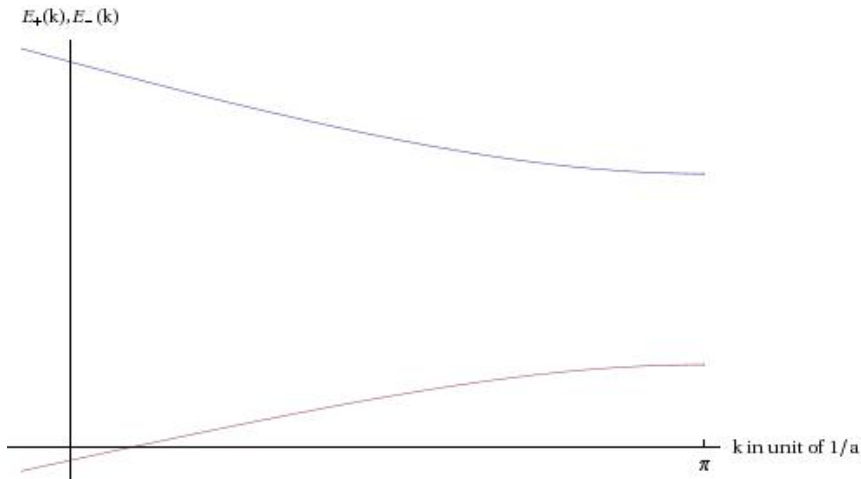

Figure 1: Band dispersion when a small perturbing periodic potential is present. We see clearly a gap opening between the two dispersions at $k = \frac{\pi}{a}$.

Remark: everything done in this exercise is discussed in detail in chapter 3, pages 23 to 26 of the Singleton book. Take a look at it and try to rederive everything in this exercise without looking at the book. The physical consequences of this analysis are very important and should be remembered.