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3.23 Electrical, Optical, and Magnetic Properties of Materials

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Homework # 5

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Homework is due on Wednesday October 17th, 5pm

1 Density of states

We saw both in recitation and in class, that we can calculate the 3D density of state corresponding to a given *dispersion formula* $E(\vec{k})$, by using the following formula:

$$g(E) = \frac{V}{(2\pi)^3} \int_{E(\vec{k})=E} \frac{dS}{\|\nabla_{\vec{k}} E(\vec{k})\|} \text{ for the 3D case}$$

where the integral is carried out over the "isosurface" of energy E , i.e the **surface** defined by the equation $E(k_x, k_y, k_z) = E$. The infinitesimal surface element is dS and V is the volume of the 3D crystal. The 2D equivalent is the following:

$$g(E) = \frac{A}{(2\pi)^2} \int_{E(\vec{k})=E} \frac{dl}{\|\nabla_{\vec{k}} E(\vec{k})\|} \text{ for the 2D case}$$

where the integral is carried out over the "isosurface" of energy E , i.e the **curve** defined by the equation $E(k_x, k_y) = E$. The infinitesimal element of length along the isosurface is dl and A is the area of the 2D crystal. Finally for the 1D case we have:

$$g(E) = \frac{L}{(2\pi)} \sum_{k_0} \frac{1}{\left| \frac{dE(k)}{dk} \right|_{(k=k_0)}} \text{ for the 1D case}$$

where k_0 are all the k points such that $E(k_0) = E$, and L is the length of the 1D crystal.

1.1 Free electron gas in 1D, 2D and 3D

Now we will apply this to the 1D, 2D and 3D free electron gas.

1) Write down the dispersion relations $E(\vec{k})$ for a free electron gas in 1D, 2D and 3D. From those relations, describe the corresponding isosurfaces, i.e draw a typical isosurface for each case (1D, 2D, 3D).

2) For the 2D and 3D cases, find the appropriate set of coordinates to describe an isosurface. Using this set of coordinates, give a mathematical expression for the "surface" element dS . Finally give an analytical form for the density of states.

3) For the one dimensional case, use the third formula above to calculate the density of states.

4) Plot the 1D, 2D and 3D density of states as a function of the energy E .

1.2 The case of tightly bound electrons in 1D

Let's consider tightly bound electrons described by the following band dispersion (for a 1D linear chain of atoms):

$$E(k) = \epsilon_0 - 2\gamma \cos(ka)$$

1) Define the interval of all possible values for $E(k)$ when k is in the first Brillouin Zone. Plot the band dispersion for k in the first Brillouin Zone.

2) Using the formula for the 1D case, calculate the density of states. Plot this density of states as a function of the energy in the appropriate interval (defined in question 1)).

2 Tight-binding method

2.1 geometrical description of the crystal

Let us consider a simple cubic lattice (3D) of lattice parameter a , with one atom per unit cell centered at the origin of the coordinate system. Each atom has one *valence* electron and in the atomic limit (i.e in the limit where the atoms are far from each other) this electron is described by an s-type atomic orbital $\phi_s(\vec{r})$.

1) Give a mathematical expression for the primitive basis vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ that describe this simple cubic lattice. Calculate the expression for the reciprocal primitive vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$. What is the volume of the unit cell in real space? What is the volume of the unit cell in reciprocal space, i.e the first Brillouin Zone? Relate those two volumes by an equation.

2) Express the equilibrium position vectors \vec{R} for the atoms in this simple cubic crystal in terms of the $\vec{a}_1, \vec{a}_2, \vec{a}_3$ basis. Sketch the first Brillouin Zone in reciprocal space.

2.2 calculation of the band dispersion

The tight-binding method is an extension of the LCAO method, used in Chemistry, to periodic systems like solids. The spirit of the technique is the following: If one looks at the wavefunction for an electron in the atomic limit (when the atoms of the solid are far from each other), then this wavefunction looks very much like the atomic orbital $\phi_s(\vec{r})$. Now if we bring the atoms closer and closer to each other, the wavefunction for the electron will be perturbed and at sufficiently small distances between atoms, the electron will be able to "hop" from atom to atom, and it will delocalize over the entire solid. Nevertheless when the electron is localized around one particular atom, let say the atom centered around position \vec{R} , the wavefunction must still look very much like $\phi_s(\vec{r} - \vec{R})$. So the idea of the tight-binding method is to write down the electronic wavefunction as a linear combination of all the atomic orbitals $\phi_s(\vec{r} - \vec{R})$, centered around each atom \vec{R} **in the crystal** (the summation over \vec{R} below concerns all atoms in the crystal):

$$\psi_s(\vec{r}) = \sum_{\vec{R}} c_{\vec{R}} \phi_s(\vec{r} - \vec{R})$$

But in order to be an "acceptable" wavefunction, $\psi_s(\vec{r})$ must satisfy Bloch's theorem. This is a big constraint for $\psi_s(\vec{r})$, and as a consequence, we can write down an expression for $\psi_s(\vec{r})$ for each wavevector \vec{k} :

$$\psi_{s\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \phi_s(\vec{r} - \vec{R})$$

The $\frac{1}{\sqrt{N}}$ is just a normalization factor (N being the number of unit cells in our crystal), and the coefficients $c_{\vec{R}}$ are given by $e^{i\vec{k}\vec{R}}$.

We are interested in the eigenenergy $E_s(\vec{k})$ of the periodic one-electron effective hamiltonian \hat{H} . To calculate this eigenenergy we use the following result:

$$E_s(\vec{k}) = \frac{\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \rangle}{\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle}$$

1) Give the mathematical expression for $\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle$ in terms of integrals over the volume of the crystal. In this expression you should obtain terms of the form:

$$\int_{\text{crystal}} \phi_s^*(\vec{r} - \vec{R}) \phi_s(\vec{r} - \vec{R}') d\vec{r}$$

Because of the Born-Von Karman boundary conditions, one can show that this integral is equal to the following one:

$$\int_{\text{crystal}} \phi_s^*(\vec{r}) \phi_s(\vec{r} - (\vec{R}' - \vec{R})) d\vec{r}$$

So you see that this integral **only depends** on the relative distance $\vec{R}' - \vec{R}$. Using this, simplify the expression for $\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle$? If the set of atomic orbitals $\left\{ \phi_s(\vec{r} - \vec{R}) \right\}_{\vec{R}}$ form an orthonormal basis, what is the mathematical expression for $\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle$?

We will now consider that the set of atomic orbitals form an orthonormal basis

2) Now that we have expressed $\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle$, we need to focus on the numerator $\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \rangle$. Because \hat{H} is a periodic hamiltonian we can show that the numerator can be written as:

$$\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \rangle = \sum_{\vec{R}} e^{i\vec{k}\vec{R}} \int_{\text{crystal}} \phi_s(\vec{r}) \hat{H} \phi_s(\vec{r} - \vec{R}) d\vec{r}$$

Let us denote by ϵ_s and γ the following integrals: $\epsilon_s = \int_{\text{crystal}} \phi_s(\vec{r}) \hat{H} \phi_s(\vec{r}) d\vec{r}$ and $\gamma = \int_{\text{crystal}} \phi_s(\vec{r}) \hat{H} \phi_s(\vec{r} - \vec{R}) d\vec{r}$ (when \vec{R} is a nearest-neighbour to the atom centered around the origin $\vec{0}$). Using those parameters, give a mathematical expression for $\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \rangle$ when one considers the sum over \vec{R} only up to nearest neighbours.

3) Using the results of question 1) and 2), plot the function $E_s(\vec{k})$ along the following lines in the first Brillouin Zone: from Γ ($\frac{2\pi}{a}(0, 0, 0)$) to X ($\frac{2\pi}{a}(1, 0, 0)$), then from X to L ($\frac{2\pi}{a}(1/2, 1/2, 1/2)$), and finally from L to Γ .

4) Using a Taylor expansion for $E_s(\vec{k})$ around $\vec{k} \approx \vec{0}$, show that the band dispersion can be written as:

$$E_s(\vec{k}) \approx \alpha - \frac{\hbar^2 \vec{k}^2}{2m^*}$$

and relate α and m^* to the parameters ϵ_s , γ and a . From that expression what can you infer about the behavior of electrons with a wavevector close to the Γ point? How does the effective mass m^* vary with the "hopping integral" γ ?

5) If one considers that this crystal has only one *valence* electron per unit cell, will it be a metal or an insulator (explain your answer)? If this is a metal, what is the value of the Fermi energy? Show a 3D plot of the Fermi surface in the first Brillouin Zone (k_x, k_y and k_z all vary between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$).

3 Si and GaAs

Silicon and Gallium Arsenide crystals can be described by an fcc lattice with two atoms per unit cell. The primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ for the fcc lattice expressed in a cartesian basis are given by:

$$\vec{a}_1 = \frac{a}{2}(0, 1, 1), \vec{a}_2 = \frac{a}{2}(1, 0, 1), \text{ and } \vec{a}_3 = \frac{a}{2}(1, 1, 0)$$

a is the lattice parameter. The basis vectors, that describe the positions of atoms inside a unit cell, are given by:

$$\vec{\tau}_1 = \frac{a}{4}(1, 1, 1) \text{ and } \vec{\tau}_2 = -\frac{a}{4}(1, 1, 1)$$

1) Find an expression for the reciprocal space primitive vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$. Give the expression for the Fourier coefficient $V_{\vec{G}}$ in terms of the periodic potential $V(\vec{r})$. Establish a relationship between $V_{-\vec{G}}$ and $V_{\vec{G}}^*$.

2) Does Silicon have an inversion symmetry, i.e $V(-\vec{r}) = V(\vec{r})$? Explain your answer. What about GaAs?

3) If a crystal have an inversion symmetry, show that $V_{\vec{G}} = V_{-\vec{G}} = V_{\vec{G}}^*$.