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

Homework # 5, solution

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Homework is due on Wednesday October 17th, 5pm

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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:

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

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:

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

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:

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

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

Remark: in this exercise we are interested in the energy density of states without taking into account the spin degeneracy! If we were interested in the FULL density of states, we would have to multiply all our results by 2.

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).

solution:

The dispersion relations are the following:

$$E(k_x) = \frac{\hbar^2 k_x^2}{2m} \text{ in 1D}$$

$$E(k_x, k_y) = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m} \text{ in 2D}$$

and

$$E(k_x, k_y, k_z) = \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} \text{ in 3D}$$

One can visualize the 1D and 2D dispersion by looking at the plots shown on figure 1. The isosurfaces are the regions of space where the energy is kept
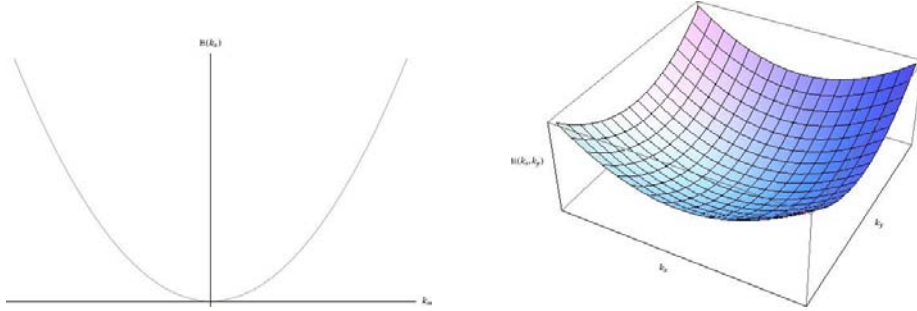

Figure 1: 1D and 2D energy dispersions for a free electron

constant. As a consequence, we have the following results:

1. In the 1D case, the isosurface is defined by the equation $\frac{\hbar^2 k_x^2}{2m} = E$, so we see that this **isosurface** reduces to **two points**, k_0 and $-k_0$, where $k_0 = \sqrt{\frac{2mE}{\hbar^2}}$

2. In the 2D case, the **isosurface** is defined by $\frac{\hbar^2 (k_x^2 + k_y^2)}{2m} = E$. This equation is nothing but the equation of **a circle** in k_x, k_y space of radius $R = \sqrt{\frac{2mE}{\hbar^2}}$.

3. In the 3D case, the equation that defines the isosurface is the following: $\frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m} = E$. So we see that we define **a sphere** in the k_x, k_y, k_z space with a radius $R = \sqrt{\frac{2mE}{\hbar^2}}$.

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.

solution:

Given the geometry of the isosurfaces in 2D and 3D, we see that the appropriate sets of coordinates are the following:

- In the 2D case, we will use a set of **planar polar coordinates** r, θ ($r^2 = k_x^2 + k_y^2$, $\tan(\theta) = \frac{k_y}{k_x}$). The "element of length" along the circle of radius r is $dl = rd\theta$.

- In the 3D case, we will use the natural extension of the planar polar coordinates to 3 variables, which is nothing less than the set of **spherical coordinates** r, θ, ϕ ($r^2 = k_x^2 + k_y^2 + k_z^2$, $\tan(\phi) = \frac{k_y}{k_x}$, $\sin(\theta) = \frac{k_x}{k_z}$). The "element of surface" on a sphere of radius r is $dS = r^2 \sin(\theta) d\theta d\phi$.

Let us now use the formulas given at the beginning of this exercise. For the 2D case, we have: $\|\vec{\nabla}_{\vec{k}} E(\vec{k})\| = \frac{\hbar^2}{m} \sqrt{k_x^2 + k_y^2} = \frac{\hbar^2}{m} r$ using the polar coordinates. We need to integrate the inverse of $\|\vec{\nabla}_{\vec{k}} E(\vec{k})\|$ along the circle of radius $r = \sqrt{\frac{2mE}{\hbar^2}}$. So the density of states in 2D is:

$$g_{2D}(E) = \frac{A}{(2\pi)^2} \int_0^{2\pi} \frac{r d\theta}{\frac{\hbar^2}{m} r} = \frac{mA}{2\pi \hbar^2}$$

We see an interesting feature of the 2D density of states for the free electron gas: it is **a constant!**

Let us move on to the 3D case. This time the integral is carried out over a sphere of radius $r = \sqrt{\frac{2mE}{\hbar^2}}$. We have $\|\vec{\nabla}_{\vec{k}} E(\vec{k})\| = \frac{\hbar^2}{m} \sqrt{k_x^2 + k_y^2 + k_z^2} = \frac{\hbar^2}{m} r$ and so the density of states is:

$$g_{3D}(E) = \frac{V}{(2\pi)^3} \int_0^{2\pi} \int_0^{\pi} \frac{r^2 \sin(\theta) d\theta d\phi}{\frac{\hbar^2}{m} r}$$

In this integral the remaining r term is independant of θ and ϕ, because $r = \sqrt{\frac{2mE}{\hbar^2}}$. So the integral is just 4π and the final answer is:

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

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

solution:

For the 1D case, we use the formula given at the beginning of this exercise. We see that there are 2 k_0 for which the dispersion relation is verified in the expression for the density of states $g(E) = \frac{L}{(2\pi)} \sum_{k_0} \frac{1}{|\frac{dE(k)}{dk}(k=k_0)|}$. The direct use of this formula gives us:

$$g_{1D}(E) = \frac{L}{\pi} \sqrt{\frac{m}{2\hbar^2}} \frac{1}{\sqrt{E}}$$

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

solution:

I give here the plots of $\frac{g_{1D}(E)}{\frac{L}{\pi}\sqrt{\frac{m}{2\hbar^2}}}$, $\frac{g_{2D}(E)}{\frac{mA}{2\pi\hbar^2}}$ and $\frac{g_{3D}(E)}{\frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}}$ as a function of E on figure 2.

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):

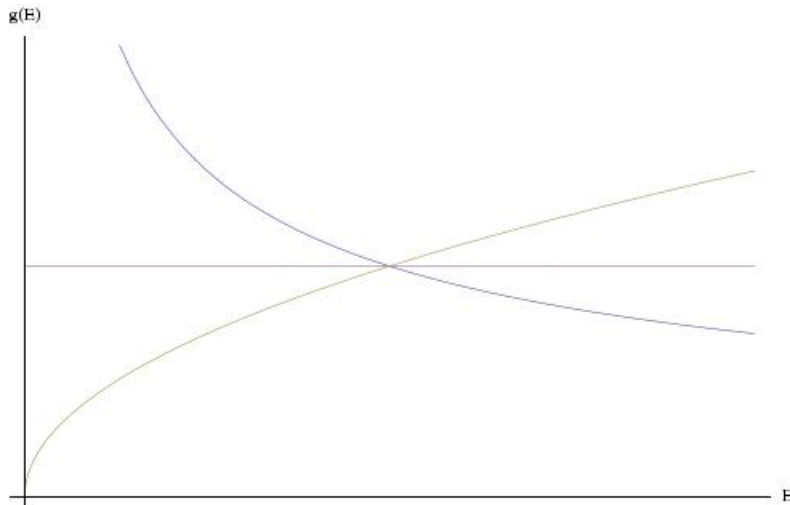$$E(k) = \epsilon_0 - 2\gamma \cos(ka)$$

Figure 2: 1D, 2D and 3D normalized density of states for a free electron. The 1D curve blows up when $E \rightarrow 0$, the 2D one is constant, and the 3D grows continuously from 0.

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.

solution:

We see on the band dispersion that the periodicity in k is given by the cosine term. This term is periodic in k with the following period $\frac{2\pi}{a}$. Moreover since the cosine is an even function in k, it is convenient to represent the band structure on a plot centered around $k = 0$, starting at $k = -\frac{\pi}{a}$ and ending at $k = \frac{\pi}{a}$. The band dispersion is shown on figure 3. **In order to plot this dispersion i considered γ to be positive**.

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)).

solution:

Given the mathematical expression for the band dispersion, we see that: $\frac{dE(k)}{dk} = 2\gamma a \sin(ka)$. In the formula given for the 1D case, we see that we need to calculate this derivative at points k_0 such that $E(k_0) = E$. Before to calculate k_0, let's have a look at what is the energy range for E. We see that because the cosine takes values only between -1 and 1, then the energy E must be located between $\epsilon_0 - 2\gamma$ and $\epsilon_0 + 2\gamma$. In this interval of energy, k_0 can be expressed as $k_0 = \pm \frac{1}{a} \arccos(\frac{\epsilon_0 - E}{2\gamma})$.

If we go back to the expression for the derivative of $E(k)$, and if we use the well-known trigonometric formula $\sin(x) = \pm\sqrt{1 - \cos^2(x)}$, then we see that:

$$\frac{1}{|\frac{dE(k)}{dk}|_{k=k_0}|} = \frac{1}{|2\gamma a \sin(k_0 a)|} = \frac{1}{|2\gamma a \pm \sqrt{1 - (\frac{\epsilon_0 - E}{2\gamma})^2}|}$$

We can now express the density of states for a one dimensional nearest-neighbour tight-binding as:

$$g(E) = \frac{L}{2\pi\gamma a} \frac{1}{\sqrt{1 - (\frac{\epsilon_0 - E}{2\gamma})^2}}$$
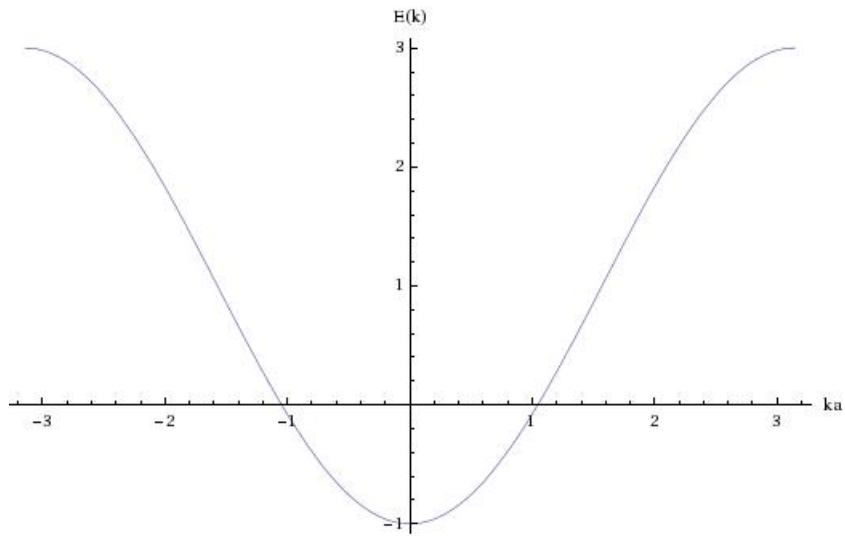
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Figure 3: Energy dispersion for a one dimensional nearest neighbour tight-binding model. The first Brillouin Zone runs from $k = -\frac{\pi}{a}$ to $k = \frac{\pi}{a}$. On this plot ϵ_0 is 1 and so is γ.

A plot of this density of state is shown on figure 4.
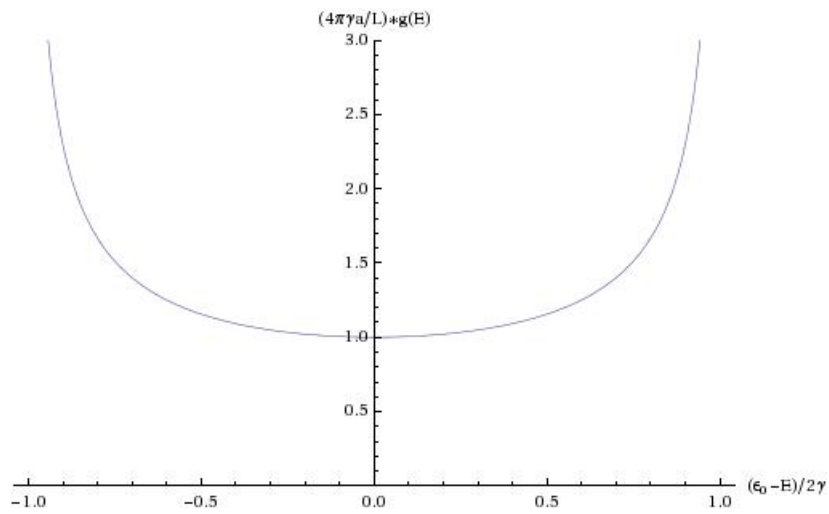

Figure 4: Density of state of a 1D nearest-neighbour tight-binding model.

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.

solution:

The simple cubic lattice is a **Bravais lattice**. As such all the lattice points are equivalent to each other. The most natural basis of primitive vectors are of course the cartesian vectors:

$$\vec{a}_1 = a\vec{e}_x \quad \vec{a}_2 = a\vec{e}_y \quad \vec{a}_3 = a\vec{e}_z$$

By definition, the primitive vectors of the reciprocal lattice $\vec{b}_1, \vec{b}_2, \vec{b}_3$ are such that: $\vec{a}_1 \cdot \vec{b}_1 = 2\pi$, $\vec{a}_2 \cdot \vec{b}_1 = 0$ and $\vec{a}_3 \cdot \vec{b}_1 = 0$ (and equivalent expressions for $\vec{b}_2$ and $\vec{b}_3$). For $\vec{b}_1$, we can easily conclude from the three relations above that this vector must be perpendicular to $\vec{a}_2$ and $\vec{a}_3$. So in the case of the simple cubic lattice, this induces that this vector is perpendicular to $\vec{e}_y$ and $\vec{e}_z$. So $\vec{b}_1$ is a vector proportional to $\vec{e}_x$. Now if we use the fact that $\vec{a}_1 \cdot \vec{b}_1 = 2\pi$, we can conclude that $\vec{b}_1 = \frac{2\pi}{a}\vec{e}_x$. The same kind of analysis for $\vec{b}_2$ and $\vec{b}_3$ leads us to the following final expressions for the primitive vectors in reciprocal space:

$$\vec{b}_1 = \frac{2\pi}{a}\vec{e}_x \quad \vec{b}_2 = \frac{2\pi}{a}\vec{e}_y \quad \vec{b}_3 = \frac{2\pi}{a}\vec{e}_z$$

The volume of the unit cell in real space is given by the volume of the parallelepiped delimited by $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$, which is nothing but $\Omega = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3$. The volume of the first Brillouin Zone is nothing but the volume of the unit cell in reciprocal space. Similarly to the real space case, this volume is given by $\Omega^{'} = \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{a^3}$. We see that the relationship between the volume of the unit cell in real space Ω and the volume of the unit cell in reciprocal space $\Omega^{'}$ is :

$$\Omega^{'} = \frac{(2\pi)^3}{\Omega}$$

This relationship is valid for ANY crystal structure.

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.

solution:

The direct space translation vectors $\vec{R}$ are given by:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

where n_1, n_2, n_3 are integer numbers. The first Brillouin Zone centered on the origin of the coordinate system in reciprocal space is defined by all the possible k vectors $\vec{k} = k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3$, where k_1, k_2, k_3 are in the interval $\left[-\frac{1}{2}, \frac{1}{2}\right]$.

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 combinaison 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 coefficiants $c_{\vec{R}}$ 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 $\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle$?
solution:
Let's write down the scalar product of $\psi_{s\vec{k}}(\vec{r})$ with itself: $\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle$.

$$\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \rangle = \int_{\text{crystal}} \psi_{s\vec{k}}^*(\vec{r}) \psi_{s\vec{k}}(\vec{r}) d\vec{r}$$

By plugging in the mathematical expression for $\psi_{s\vec{k}}(\vec{r})$, this expression becomes:

$$\left\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \right\rangle = \frac{1}{N} \sum_{\vec{R},\vec{R}'} e^{i\vec{k}(\vec{R}'-\vec{R})} \int_{\text{crystal}} \phi_s^*(\vec{r}-\vec{R})\phi_s(\vec{r}-\vec{R}')d\vec{r}$$

At this stage, we will use the hint given in the text above. Indeed if one considers the integral $\int_{\text{crystal}} \phi_s^*(\vec{r}-\vec{R})\phi_s(\vec{r}-\vec{R}')d\vec{r}$, it is quite easy to see that translating $\vec{r}$ by a direct space vector $\vec{R}$ does not change the value of the integral because of the Born-Von Karman boundary conditions on the solid. So we can simplify the expression above to the following one:

$$\left\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \right\rangle = \frac{1}{N} \sum_{\vec{R},\vec{R}'} e^{i\vec{k}(\vec{R}'-\vec{R})} \int_{\text{crystal}} \phi_s^*(\vec{r})\phi_s(\vec{r}-(\vec{R}'-\vec{R}))d\vec{r}$$

It doesn't seem that we have achieved a lot here, but actually it is not true! Indeed if we change the summation variable from $\vec{R}$ and $\vec{R}'$ to $\vec{R}$ and $\vec{R}'' = \vec{R}' - \vec{R}$, we see that the argument of the double sum does NOT depend on $\vec{R}$. This means that the sum over $\vec{R}$ just gives us **the total number of unit cell** in the crystal, N, which cancels out with the $\frac{1}{N}$ term. So in the end, we end up with the following expression for $\left\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \right\rangle$:

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

Moreover **if the basis of atomic orbitals is orthonormal** then those integrals are all zero, exept the one for $\vec{R}'' = \vec{0}$. And the final result is:

$$\left\langle \psi_{s\vec{k}} | \psi_{s\vec{k}} \right\rangle = 1 \text{ if orthonormal atomic orbitals}$$

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

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

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

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 $\left\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \right\rangle$ when one considers the sum over $\vec{R}$ only up to nearest neighbours.

solution:

Using the expression for $\left\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \right\rangle$ given above and the definition for the nearest-neighbour transfert integral, wee find the following result:

$$\left\langle \psi_{s\vec{k}} | \hat{H} | \psi_{s\vec{k}} \right\rangle = \epsilon_s + \sum_{\vec{R}} e^{i\vec{k}\vec{R}}\gamma$$

where the sum runs over the nearest neighbours of the atom centered at the origin. Those nearest neighbours have the following coordinates $\vec{R} = \pm\vec{a}_1$, $\vec{R} = \pm\vec{a}_2$ and $\vec{R} = \pm\vec{a}_3$.

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 form L to Γ.

solution:

From questions 1) and 2), we see that the energy dispersion can be written as:

$$E(\vec{k}) = \epsilon_s + 2\gamma(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$

We can then plot this dispersion along high-symmetry lines. This plot is shown on figure 5.
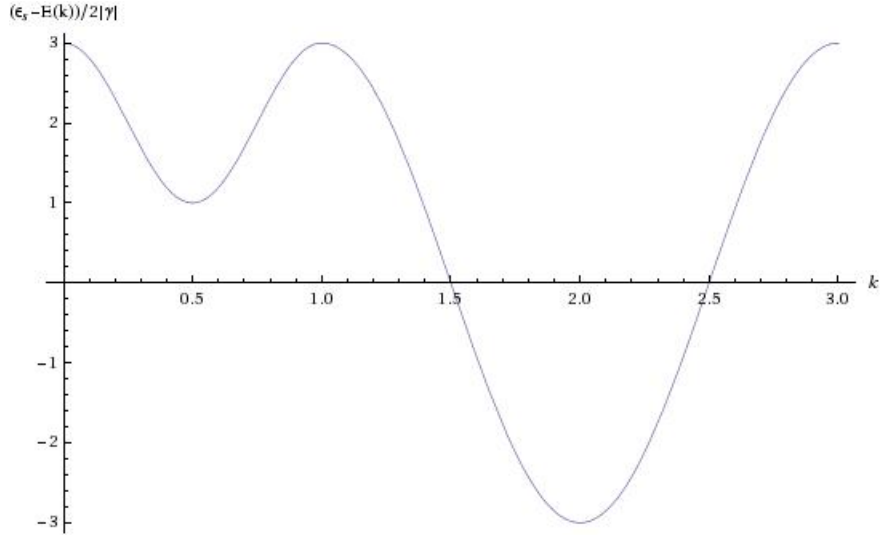

Figure 5: Band structure of our 3D nearest-neighbour tight-binding model in a simple cubic structure.

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?

solution:

Using a Taylor expansion for the cosines around $\vec{k} \approx 0$, we find:

$$E(\vec{k}) \approx \epsilon_s + 2\gamma * (1 - \frac{(k_x a)^2}{2} + 1 - \frac{(k_y a)^2}{2} + 1 - \frac{(k_z a)^2}{2}) = (\epsilon_s + 6\gamma) - a^2\gamma\vec{k}^2$$

By identification, we can extract the values for m^* and α:

$$\alpha = \epsilon_s + 6\gamma \text{ and } m^* = \frac{\hbar^2}{2a^2\gamma}$$

Remark: it is interesting and physically appealing that the effective mass is proportional to the INVERSE of the transfert integral γ. Indeed this coefficiant is a measure of how "easy" it is for an electron to "hop" from an atom to its nearest neighbour. It is then logical that when γ is big, meaning that the electron easily transfer to a neighbouring atom, then the effective mass is small, such that this

particle is very "light". On the contrary, when γ is very small, then the particle hardly moves away corresponding to the physical picture of a very "heavy" particle.

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 $\frac{\pi}{a}$).

solution:

We saw in recitation, that a band can accomodate **2N** electrons, where N is the number of unit cell in the crystal and the coefficiant 2 takes nto account the spin degeneracy. In our case, we have *one electron per unit cell*, so N electrons in total and the band is half-filled. Our system is then a metal because empty energy states are arbitrarily close to the highest occupied energy, the **Fermi energy**. The Fermi energy is exactly the middle energy of our band because this band is symmetric with respect to the middle energy. So $E_{\mathrm{F}} = \epsilon_s$. The **Fermi surface** is defined to be the location of all the $\vec{k}$ vectors in the first Brillouin Zone, such that the energy $E(\vec{k})$ is equal to the Fermi energy. The equation that defines the **Fermi surface** is then:

$$E(\vec{k}) = \epsilon_s + 2\gamma(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)) = E_{\mathrm{F}} = \epsilon_s$$

A 3D plot of the Fermi surface in the first Brillouin Zone is shown on figure 6.
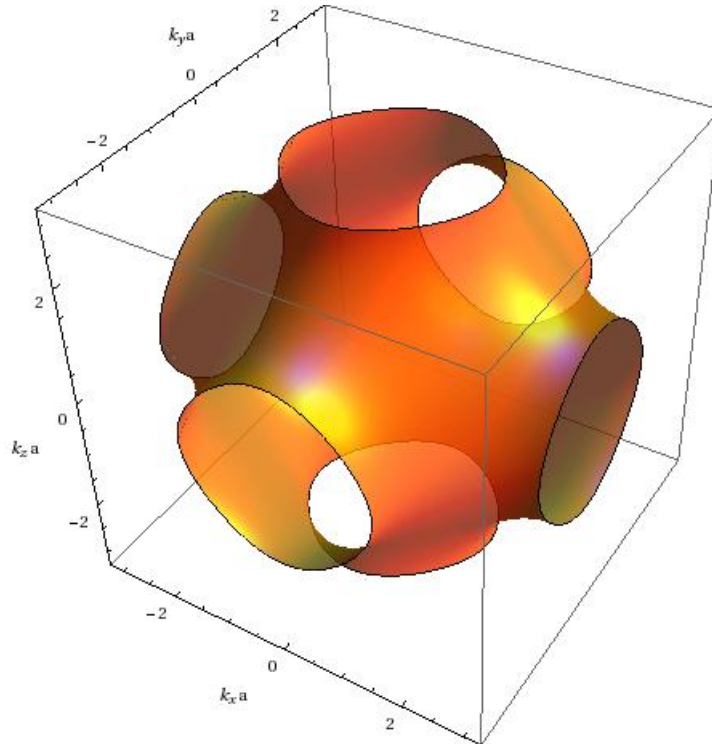

Figure 6: Fermi surface corresponding to a half-filled s band in a 3D simple cubic crystal in a nearest neighbour tight-binding model.

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:

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

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

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

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 coefficiant $V_{\vec{G}}$ in terms of the periodic potential $V(\vec{r})$. Establish a relationship between $V_{-\vec{G}}$ and $V_{\vec{G}}^*$.

solution:

In general, the primitive basis vectors in reciprocal space are given by the following formulas:

- $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

- $\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

- $\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

Calculating those cross products gives us:

$$\vec{b}_1 = \tfrac{2\pi}{a}(-1,1,1),\ \vec{b}_2 = \tfrac{2\pi}{a}(1,-1,1),\ \vec{b}_3 = \tfrac{2\pi}{a}(1,1,-1)$$

We have seen in the lectures on Bloch theorem (yes we saw it!), that the fourier coefficients $V_{\vec{G}}$ of the effective periodic potential $V(\vec{r})$ can be written as:

$$V_{\vec{G}} = \tfrac{1}{\Omega} \int_{\text{unit cell}} V(\vec{r}) e^{i\vec{G}\cdot\vec{r}} d\vec{r}$$

where Ω is the volume of the unit cell. Now let us take the complex conjuguate of $V_{\vec{G}}$. We end up with:

$$(V_{\vec{G}})^* = (\tfrac{1}{\Omega} \int_{\text{unit cell}} V(\vec{r}) e^{i\vec{G}\cdot\vec{r}} d\vec{r})^* = \tfrac{1}{\Omega} \int_{\text{unit cell}} (V(\vec{r}) e^{i\vec{G}\cdot\vec{r}})^* d\vec{r}$$

But since the potential is a real valued function, we see that $V(\vec{r})^* = V(\vec{r})$, and so we find:

$$(V_{\vec{G}})^* = \tfrac{1}{\Omega} \int_{\text{unit cell}} (V(\vec{r}) e^{i\vec{G}\cdot\vec{r}})^* d\vec{r} = \tfrac{1}{\Omega} \int_{\text{unit cell}} V(\vec{r}) (e^{i\vec{G}\cdot\vec{r}})^* d\vec{r} = V_{-\vec{G}}$$

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

solution:

The origin of the coordinate system being in the middle of two nearest neighbour silicon atoms, we see that Silicon has an inversion symmetry. And so the potential function must have this symmetry too, so $V(\vec{r}) = V(-\vec{r})$. GaAs does not have that symmetry because in the process of changing $\vec{r}$ to $-\vec{r}$, a Gallium atom becomes an Arsenide atom.

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

solution:

If a crystal have an inversion symmetry, then because of question 1) and 2), we see that:

$$V_{\vec{G}}^* = V_{-\vec{G}} = V_{\vec{G}}$$

Indeed the first equality comes from question 1), and the second comes from the identification of like terms in the two sums $V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}\vec{r}} = V(-\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G}(-\vec{r})}$.