Phys 507A - Solid State Physics I

Assignment 1: Electrons in crystals. *Due Jan. 26th*

1. *Periodic potential in 1d.*

   Consider an electron subject to a 1d periodic potential,

   $$U(x) = \sum_{n=-\infty}^{\infty} v(x - na), \tag{1}$$

   where $v(x - na)$ represents the potential barrier against an electron tunnelling between the ions on opposite sides of the point na. For simplicity we assume that $v(x) = v(-x)$ (inversion symmetry), and $v(x) = 0$ for $|x| \geq a/2$. But other than this the potential $U(x)$ is quite general.

   Remarkably, the band structure of the 1d solid can be expressed quite simply in terms of the transmittance and reflectance of an electron hitting the barrier $v(x)$. Denote the energy of the incident electron to be $\epsilon = \hbar^2 K^2/2m$. The variable $K = \sqrt{2m\epsilon}/\hbar$ parametrizes the energy of the electron. Consider an electron incident from the left on the potential barrier $v(x)$; since $v(x) = 0$ for $x \geq a/2$, in these regions the wave function $\psi_l(x)$ will have the form

   $$\begin{aligned} \psi_l(x) &= e^{iKx} + re^{-iKx}, x \leq -\frac{a}{2} \\ &= te^{iKx}, x \geq \frac{a}{2}. \end{aligned} \tag{2}$$

   Here t and r are the transmission and reflection coefficients, respectively. Their actual dependence on K is given by the form of the barrier $v(x)$. However, one can deduce the properties of the band structure of the periodic potential U by appealing only to very general properties of t and r. Because $v(x)$ is even, $\psi_r(x) = \psi_l(-x)$ is also a solution to the Schröedinger equation with energy ϵ. From Eq. (2) it follows that

   $$\begin{aligned} \psi_r(x) &= te^{-iKx}, x \leq -\frac{a}{2}, \\ &= e^{-iKx} + re^{iKx}, x \geq \frac{a}{2}. \end{aligned} \tag{3}$$

   Since ψ_l and ψ_r are two independent solutions to the single-barrier Schröedinger equation with the same energy, any other solution with that energy will be a linear combination of these two; in addition, since the crystal potential is identical to $v(x)$ in the region $|x| \leq a/2$, any solution to the crystal Schröedinger equation with energy ϵ in the $|x| \leq a/2$ region must be given by

   $$\psi(x) = A\psi_l(x) + B\psi_r(x). \tag{4}$$

Now Bloch's theorem asserts that ψ can be chosen to satisfy

$$\psi(x+a) = e^{ika}\psi(x), \tag{5}$$

for a suitable k (different than K!). Differentiating the above equation we also find that

$$\psi'(x+a) = e^{ika}\psi'(x). \tag{6}$$

(a) By imposing the conditions (5) and (6) at $x = -a/2$, and using Eqs. (2)–(4), show that the energy of the Bloch electron is related to its wavevector k by:

$$\cos(ka) = \frac{t^2 - r^2}{2t}e^{iKa} + \frac{1}{2t}e^{-iKa}, \epsilon = \frac{\hbar^2 K^2}{2m}. \tag{7}$$

Verify that this gives the right answer in the free electron case $(v = 0)$.

We write the complex number t in terms of its magnitude and phase:

$$t = |t|e^{i\delta}. \tag{8}$$

The real number δ is known as the phase shift, since it represents the change in phase of the transmitted wave relative to the incident one. Electron conservation requires that the probability of transmission plus the probability of reflection be unity,

$$|t|^2 + |r|^2 = 1. \tag{9}$$

This, and some other useful information, can be proved as follows. Let ϕ_1 and ϕ_2 be any two solutions to the one-barrier Schröedinger equation with the same energy:

$$-\frac{\hbar^2}{2m}\phi_i'' + v(x)\phi_i = \frac{\hbar^2 K^2}{2m}\phi_i, i = 1, 2. \tag{10}$$

Define the Wronskian $w(\phi_1, \phi_2)$ by

$$w(\phi_1, \phi_2) = \phi_1'(x)\phi_2(x) - \phi_1(x)\phi_2'(x). \tag{11}$$

(b) Prove that w is independent of x by deducing from Eq. (10) that its derivative vanishes.

(c) Prove Eq. (9) by evaluating $w(\psi_l, \psi_l^*)$ for $x \le -a/2$ and $x \ge a/2$, noting that because $v(x)$ is real, ψ_l^* will be a solution to the same Schröedinger equation as ψ_l.

(d) By evaluating $w(\psi_l, \psi_r^*)$ prove that rt^* is pure imaginary, so r must have the form

$$r = \pm i|r|e^{i\delta}, \tag{12}$$

where δ is the same as in Eq. (8).

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(e) Show that as a consequence of Eqs. (7), (9), and (12) that the energy and wavevector of the Bloch electron are related by

$$\frac{\cos\left(Ka + \delta\right)}{|t|} = \cos\left(ka\right). \tag{13}$$

(f) Since $|t|$ is always less than one, the left hand side of Eq. (13) will be larger than one for K values in the neighbourhood of $(Ka + \delta) = n\pi$. In this case Eq. (13) has no solutions for real k; the corresponding regions of energy are the energy gaps.

Sketch the left hand side of Eq. (13) as a function of K, and show graphically that real solutions for k can only exist within certain "bands" of K. These are the energy bands. Note that $|t|$ approaches unity for large K (the barrier becomes increasingly less effective as the incident energy grows); therefore the K bands become wider as K becomes larger (accordingly, the "forbidden" regions become narrower).

(g) As a concrete example, consider

$$v(x) = g\delta(x), \tag{14}$$

where $\delta(x)$ is the Dirac delta function. The resulting crystal potential $U(x)$ is the so called "Dirac comb", or "Kronig-Penney model". Show that in this case

$$\cot\left(\delta\right) = -\frac{\hbar^2 K}{mg}, \quad |t| = \cos\left(\delta\right). \tag{15}$$

(h) Substitute Eq. (15) into Eq. (13) and determine the allowed values of K graphically (Plot using numerical software such as Mathematica or Gnuplot).

The Kronig-Penney model is the textbook example of a one-dimensional periodic potential. Note, however, that most of the structure we have established is independent of the particular functional dependence of $|t|$ and δ on K.

2. *Bravais lattices, primitive vectors, basis.*

In each of the following cases indicate whether the structure is a Bravais lattice. If it is, give three primitive vectors; if it is not, describe it as a Bravais lattice with as small as possible a basis.

(a) Base-centered cubic (simple cubic with additional points in the centers of the horizontal faces of the cubic cell).

(b) Side-centered cubic (simple cubic with additional points in the centers of the vertical faces of the cubic cell).

(c) Edge-centered cubic (simple cubic with additional points at the midpoints of the lines joining nearest neighbors).

3. *Diamond lattice.*

The diamond lattice, that is formed by the carbon atoms in a diamond crystal, is also the lattice of several other important materials such as silicon, germanium, and grey tin. The diamond lattice consists of two interpenetrating face-centered Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal. It can be regarded as a fcc with a two-atom basis at $\mathbf{0}$ and $\frac{a}{4}(\hat{\boldsymbol{x}} + \hat{\boldsymbol{y}} + \hat{\boldsymbol{z}})$.

(a) Sketch the conventional cubic cell of the diamond lattice (a cube with side a).

(b) Calculate the nearest neighbor bond length in terms of the lattice parameter a.

(c) The diamond crystal has $a = 3.57$ Å; look up the mass for each carbon atom and find the density for the diamond crystal.

(d) Prove that the diamond lattice has an inversion center at the midpoint of any nearest-neighbor bond.

4. *Packing fraction for a lattice.*

The fcc is the most dense and the sc (simple cubic) is the least dense of the three cubic Bravais lattices. The diamond structure is less dense than any of these. One measure of this is that the coordination numbers are: fcc, 12; bcc, 8; sc, 6; diamond, 4. Another is the following: Suppose identical solid spheres are distributed through space in such a way that their centers lie on the points of each of these four structures, and spheres on neighboring points just touch, without overlaping. Such an arrangement of spheres is called a close-packing arrangement. Assuming that the spheres have unit density, show that the density of a set of close packed spheres on each of the four structures (the "packing fraction") is:

fcc: $\sqrt{2}\pi/6 = 0.74$.

bcc: $\sqrt{3}\pi/8 = 0.68$.

sc: $\pi/6 = 0.52$.

diamond: $\sqrt{3}\pi/16 = 0.34$.

5. *Simple hexagonal lattice.*

The simple hexagonal Bravais lattice (sh) is given by stacking 2d triangular nets directly above each other. The direction of stacking ($\boldsymbol{a}_3$ below) is known as the c-axis. Three primitive vectors are:

$$\boldsymbol{a}_1 = a\hat{\boldsymbol{x}}, \boldsymbol{a}_2 = \frac{a}{2}\hat{\boldsymbol{x}} + \frac{\sqrt{3}a}{2}\hat{\boldsymbol{y}}, \boldsymbol{a}_3 = c\hat{\boldsymbol{z}}. \tag{16}$$

The first two generate a triangular lattice in the $x - y$ plane and the third stacks the planes a distance c above one another.

(a) Using the explicit construction of the reciprocal lattice primitive vectors [Eq. (1.23) in Snoke] show that reciprocal of the sh lattice is also sh, with lattice constants $2\pi/c$ and $4\pi/(\sqrt{3}a)$, rotated through $30°$ about the c-axis with respect to the direct lattice.

The hexagonal close-packed (hcp) structure ranks in importance with the bcc and the fcc Bravais lattices; about 30 elements crystallize in the hcp form. The hcp consists of two interpenetrating sh Bravais lattices, displaced from one another by $\frac{1}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + \frac{1}{2}\boldsymbol{a}_3$. The name hcp reflects the fact that close-packed hard spheres can be arranged in such a structure. Consider stacking cannonballs, starting with a close packed triangular lattice as the first layer; the next layer is formed by placing a ball in the depressions left in the center of every other triangle in the first layer, thereby forming a second triangular layer, shifted with respect to the first. The third layer is formed by placing balls in alternate depressions of the second layer, so that the third layer lies directly above the balls in the first layer. The fourth layer lies directly above the second, and so on.

(b) For the case of cannon balls, prove that $c/a = \sqrt{8/3} = 1.63$. This value of c/a is called "ideal"; of course, atoms are not cannon balls, and in nature the hcp structure is found with c/a ranging from 1.56 (for Be) to 1.89 (for Cd).

(c) For what value of c/a does the ratio have the same value in both direct and reciprocal lattices? If c/a is ideal in the direct lattice, what is its value in the reciprocal lattice?

6. *Free electron energies in the reduced zone scheme.*

   Consider the free electron energy bands of an fcc crystal in the approximation of an empty lattice, but in the reduced zone scheme in which all $\boldsymbol{k}'s$ are transformed to lie in the first Brillouin zone. Plot roughly in the [111] direction the energies of all bands up to six times the lowest band energy at the zone boundary at $\boldsymbol{k} = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Let this be the unit of energy. This problem shows why band edges need not necessarily be at the zone center. Several of the degeneracies (band crossings) will be removed when account is taken of the crystal potential.

7. *Density of states for a 2d system.*

   Show that the density of states in an isotropic 2d system near a band minimum or maximum does not depend on the energy of the electrons.

8. *Density of states for a 1d tight-binding model.*

The band energy dispersion for a 1d tight-binding model is given by

$$\epsilon_k = \epsilon_0 - 2t\cos(ka), \tag{17}$$

for $k \in (-\pi/a, \pi/a]$ (1st Brillouin zone). Find the energy density of states.

9. *Effect of disorder on the semi-circle density of states.*

A simple model for an energy band in a 3d crystal is given by the semi-circle density of states,

$$\rho(\epsilon) = \frac{8N}{\pi W^2}\sqrt{\left(\frac{W}{2}\right)^2 - \epsilon^2}. \tag{18}$$

We assumed the energy band is centered at $\epsilon = 0$, and that W is the bandwidth (N is the number of atoms). Of course, Eq. (18) has sharp cut-offs at the band edges $\epsilon = \pm W/2$.

Let's assume the presence of "long wavelength" disorder, meaning that some regions of the crystal have lattice spacings greater than others. By long wavelength we mean that the length scale for variations of the lattice spacing is much larger than the lattice spacing itself. In the absence of any additional information, we may assume that W is normal distributed:

$$P(W) = \frac{1}{\sqrt{2\pi\Delta^2}}e^{-\frac{(W-W_0)^2}{2\Delta^2}}, \tag{19}$$

with W_0 as the mean and Δ as the root-mean-square deviation.

Show that the resulting density of states is given by

$$\langle\rho(\epsilon)\rangle = \frac{4N}{\pi W_0}\int_{|\epsilon'|}^{\infty} dx \frac{e^{-\frac{1}{2\xi^2}(1-x)^2}}{x\sqrt{2\pi\xi^2}}\sqrt{1 - \left(\frac{\epsilon'}{x}\right)^2}. \tag{20}$$

For notational simplicity we defined $\epsilon' = 2\epsilon/W_0$, $\xi = \Delta/W_0$, and $x = W/W_0$. Use Mathematica to plot $\langle\rho(\epsilon')\rangle/[4N/(\pi W_0)]$ for $\xi = 0.01, 0.1, 0.3, 0.5, 1$, and show that the second term in Eq. (20) gives rise to exponential "smoothing" of the band edge.