Solved Exercises in Solid State Physics

Notes from the Exercises component of the third-year undergraduate course *Fizika trdne snovi* (Solid State Physics), led by doc. dr. Tomaž Rejec at the Faculty of Mathematics and Physics at the University of Ljubljana in the academic year 2020-21. The course covers solid state physics at an upper-undergraduate level. Credit for the material covered in these notes is due to professor Rejec, while the voice, typesetting, and translation to English in this document are my own.

Disclaimer: Mistakes—both simple typos and legitimate errors—are likely. Keep in mind that these are the notes of an undergraduate student in the process of learning the material himself—take what you read with a grain of salt. If you find mistakes and feel like telling me, for example by [email](), I'll be happy to hear from you, even for the most trivial of errors.

Elijan J. Mastnak
Faculty of Mathematics and Physics, University of Ljubljana
Summer semester 2020-21

Contents

1   First Exercise Set

Theoretical Background: Crystal Structure and the Packing Factor

- We model matter a periodic structure of identical *unit cells*, which are formed of atoms arranged in a well-defined geometric structure, periodically arranged throughout a crystal lattice.

- The atoms within the unit cells are rigid spheres, which we assume take up enough space to just touch each other. Unit cells are separated by the lattice constant a.

- The *atomic packing factor*, denoted by η, is the ratio of the volume of atoms inside a given unit cell to the cell's total volume

$$\eta = \frac{\text{Volume of atoms } \textit{fully inside} \text{ a unit cell}}{\text{Volume of a unit cell}}. \tag{1.1}$$

- For the sake of completeness, unit cells may be either *primitive* or *non-primitive*, although this distinction is not required for this problem. A primitive unit cell, while in general not uniquely defined for a given lattice structure, is always the smallest possible cell (by volume) periodically spanning the lattice structure and always contains a net total of exactly one atom.

  Two conventional choices of primitive unit cell are the parallelepiped spanned by the primitive vectors, and the Wigner-Seitz primitive cell, which is discussed more in the accompanying lecture notes.

  Non-primitive unit cells are larger in volume than primitive cells, generally form more familiar geometric shapes better reflecting the entire lattice's symmetry, and often contain a net total of more than one atom. The unit cells discussed in the problem below are generally non-primitive unit cells.

1.1   The Atomic Packing Factor

Find the atomic packing factor η for each of the crystal lattice structures listed below.

Each problem is solved with the same general procedure:

1. Determine how many atoms are fully inside a given unit cell.

2. Determine the radius of the cell's constituent atoms.

3. Use Equation 1.1 to find the packing factor.

Think of the this problem as an introduction to the learning the crystal structures. The mathematics itself is elementary; we begin our course with this problem as an introduction to common crystal structures and for lack of lecture material to build on during the first day of the new semester.

1.1.1 Simple Cubic

A simple cubic structure is shown in the figure to the right. A simple cubic structure...

- is abbreviated SC.

- consists of 8 atoms placed at the verticies of a perfect cube.
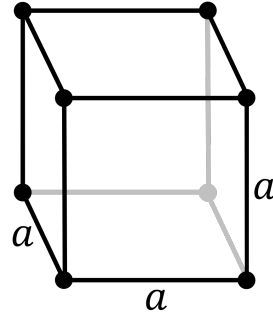
- Each atom at a given vertex of a simple cubic cell is equally shared by the eight cells surrounding the vertex. A simple cubic cell has eight atoms, each of which is only one-eighth inside a given cell. There is thus a net total of $8 \cdot (1/8) = 1$ atom fully inside a simple cubic cell.

- The radius of an atom in a simple cubic cell is $a/2$, and the corresponding volume is

$$V_{\text{atom}} = \frac{4\pi}{3} \left(\frac{a}{2}\right)^3 = \frac{\pi a^3}{6}.$$

The volume of an entire simple cubic cell is simply $V_{\text{cell}} = a^3$.

- Using Equation 1.1 and the just-derived volumes, the packing factor is thus

$$\eta_{\text{SC}} = \frac{\left(8 \cdot \frac{1}{8}\right) \cdot V_{\text{atom}}}{V_{\text{cell}}} = \frac{1}{a^3} \frac{\pi a^3}{6} = \frac{\pi}{6}.$$

1.1.2 Body-Centered Cubic

A body-centered cubic structure is shown in the figure to the right. A body-centered cubic structure...

- is abbreviated BCC.

- consists of 8 atoms placed at the verticies of a perfect cube, with one additional atom at the cube's center.
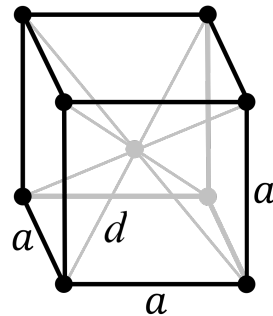
- Like in the simple cubic structure, each outer atom in a BCC cell is equally shared by the eight cells surrounding a given vertex. This makes for net total of $8 \cdot \left(\frac{1}{8}\right) = 1$ outer atoms in a given cell. Together with the singly central atom, which is completely within the cell, there are 2 atoms fully inside a BCC cell.

- To determine the radius of an atom, we imagine expanding the atoms spherically outward until atoms just touch each other. The first contact occurs between a vertex atom and the center atom a quarter of the way along the main diagonal

connecting two opposite vertices. The length of the main diagonal is $d = \sqrt{3}a$, and the radius of an atom is thus

$$r = \frac{d}{4} = \frac{a\sqrt{3}}{4}.$$

The corresponding volume of an atom is

$$V_{\text{atom}} = \frac{4\pi}{3}\left(\frac{a\sqrt{3}}{4}\right)^3 = \frac{\pi\sqrt{3}}{16}a^3.$$

As before, the volume of a primitive cell is $V_{\text{cell}} = a^3$.

- Using Equation 1.1 and the just-derived atomic volume, the packing factor is thus

$$\eta_{\text{BCC}} = \frac{\left(8 \cdot \frac{1}{8} + 1\right) \cdot V_{\text{atom}}}{V_{\text{cell}}} = \frac{2}{a^3}\frac{\pi\sqrt{3}}{16}a^3 = \frac{\pi\sqrt{3}}{8}.$$

1.1.3 Face Centered Cubic

A face-centered cubic structure is shown in the figure to the right. A face-centered cubic structure...

- is abbreviated FCC.

- is similar to the SC structure, with eight atoms at each cell vertex, but with an additional six atoms in the center of each of the cell's six faces.
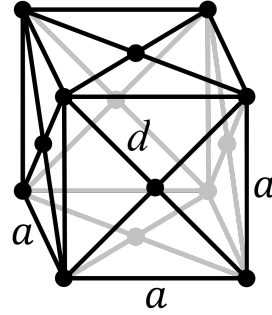
- Like in the SC and FCC structures, each of the eight vertex atoms is shared by eight cells, making for a total of $8 \cdot \left(\frac{1}{8}\right) = 1$ vertex atoms in a given FCC cell. Meanwhile, the six face-centered atoms are equally shared by only two cells, making for a net total of $6 \cdot \frac{1}{2} = 3$ face-centered atoms in a given FCC cell.

- To find the radius of a sphere, we again imagine expanding out the atoms until they just begin to touch each other. The first contact point occurs between a vertex and face-centered atom a quarter of the way along the face diagonal. The length of the face diagonal is $d = \sqrt{2}a$, and the radius of an atom is thus

$$r = \frac{d}{4} = \frac{a\sqrt{2}}{4}.$$

The corresponding volume of an atom is

$$V_{\text{atom}} = \frac{4\pi}{3}\left(\frac{a\sqrt{2}}{4}\right)^3 = \frac{\pi\sqrt{2}}{24}a^3.$$

As before, the volume of a primitive cell is $V_{\text{cell}} = a^3$.

- Using Equation 1.1 and the just-derived atomic volume, the packing factor is

$$\eta_{\text{FCC}} = \frac{\left(8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2}\right) \cdot V_{\text{atom}}}{V_{\text{cell}}} = \frac{4}{a^3}\frac{\pi\sqrt{2}}{24}a^3 = \frac{\pi\sqrt{2}}{6}.$$

1.1.4 Diamond Cubic

- A diamond cubic structure is so tightly packed with atoms that I have not included a diagram, which would be too crowded to be particularly insightful. Instead, we imagine a diamond cubic structure as follows:

  > Imagine two FCC primitive cells exactly superimposed on each other, then shift one cell relative to the other a quarter of the way along the main body diagonal. The result is a diamond cubic cell.

- Instead of finding the total number of atoms in a given cell geometrically, we use a slight trick: take the net number of atoms in a FCC cell, i.e. $N_{\text{FCC}} = 8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{2} = 4$, and double it. The result is $N_{\text{diamond}} = 4 + 4 = 8$.

- And for the radius of an atom in a diamond cubic cell: the shortest distance is between two atoms is one eighth of the body diagonal $d = \sqrt{3}a$. The radius is thus

$$r = \frac{d}{8} = \frac{a\sqrt{3}}{8},$$

  and the corresponding volume is

$$V_{\text{atom}} = \frac{4\pi}{3}\left(\frac{a\sqrt{3}}{8}\right)^3 = \frac{\pi\sqrt{3}}{128}a^3.$$

  As for any cubic cell, the cell volume is $V_{\text{cell}} = a^3$.

- Using Equation 1.1 and the just-derived atomic volume, the packing factor is

$$\eta_{\text{diamond}} = \frac{(4+4) \cdot V_{\text{atom}}}{V_{\text{cell}}} = \frac{8}{a^3}\frac{\pi\sqrt{3}}{128}a^3 = \frac{\pi\sqrt{3}}{16}.$$

1.1.5 Regular Hexagonal

A regular hexagonal structure is shown in the figure to the right. This structure can be equivalently interpretted with either

- a rhombohedral lattice system (in black), with layers vertically separated by the distance c, or

- a hexagonal lattice system (in grey), with layers vertically separated by the same distance c.
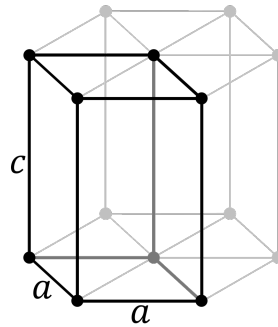
- We will work with a rhomboid lattice system. There are 8 atoms in a given cell— four in the bottom and four in the top plane. The radius of an atom in any given layer is $a/2$. The vertical spacing c must be such that atoms in successive layers just touch, and is thus $c = a$.

- How much of a sphere is shared by other cells? The atoms at 120° vertices contribute twice as much volume to a cell as the toms at 60° vertices. But the net effect is the same as if all vertices were 90°—just like for a simple cubic structure. As a result, on average 1/8 of a single atom occupies a given cell, for a net total of $8 \cdot \frac{1}{8} = 1$ atom in a primitive cell.

- The volume of an atom, which is just a sphere of radius $a/2$, is

$$V_{\text{atom}} = \frac{4\pi}{3}\left(\frac{a}{2}\right)^3 = \frac{\pi}{6}a^3.$$

The volume of a cell, found by multiplying the rhombic area $\frac{a^2\sqrt{3}}{2}$ by the known height $c = a$, is

$$V_{\text{cell}} = \frac{a^2\sqrt{3}}{2} \cdot a = \frac{a^3\sqrt{3}}{2}.$$

- The corresponding packing factor, using the just derived atomic and cell volumes, is

$$\eta_{\text{hexagonal}} = \frac{\left(8 \cdot \frac{1}{8}\right) \cdot V_{\text{atom}}}{V_{\text{cell}}} = \frac{\pi a^3}{6} \cdot \frac{2}{a^3\sqrt{3}} = \frac{\pi\sqrt{3}}{9}.$$

1.1.6 Hexagonal Close Packed

A hexagonal close-packed (HCP) structure is shown in the figure to the right. This structure can be viewed as

- a regular hexagonal structure (with atoms in the top layer shown in black), as in the previous problem...

- with an additional three atoms in the "gaps" between the top and bottom layers.
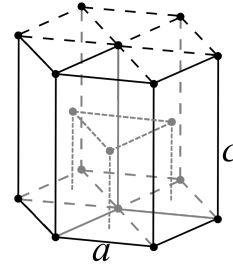
- As for a regular hexagonal structure, the radius of a given atom is $a/2$, and the corresponding atomic volume is

$$V_{\text{atom}} = \frac{4\pi}{3}\left(\frac{a}{2}\right)^3 = \frac{\pi}{6}a^3.$$

To determine the cell height c, we first consider a triangle in one layer and the atom in the center of the triangle in the intermediate layer above. The result is a regular tetrahedron with side length a and height

$$h_{\text{tetrahedron}} = a\sqrt{\frac{2}{3}}.$$

The height of the entire cell is then twice the tetrahedron height, so $c = 2a\sqrt{\frac{2}{3}}$.

The volume of a cell, found by multiplying the rhombic area $\frac{a^2\sqrt{3}}{2}$ by the height c, is

$$V_{\text{cell}} = \frac{a^2\sqrt{3}}{2} \cdot \left(2a\sqrt{\frac{2}{3}}\right) = \sqrt{2}a^3.$$

- A single rhombohedral cell contains 8 vertex atoms, each occupying one-eighth of the given cell, along with one entire atom in the center. There are thus $8 \cdot \frac{1}{8} + 1 = 2$ net atoms in a given HCP cell. The HCP packing factor is thus

$$\eta = \frac{(8 \cdot \frac{1}{8} + 1) \cdot V_{\text{atom}}}{V_{\text{cell}}} = 2 \cdot \frac{\pi a^3}{6} \cdot \frac{1}{\sqrt{2}a^3} = \frac{\pi\sqrt{2}}{6}.$$

Note that this is the same packing factor as a FCC cell. Without proof, this is in fact the maximum possible packing factor for primitive cell with spherical building blocks.

2 Second Exercise Set

2.1 Close Packed Crystal Structures

2.1.1 Theory: Hexagonal Close-Packed Structures

- Begin by considering a two-dimensional Bravais hexagaonal (triangular) lattice in the xy plane. We then generalize this hexagonal lattice to three dimensions by stacking multiple 2D hexagonal layer directly above the the other. Formally, we might say that all layers have identical projections onto the xy plane. This resulting structure is called a *simple hexagonal* lattice.

- We need to introduce some terminology before moving to more complicated structures. Namely, the empty region between spheres in a 2D hexagonal lattice is called a *trigonal gap*. **TODO:** figure. The trigonal gaps are centered at the centroids of the equilateral triangles formed by the hexagonal lattice points.

- Having defined the trigonal gap, we can construct a *hexagonal close-packed* lattice by beginning with a 2D hexagonal lattice, which we'll call layer A, and stacking a second 2D hexagonal lattice (layer B) on top of layer A such that the lattice points of layer B align with the trigonal gaps in layer A. If we then repeat the pattern, i.e. stacking a layer of type A above layer B, then adding B onto layer A, and so on, the resulting $ABABAB...$ structure is a hexagonal close-packed (HCP) lattice.

- Once again, we need some terminology before defining the next lattice structure. Consider a two-layer AB lattice from above. The trigonal gaps in layer B positioned directly above lattice points in layer A are called *tetrahedral gaps*, while the trigonal gaps in layer B positioned directly above trigonal gaps in layer A are called *octahedral gaps*. Note that in the $ABABAB$ structure, the lattice points in the A layers align with the tetrahedral gaps in the B layers.

- Having defined tetrahedral and octahedral gaps, we can now construct a *cubic close-packed* lattice, which we will later show is equivalent to a FCC lattice. We begin with a single 2D hexagonal lattice (layer A), stack a second 2D hexagonal lattice (layer B) such that the lattice points in B align with the trigonal gaps in A, then stack a third 2D hexagonal lattice (layer C) such that the lattice points in C align with the octahedral[1] gaps in layer B. When repeated, the resulting $ABCABCABC...$ structure forms a cubic close-packed lattice.

- In general, any lattice consisting of vertically superposed 2D hexagonal layers such that lattice points in one layer align with the trigonal gaps (either of the tetrahedral or octahedral type) in the previous layer is called a close-packed lattice. The only restriction is that a given layer cannot repeat the layer directly below it.

- Note that showing FCC is equivalent to ABC will help explain why

$$\eta_{\text{FCC}} = \eta_{\text{HCP}}$$

from the previous exercise.

---

[1]Note that placing C in the tetrahedral gaps of layer B would result in an $ABABAB$ structure.

2.1.2 Hexagonal Close-Packed (ABABAB)

- We begin by considering a 2D hexagonal lattice as layer A, and define a Cartesian coordinate system in which the xy plane is parallel to the lattice planes, while the z axis is normal to the lattice. We will describe the 2D lattice in terms of the lattice constant a and the primitive vectors

$$\boldsymbol{a}_1 = (a, 0, 0) \qquad \boldsymbol{a}_2 = \left(\tfrac{a}{2}, \tfrac{a\sqrt{3}}{2}, 0\right).$$

  Note that the two primitive vectors define an equilateral triangle with side length a, as expected for a 2D hexagonal lattice.

- We construct the next layer in the lattice, layer B, by stacking a second 2D hexagonal lattice such that the lattice points in the second lattice align with the trigonal gaps in layer A.

  Any three neightboring atoms arranged in an equilateral triangle in layer A, together with the atom in layer B directly above the triangle's centroid, form a regular tetrahedron.

  The height of the layer B atom above layer A is simply the height of a regular tetrahedron with side length a, which, from e.g. introductory geometry, is

$$h_{\text{tetrahedron}} = a\sqrt{\frac{2}{3}}. \tag{2.1}$$

  For our choice of origin (TODO picture), the position vector of the the layer B atom at the top of the aforementioned tehtrahedron is thus

$$\boldsymbol{r}_{\text{top}} = \left(\tfrac{a}{2}, \tfrac{a\sqrt{3}}{6}, a\sqrt{\tfrac{2}{3}}\right)$$

  Note the (x, y) position is the equilateral triangle's centroid.

- We already know the primitive vectors a_1 and a_2; our next step is to find a primitive vector $\boldsymbol{a}_3$ with which we can completely describe the 3D HCP lattice.

  Perhaps the first, most obvious choise, is simply $\boldsymbol{a}_3 = \boldsymbol{r}_{\text{top}}$, i.e. the position of the layer B atom at the top of the regular tetrahedron.

  It turns out $\boldsymbol{r}_{\text{top}}$ is not a valid choice for $\boldsymbol{a}_3$, since we cannot encode the position of every atom in the HCP lattice with the linear combination

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

  For example, using $\boldsymbol{a}_3 = \boldsymbol{r}_{\text{top}}$ and choosing $n_1 = n_2 = 0$ and $n_3 = 2$ would predict an atom at the position $\boldsymbol{R} = 2\boldsymbol{a}_3 = 2\boldsymbol{r}_{\text{top}}$. But $2\boldsymbol{r}_{\text{top}}$ corresponds to the position of a layer C atom from the $ABCABC$ cubic close-packed structure, not to the HCP $ABABAB$ structure.

- Instead, we choose the third HCP primitive vector $\boldsymbol{a}_3$ to be the position of the atom directly above the origin. An atom in layer A, but one level above the layer A containing the origin. This vertical position is simply twice the height between layers, i.e. twice the tetrahedron height in Equation 2.1, and the vector $\boldsymbol{a}_3$ is thus

$$\boldsymbol{a}_3 = \left(0, 0, 2a\sqrt{\tfrac{2}{3}}\right).$$

- Note, however, that the primitive vectors $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ do note completely encode the the HCP lattice; in fact, the $\boldsymbol{a}_i$ represent only atoms in layers of type A, since only those atoms can be reached with a linear combination of the $\boldsymbol{a}_i$. As such, the HCP lattice is not a Bravais lattice.

- To represent all atoms in the HCP lattice, including those in layers of type B, we introduce two additional *basis vectors*

$$\boldsymbol{d}_1 = (0, 0, 0) \qquad \text{and} \qquad \boldsymbol{d}_2 = \left(\tfrac{a}{2}, \tfrac{a\sqrt{3}}{6}, a\sqrt{\tfrac{2}{3}} \right).$$

The first vector represents atoms in layer A and is thus zero, while the second vector represents atoms in layer B. We can then describe the position of every atom in the entire HCP $ABAB$ lattice with the linear combination

$$\boldsymbol{R} = n_1 \boldsymbol{a}_1 + n_2 \boldsymbol{a}_2 + n_3 \boldsymbol{a}_3 + \sum_k \boldsymbol{r}_k.$$

In other words, we take $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$, which form a simple hexagonal Bravais lattice (layer A), and add the basis vectors $\boldsymbol{d}_1$ and $\boldsymbol{d}_2$ to represent the B layer atoms. Together, the simple hexagonal Bravais lattice and the basis form an HCP lattice.

2.1.3 Cubic Close-Packed (ABCABC)

- As for the hexagonal close-packed $ABAB$ lattice, we begin with a 2D hexagonal lattice, described by the primitive vectors

$$\boldsymbol{a}_1 = (a, 0, 0) \qquad \text{and} \qquad \boldsymbol{a}_2 = \left(\tfrac{a}{2}, \tfrac{\sqrt{3}}{2}a, 0 \right).$$

As above, it remains to find the primitive vector $\boldsymbol{a}_3$ with which to fully encode the cubic close-packed $ABCABC$ lattice. We will first quote the correct result, and then prove it; the correct $\boldsymbol{a}_3$ reads

$$\boldsymbol{a}_3 = \left(\tfrac{a}{2}, \tfrac{\sqrt{3}}{6}a, \sqrt{\tfrac{2}{3}}a \right).$$

For this choice of $\boldsymbol{a}_3$,

- the atom at $\boldsymbol{R} = 0 \cdot \boldsymbol{a}_3$ lies at the origin in layer A,
- the atom at $\boldsymbol{R} = 1 \cdot \boldsymbol{a}_3$ lies in layer B,
- the atom at $\boldsymbol{R} = 2\boldsymbol{a}_3$ lies in layer C, and
- the atom at $\boldsymbol{R} = 3\boldsymbol{a}_3$ is again in layer A.

Since we can reach all layers with only the primitive vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$, the cubic close-packed $ABCABC$ is a Bravais lattice, and we do not need a basis.

Equivalence of Cubic Close-Packed and FCC

- The cubic close-packed lattice spanned by the above $\boldsymbol{a}_1, \boldsymbol{a}_2$ and $\boldsymbol{a}_3$ is equivalent to a FCC lattice. To show this, we begin by showing the three CCP primitive vectors are equally long, i.e.

$$|\boldsymbol{a}_1| = |\boldsymbol{a}_2| = |\boldsymbol{a}_3| = a.$$

Interpretted geometrically, the primitive vectors' equal length means the atoms in any given *A*, *B* or *C* layer are arranged in equilateral triangles, while any three triangularly spaced atoms in one layer and the atom in the next layer above the triangle's centroid form a regular tetrahedron. Because of this tetrahedron structure, the angle between all CCP vectors is equal, i.e.

$$\measuredangle(\boldsymbol{a}_i, \boldsymbol{a}_j) = 60°, \qquad i \neq j.$$

Our goal is to show that the primitive vectors in a FCC lattice obey the same angular relationship, i.e. that $\measuredangle(\boldsymbol{a}_i, \boldsymbol{a}_j) = 60°$ for *both* FCC and CCP structures. We will use that result as proof that the FCC and CCP (*ABCABC*) lattices are equivelent.

- We thus consider the FCC lattice, (see the unit cell in *figs2/2-FCC-ABC-equivalence*), for which the primitive vector read

$$\boldsymbol{a}_1 = \tfrac{a}{2}(1,1,0) \qquad \boldsymbol{a}_2 = \tfrac{a}{2}(1,0,1) \qquad \boldsymbol{a}_3 = \tfrac{a}{2}(0,1,1). \tag{2.2}$$

Without rigorous proof, we note that all lattice points in the FCC lattice can be constructed from a linear combination of these $\boldsymbol{a}_i$, which ensures that these vectors are the correct choice for a FCC lattice.

- Next, we note that the FCC primitive vectors have equal magnitude:

$$|\boldsymbol{a}_1| = |\boldsymbol{a}_2| = |\boldsymbol{a}_3| = \frac{a}{\sqrt{2}}.$$

With these magnitudes known, we can then show that the angle α between all FCC primitive vectors is equal to 60°, just like for the CCP lattice. For example, for the FCC $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$, we have

$$\cos\alpha = \frac{\boldsymbol{a}_1 \cdot \boldsymbol{a}_2}{|\boldsymbol{a}_1||\boldsymbol{a}_2|} = \frac{a^2}{4} \cdot \frac{2}{a^2} = \frac{1}{2} \implies \alpha = 60°$$

A similar calculation for the other $\boldsymbol{a}_i$ gives the same result $\alpha = 60°$, although we could reach this conclusion on grounds of cubic symmetry alone.

- Since the angle between the primitive vectors is 60° degrees for both the FCC and ABC HCP lattices, we conclude that the two lattices are geometrically equivalent. Note that the magnitudes of the FCC and CCP $\boldsymbol{a}_i$ being different is not a problem; the important thing is the side lengths having the same ratios and angles between them in both structures.

2.2   Symmetry Group of a Cubic Lattice

Find all symmetry operations that map a cubic lattice back into itself. After identifying the operators, show the operations form a group.

Symmetry operations mapping a cubic unit cell back into itself are:

1. Rotation by an angle $n\pi/2$, $n \in \mathbb{N}$, about a four-fold axis through any two opposite face centers. The axis is called a four-fold axis, since four rotations of $\pi/2$ map the cell into its original orientation.

A cubic cell has 6 faces, and thus 3 four-fold axes, one for each pair of opposite faces.

As a side note, a four-fold axis is denoted by C_4, while two repeated four-fold axis rotations would be written C_4^2. A rotation of C_4^4, i.e. rotation by 2π, maps the unit cell into its original orientation, and thus corresponds the unit operation.

2. Rotation by an angle $n\pi/3$ about a three-fold axis along the main body diagonal connecting two opposite vertices.

   A cubic cell has four C_3 axes, one for each of the cube's four main diagonals.

3. Rotation by an angle π about a two-fold diagonal axis connecting the midpoints of two opposite edges (see *figs2/3-rotations*).

   A cube has 12 diagonally opposite edges, and thus $12/2 = 6$, two-fold axes, one for each pair of opposite edges.

- Since multiple rotations about a given axis are also valid symmetry operations, the complete set of rotation axes for a cubic cell is

$$C_4, C_4^2, C_4^3 \qquad C_3, C_3^2 \qquad C_2 \qquad E,$$

where E is the unit operation. After accounting for the fact that a cubic cell contains multiple instances of a given axis, the total number of rotation axes is

$$\underbrace{3 \cdot 3}_{C4} + \underbrace{4 \cdot 2}_{C3} + \underbrace{6 \cdot 1}_{C2} + 1 = 24.$$

The accounting reads: three four-fold axes, each of which can be any of the three C_4, C_4^2 or C_4^3, four three-fold axies, each of which can be any of the two C_3 or C_3^2, and six two-fold axes, each of which can be only C_2, and the unit operation.

- Next, we consider space inversion about the cube's center, denoted by I. The space inversion operator switches of positions of opposite vertices long the body diagonal—for example a rear, bottom, right vertex maps into a front, top, left vertex after space inversion. These details aren't strictly necessary for our problem, though; all we need to know is that the combination of any of the above 24 proper rotations with space inversion I generates a pseudorotation, which is just the product of a proper rotation an space inversion. The result is a further 24 symmetry operations, for a total of

$$N_\text{tot} = N_\text{rotation} + N_\text{pseudo-rotation} = 24 + 24 = 48$$

symmetry operations mapping a cubic lattice into itself.

- As a side note, reflections about a plane can be interpretted as combinations of pseudorotations—thus reflections are not independent transformations, and do not add to the count of 48 cubic cell symmetry transformations.

Groups

- We will only qualitatively sketch that the above 48 cubic symmetry operations form a group, by reviewing each of a general group's required properties in turn. For review, a group is a set of elements $\{A, B, C, \ldots\}$, together with a product $\cdot$, for which the following properties hold.

1. There exists an identity element E for which $E \cdot X = X = X \cdot E$ for all X in the group.

2. The group is associative, i.e. $(X \cdot Y) \cdot Z = X(Y \cdot Z)$ for all X, Y, Z in the group.

3. The group obeys the closure property, i.e. for all X and Y in the group, the product $X \cdot Y$ is also an element of the group.

4. The every element X, the inverse element X^{-1} is also an element of the group.

- First, we note that our group contains an identity element E. Formally, the identity element must satisfy $EA = A = AE$ for all elements A in the group. Physically, E simply represents the operation returning the cube to its exact original orientation. We could in interpret this in multiply ways, for instance twice-applied space inversion, $E = I^2$, or four rotations about a C_4 axis, i.e. $E = C_4^4$.

- Our (sketched) proof of associativity takes three steps: first, we note that every element of our group is either a rotation, a pseudorotation, or the unit operation. Second, we note that each of these operations, at least in three-dimensional space, can be written as a 3×3 matrix. Finally, we argue that since matrix multiplication is associative, then $(AB)C = A(BC)$ must hold for all elements of our group.

- We simply quote the close property, although we do give a single concrete example. Namely, a C_2 rotation is equivalent to C_4 rotation followed by a C_3 rotation. We gave a nice visual proof in class, but giving an equivalent explanation in words is hopeless, and I simply quote the result on faith.

- We also simply quote the general existance of an inverse for every element in the group, although we do give two concrete examples: space inversion I is a trivial example, since $I^{-1} = I$. For rotations, for example, we have $(C_4)^{-1} = C_4^3$. However, we simply quote the existence of an inverse for the other transformations, without derivation.

- Having, at least to some extent, shown the existence of an identity element, the associative, and closure properties; and stated the fact that the product of any two cubic symmetry operations is again a cubic symmetry operation, we can conclude that the 48 cubic symmetry operations form a group.

- Finally, we note that the group is not commutative, i.e. the equality $AB = BA$ does not hold for all A and B in the group. For example, a $C_4 C_3 \neq C_3 C_4$. As a result, the 48 cubic symmetries do not form an Abelian group.

2.3 Theory: The Wigner-Seitz Primitive Unit Cell

We have two standard choices for generating a primitive unit cell from a given set of primitive vectors $\boldsymbol{a}_i$.

- The first option is the parallelepiped spanned by the three primitive vectors. While the resulting cell is a primitive unit cell, this construction does not preserve the symmetry of the underlying BCC cubic lattice. In other words, the paralleliped is not invariant under the 48 symmetry operations associated with a BCC cubic lattice, which we discussed in the previos exercise.

- The second option is called a Wigner-Seitz cell, and is constructed in such a way that the unit cell preserves the symmetry of the entire lattice.

- A Wigner-Seitz cell is constructed as follows:

  1. Choose any lattice site in the lattice to be the origin; this will also be the center of the Wigner-Seitz cell.

  2. Draw lines connecting the central lattice point to each of its nearest neighbors, i.e. those lattice sites that are closer to the origin than to any other lattice point.

  3. For each of these lines, draw the plane normal to the line bisecting the line at its midpoint. The resulting three-dimensional body surrounding the origin and enclosed by these bisecting planes is the Wigner-Seitz primitive cell.

2.4   TODO: Wigner-Seitz Cell for a BCC Structure

- We begin by drawing a cubic BCC unit cell, which we will describe with the primitive vectors

$$\boldsymbol{a}_1 = (a, 0, 0) \qquad \boldsymbol{a}_2 = (0, a, 0) \qquad \boldsymbol{a}_3 = \frac{a}{2}(1, 1, 1). \tag{2.3}$$

Note that this unit cell is not a primitive cell—it contains a net total of two atoms and is not the smallest cell that can periodically span an entire BCC lattice. Our goal in this exercise is to find the corresponding BCC Wigner-Seitz cell.

TODO: figure.

- We begin by finding the bisecting plane for the line connecting the origin lattice point at $\boldsymbol{R} = (0, 0, 0)$ to the origin's nearest neighbor at the point $\boldsymbol{R} = (a, 0, 0)$. The halfway point on the line is at $(a/2, 0, 0)$, the equation of the bisecting plane is simply

$$x = \frac{a}{2}.$$

- Next, we consider the bisecting plane for the points $(0, 0, 0)$ and $\frac{a}{2}(1, 1, 1)$, which is the atom at the center of the cubic unit cell.

  The direction of this line, and thus the normal $\hat{\mathbf{n}}$ to the perpendicularly-bisecting plane, is

$$\hat{\mathbf{n}} = \frac{1}{\sqrt{3}}(1, 1, 1),$$

which is just the normalized vector pointing from the origin to the body-centered atom.

  The distance d from the origin to the line's midpoint, which occurs a quarter of the way along the cubic cell's main body diagonal, is

$$d = \frac{a\sqrt{3}}{4}.$$

  Equation of a plane take normal $\hat{\mathbf{n}}$ and then vector in the plane $\boldsymbol{r}$ and this should equal

$$\hat{\mathbf{n}} \cdot \boldsymbol{r} = d \implies \frac{1}{\sqrt{3}}(1, 1, 1) \cdot (x, y, z) = \frac{a\sqrt{3}}{4}.$$

The equation of the bisecting plane, after rearranging, is thus

$$x + y + z = \frac{3}{4}a.$$

- Next from the origin to the point $\frac{a}{2}(1, -1, 1)$. The direction of the connecting line is

$$\hat{\mathbf{n}} = \frac{1}{\sqrt{3}}(1, -1, 1).$$

The distance to the origin is again

$$d = \frac{a\sqrt{3}}{4},$$

and the equation of the perpendicularly-bisecting plane is

$$\hat{\mathbf{n}} \cdot \boldsymbol{r} = d \implies \frac{1}{\sqrt{3}}(1, -1, 1) \cdot (x, y, z) = \frac{a\sqrt{3}}{4}$$

Or, after rearranging,

$$x - y + z = \frac{3}{4}a.$$

- Although we have only found the equations of three bisecting planes, we will be able to leverage the BCC lattice's cubic symmetry to deduce the Wigner-Seitz cell from these three planes alone. In one plane, the three planes are given by

$$x = \frac{a}{2} \qquad x + y + z = \frac{3}{4}a \qquad x - y + z = \frac{3}{4}a$$

These planes correspond to the lines from the origin to the three circled points in the figure *WS-BCC-three-planes*. The intersection of any two planes will be the edge of a Wigner-Seitz cell, while the intersection of three planes will be the vertex of a Wigner-Seitz cell.

- We begin with the first and second planes; their equations read

$$x = \frac{a}{2} \qquad \text{and} \qquad x + y + z = \frac{3}{4}a,$$

and their intersection occurs along the line $y + z = \frac{a}{4}$, drawn in red in the figure *plus-plane*. Note also that the plane $x = \frac{a}{2}$ coincides with the plane marked by a plus in *plus-plane*.

- We then consider the first and second planes, i.e.

$$x = \frac{a}{2} \qquad \text{and} \qquad x - y + z = \frac{3}{4}a,$$

whose intersection occurs along the line $-y + z = \frac{a}{4}$, which is shown in pink in *plus-plane*. Keep in mind that, geometrically, these lines define the edges of the BCC Wigner-Seitz cell.

- Finally, we consider the second and third plane equations, i.e.

$$x + y + z = \frac{3}{4}a \qquad \text{and} \qquad x - y + z = \frac{3}{4}a,$$

  whose intersection lies along the line.

$$x + z = \frac{3}{4}a$$

  This line is shown in orange in the figure *line-orange*. The other two orange lines in the same figure arise for reasons of symmetry.

- We then consider the intersection of the two edge lines $y + z = \frac{a}{4}$ and $-y + z = \frac{a}{4}$, which occurs at

$$(x, y, z) = \left(\frac{a}{2}, 0, \frac{a}{4}\right).$$

  The coordinate $x = a/2$ is known because the lines lie in the plane $x = a/2$, as shown in *plus-plane*. So far, we have found two edges and a single vertex of the BCC Wigner-Seitz cell. In fact, because of the BCC lattice's cubic symmetry, this information is enough to determine the entire Wigner-Seitz cell.

  Unfortunately, the explanation we gave is visual, with the help of three-dimensional figures, and I see no intuitive way to transfer it into words alone.

  The dark dots in figure *points* must be the positions of other Wigner-Seitz cell vertices. These vertices must in turn be connected by the green diagonal lines in the same figure. More so, these same vertices and lines must occur on all other cube faces, as also shown in *points*.

  The three orange lines in *line-orange*, together with the green lines connecting the Wigner-Seitz vertices, form a regular hexagon. This regular hexagon is one face of the Wigner-Seitz cell.

  The entire Wigner-Seitz cell is then formed of a combination of hexagonal and square faces, shown in the figure *BCC-WS*. The three-dimensional body enclosed by these faces is called a truncated octahedron, and is the desired Wigner-Seitz cell for a BCC lattice.

  Without proof, appealing only to geometric intuition, we note that this truncated octahedron preserves all of the BCC lattice's symmetries.

3 Third Exercise Set

3.1 Theory: Classifying Bravais Lattices

This is not really an exercise, but more a theoretical discussion, and couldy reasonably be skipped without serious loss of continuity.

So far, we have discussed three types of cubic Bravais lattices—SC, BCC and FCC. It turns out that fourteen unique Bravais lattices exist in three dimensions. Our goal here is to give an overview of what these lattices are, and to discuss which geometric properties are used to classify a Bravais lattice.

Orthorhombic Lattices

- We begin with orthorhombic lattices. Unit cells in the orthorhombic family are cuboids with three different edge lengths $a \neq b \neq c$, while the angle between all edges is $\pi/2$. There are four unique orthorhombic lattices. These are:

  1. Normal (regular?). Like simple cubic, just not a cube—lattice sites only at the vertices.

  2. Then analogs of BCC and FCC—two more. These are just generalizations of cubic structures, with allowance for different side lengths.

  3. The last one—this one is new—a lattice with a centered base. Start with a simple OR, then add opposite face points in each top and bottom base (base centered).

Tetragonal Lattices

- Unit cells in the tetragonal family are cuboids with two equal side lengths: $a = b \neq c$ and an angle $\pi/2$ between all edges.

- Because of the additional property of two equal side lengths, which introduces an additional four-fold rotation axis passing through the two opposite faces with equal side lengths, a tetragonal lattice is more symmetric than an orthorhombic lattice.

- There are two types of tetragonal lattices:

  1. a regular tetragonal lattice, and

  2. a body-centered tetragonal lattice.

- Note that the primitive cell for a base-centered tetragonal lattice is a regular tetragonal with smaller side lengths $a/\sqrt{2}$ rotated by 45° in the a, a plane. Similarly, the primitive cell for a face-centered tetragonal lattice is a body-centered tetragonal lattice. As a result, there are only two types of tetragonal lattice, regular and body-centered, since the more complex base-centered and face-centered flavors can simply be constructed from regular and body-centered primitive cells.

Cubic

- We won't repeat all of them. We consider only the new version—the base-centered cubic.

  As before, we end up with a tetragonal primitive cell with the equal sides as $a/\sqrt{2}$ and $a/\sqrt{2}$ and height a.

- Note, however, that the defining charateristic of cubic lattices is their invariance under symmetries in the cubic group from previous exercise.

- As an example, the base-centered cubic—not the primitive cell, isn't invariant under 120° rotation about the main body diagonal.

  Ahah: the lesson is we could have shown this by showing the primitive cell is not cubic, so base-centered cubic is not cubic. It is tetragonal. But we didn't even need to do that, we could just make the symmetry argument and use the important definition that symmetry is the definiing characteristic of a group of Bravais lattice.

Triclinic Lattices

- The primitive cell of a triclinic lattice is a generic paraellelpipded with arbitrary side lengths $a \neq b \neq c$, and arbiatrary angles $\alpha \neq \beta \neq \gamma$ between the primitive vectors.

- There is only a single triclinic Bravais lattice.

- Note for a face-centered triclinic cells, if we look at *triclinic-red* and look at the red basis vectors, we end up with an identical regular triclinic cell, with the same properties of $a \neq b \neq c$ and $\alpha \neq \beta \neq \gamma$. And so we only need a regular triclinic to encode a face-centred triclinic.

  Same argument for body-centered triclinic. Lesson: we only need a single triclinic primitive cell to describe all triclinic structures—the regular triclinic.

3.2   Theory: The Reciprocal Lattice

- The reciprocal lattice, whose lattice positions are denoted by $\boldsymbol{K}$ (units length^{-1}), is formed of all reciprocal lattice positions $\boldsymbol{K}$ satisfying the implicit requirement that
$$e^{i\boldsymbol{K}\cdot\boldsymbol{R}} = 1$$
  for all lattice site positions $\boldsymbol{R}$ in the Bravais lattice.

- A three-dimensional reciprocal lattice is spanned by the three reciprocal primitive vectors $\boldsymbol{A}_1$, $\boldsymbol{A}_2$ and $\boldsymbol{A}_3$. In other words, all reciprocal lattice positions $\boldsymbol{K}$ can be written as the linear combination
$$\boldsymbol{K} = m_1\boldsymbol{A}_1 + m_2\boldsymbol{A}_2 + m_3\boldsymbol{A}_3, \qquad m_i \in \mathbb{N}.$$

- The primitive vectors $\boldsymbol{a}_i$ and reciprocal primitive vectors $\boldsymbol{A}_j$ obey the relationship
$$\boldsymbol{a}_i \cdot \boldsymbol{A}_j = 2\pi\delta_{ij}.$$

- Given primitive vectors $\boldsymbol{a}_i$, we find the corresponding reciprocal primitive vectors $\boldsymbol{A}_i$ according to
$$\boldsymbol{A}_1 = 2\pi\frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)} \qquad \boldsymbol{A}_2 = 2\pi\frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)} \qquad \boldsymbol{A}_3 = 2\pi\frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)}, \quad (3.1)$$
  where $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3) = \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)$ denotes the scalar triple product. Geometrically, $(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)$ is just the volume of a primitive unit cell.

3.3   The BCC and FCC Reciprocal Lattices

Find the reciprocal lattice of the simple cubic, body-centered cubic, and face-centered cubic Bravais lattices, and identify the resulting lattice structures in reciprocal space.

3.3.1   The SC Reciprocal Lattice

- We begin with the simple cubic primitive vectors, which read

$$\boldsymbol{a}_1 = a(1,0,0) \qquad \boldsymbol{a}_2 = a(0,1,0) \qquad \boldsymbol{a}_3 = a(0,0,1). \tag{3.2}$$

The corresponding primitive cell volume is

$$V_0 = |\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = a^3|(1,0,0)\cdot(1,0,0)| = a^3.$$

- Using Equation 3.1 with the above $\boldsymbol{a}_i$, the SC reciprocal primitive vectors are

$$\boldsymbol{A}_1 = 2\pi\frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{V_0} = 2\pi\frac{a^2\cdot(1,0,0)}{a^3} = \frac{2\pi}{a}(1,0,0)$$

$$\boldsymbol{A}_2 = 2\pi\frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{V_0} = 2\pi\frac{a^2\cdot(0,1,0)}{a^3} = \frac{2\pi}{a}(0,1,0)$$

$$\boldsymbol{A}_3 = 2\pi\frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{V_0} = 2\pi\frac{a^2\cdot(0,0,1)}{a^3} = \frac{2\pi}{a}(0,0,1)$$

By comparison to Equation 3.2, the simple cubic reciprocal primitive vectors $\boldsymbol{A}_i$ again form a simple cubic lattice in reciprocal space, with lattice constant $2\pi/a$.

3.3.2   The BCC Reciprocal Lattice

- Previously, e.g. in Equation 2.3, we defined a BCC lattice with the primitive vectors

$$\boldsymbol{a}_1 = a(1,0,0) \qquad \boldsymbol{a}_2 = a(0,1,0) \qquad \boldsymbol{a}_3 = \frac{a}{2}(1,1,1).$$

A more symmetric choice, which we will use in this problem, is

$$\boldsymbol{a}_1 = \frac{a}{2}(-1,1,1) \qquad \boldsymbol{a}_2 = \frac{a}{2}(1,-1,1) \qquad \boldsymbol{a}_3 = \frac{a}{2}(1,1,-1). \tag{3.3}$$

- In class we then briefly showed, with the help of a figure (see *bcc*), that we can reach any point in the BCC lattice with a linear combination of these three primitive vectors. For instance, for the choice of origin in *bcc*, we can reach the body-centered atom with the combination $n_1 = n_2 = n_3 = 1$, i.e.

$$\boldsymbol{R}_{\text{center}} = \boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3 = a\left(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\right).$$

Similarly, we can reach the bottom right lattice point in *bcc* with the combination $n_1 = 0$ and $n_2 = n_3 = 1$ (also shown in *bcc*). The construction of the other points in the BCC unit cell is analogous. This step is not vital for this problem; we simply aim to show that the $\boldsymbol{a}_i$ in Equation 3.3 are well-defined primitive vectors for a FCC lattice.

- Using Equation 3.1 with the above $\boldsymbol{a}_i$, the BCC reciprocal primitive vectors are

$$\boldsymbol{A}_1 = 2\pi \frac{(a^2/2)\cdot(0,1,1)}{(a^3/2)} = \frac{2\pi}{a}(0,1,1)$$
$$\boldsymbol{A}_2 = 2\pi \frac{(a^2/2)\cdot(1,0,1)}{(a^3/2)} = \frac{2\pi}{a}(1,0,1)$$
$$\boldsymbol{A}_3 = 2\pi \frac{(a^2/2)\cdot(1,1,0)}{(a^3/2)} = \frac{2\pi}{a}(1,1,0).$$

Really, we only needed to directly calculate $\boldsymbol{A}_1$—since the $\boldsymbol{a}_i$ are cyclic permutations of $(-1,1,1)$, it follows that $\boldsymbol{A}_2$ and $\boldsymbol{A}_3$ are just cyclic permutations of $\boldsymbol{A}_1$.

- We now aim to identify lattice structure encoded by the reciprocal primitive vectors $\boldsymbol{A}_i$. In one place, the $\boldsymbol{A}_1$ for a BCC lattice are

$$\boldsymbol{A}_1 = \frac{2\pi}{a}(0,1,1) \qquad \boldsymbol{A}_2 = \frac{2\pi}{a}(1,0,1) \qquad \boldsymbol{A}_3 = \frac{2\pi}{a}(1,1,0) \qquad (3.4)$$

Plotting these vectors shows that they form a FCC lattice in reciprocal space—see picture *A-three*. Alternatively, we could just compare the $\boldsymbol{A}_i$ to the known FCC primitive vectors in Equation 2.2, i.e.

$$\boldsymbol{a}_1 = \tfrac{a}{2}(1,1,0) \qquad \boldsymbol{a}_2 = \tfrac{a}{2}(1,0,1) \qquad \boldsymbol{a}_3 = \tfrac{a}{2}(0,1,1).$$

Conclusion: the reciprocal lattice of a BCC lattice is a FCC lattice in reciprocal space with lattice constant $4\pi/a$.

3.3.3   The FCC Reciprocal Lattice

- We begin with the FCC lattice vectors given in Equation 2.2, which for review read

$$\boldsymbol{a}_1 = \tfrac{a}{2}(1,1,0) \qquad \boldsymbol{a}_2 = \tfrac{a}{2}(0,1,1) \qquad \boldsymbol{a}_3 = \tfrac{a}{2}(1,0,1).$$

The corresponding primitive cell volume V_0 is

$$V_0 = |\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = \frac{a^3}{8}|(1,1,0)\cdot(1,1,-1)| = \frac{a^3}{4}.$$

- Using Equation 3.1 with the above $\boldsymbol{a}_i$, the FCC reciprocal primitive vectors are then

$$\boldsymbol{A}_1 = 2\pi \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{V_0} = 2\pi \frac{(a^2/4)\cdot(1,1,-1)}{(a^3/4)} = \frac{2\pi}{a}(1,1,-1)$$
$$\boldsymbol{A}_2 = 2\pi \frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{V_0} = 2\pi \frac{(a^2/4)\cdot(-1,1,1)}{(a^3/4)} = \frac{2\pi}{a}(-1,1,1)$$
$$\boldsymbol{A}_3 = 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{V_0} = 2\pi \frac{(a^2/4)\cdot(1,-1,1)}{(a^3/4)} = \frac{2\pi}{a}(1,-1,1).$$

As for the BCC case above, we only needed to directly calculate $\boldsymbol{A}_1$—since the $\boldsymbol{a}_i$ are just cyclic permutations of $(0,1,1)$, it follows that $\boldsymbol{A}_2$ and $\boldsymbol{A}_3$ are just cyclic permutations of $\boldsymbol{A}_1$.

By comparision to Equation 3.3, we can see that the FCC reciprocal primitive vectors form a BCC lattice in reciprocal space, with lattice constant $4\pi/a$.

3.4 Reciprocal Lattice of Two-Dimensional Triangular Lattice

Find the reciprocal lattice of two-dimensional triangular (or hexagonal) lattice.

- We begin by sketching the two-dimensional triangular lattice, and defining a coordinate system and and primitive vectors. The primitive vectors have equal length and an angle of 60° between them—see *triangular-angles*. These primitive vectors are

$$\boldsymbol{a}_1 = a(1,0) \qquad \text{and} \qquad \boldsymbol{a}_2 = a\left(\tfrac{1}{2}, \tfrac{\sqrt{3}}{2}\right). \tag{3.5}$$

  Next, we note that the procedure for finding the reciprocal primitive vectors $\boldsymbol{A}_j$ used in the previous problem (see Equation 3.1) works only in three dimensions, since the cross product is defined only in 3D.

- Instead, we will find the reciprocal primitive vectors for a two-dimensional lattice using the general definition

$$\boldsymbol{a}_i \cdot \boldsymbol{A}_j = 2\pi \delta_{ij}.$$

  In two dimensions, where $i, j \in \{x, y\}$, this relationship represents four equations. In matrix form, this system of equations reads

$$\begin{pmatrix} a_{1_x} & a_{1_y} \\ a_{2_x} & a_{2_y} \end{pmatrix} \begin{pmatrix} A_{1_x} & A_{2_x} \\ A_{1_y} & A_{2_y} \end{pmatrix} \equiv \begin{pmatrix} \boldsymbol{a}_1^\top \\ \boldsymbol{a}_2^\top \end{pmatrix} \begin{pmatrix} \boldsymbol{A}_1 & \boldsymbol{A}_2 \end{pmatrix} = 2\pi \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 2\pi \mathbf{I},$$

  where $\mathbf{I}$ is the identity matrix. Solving the above equation for $\begin{pmatrix} \boldsymbol{A}_1 & \boldsymbol{A}_2 \end{pmatrix}$ produces

$$\begin{pmatrix} \boldsymbol{A}_1 & \boldsymbol{A}_2 \end{pmatrix} \equiv \begin{pmatrix} A_{1_x} & A_{2_x} \\ A_{1_y} & A_{2_y} \end{pmatrix} = 2\pi \begin{pmatrix} a_{1_x} & a_{1_y} \\ a_{2_x} & a_{2_y} \end{pmatrix}^{-1}.$$

  Finally, substituting the vector components from Equation 3.5 and computing the inverse matrix produces

$$\begin{pmatrix} A_{1_x} & A_{2_x} \\ A_{1_y} & A_{2_y} \end{pmatrix} = 2\pi \begin{pmatrix} a & 0 \\ \tfrac{a}{2} & \tfrac{a\sqrt{3}}{2} \end{pmatrix}^{-1} = 2\pi \cdot \frac{2}{a^2\sqrt{3}} \begin{pmatrix} \tfrac{a\sqrt{3}}{2} & 0 \\ -\tfrac{a}{2} & a \end{pmatrix} = \frac{4\pi}{a\sqrt{3}} \begin{pmatrix} \tfrac{\sqrt{3}}{2} & 0 \\ -\tfrac{1}{2} & 1 \end{pmatrix}.$$

  The reciprocal primitive vectors $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ are thus

$$\boldsymbol{A}_1 = \frac{4\pi}{\sqrt{3}a}\left(\tfrac{\sqrt{3}}{2}, -\tfrac{1}{2}\right) \qquad \text{and} \qquad \boldsymbol{A}_2 = \frac{4\pi}{\sqrt{3}a}(0,1).$$

- Interpretation: See picture *triangular-angles* for both $\boldsymbol{a}_i$ and $\boldsymbol{A}_i$ drawn together in a single coordinate system.

  Some notes:

  - The $\boldsymbol{A}_i$ have the same length, i.e. $|\boldsymbol{A}_1| = |\boldsymbol{A}_2| = \frac{4\pi}{\sqrt{3}a}$.
  - The vectors $\boldsymbol{a}_i$ and $\boldsymbol{A}_j$ are orthonormal, i.e. $\boldsymbol{A}_2 \cdot \boldsymbol{a}_1 = \boldsymbol{A}_1 \cdot \boldsymbol{a}_2 = 0$, while $\boldsymbol{A}_1 \cdot \boldsymbol{a}_1 = \boldsymbol{A}_2 \cdot \boldsymbol{a}_2 = 2\pi$. This is of course expected, since we used the general relationship $\boldsymbol{a}_i \cdot \boldsymbol{A}_j$ to solve for the $\boldsymbol{A}_i$ in the first place, but it is good to double check.

- Finally, note that the angle between $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ is not 60°, as for an equilateral triangle, but 120°. We can resolve this by defining the reciprocal primitive vector $\widetilde{\boldsymbol{A}}_1 \equiv \boldsymbol{A}_1 + \boldsymbol{A}_2$, which comes out to

$$\widetilde{\boldsymbol{A}}_1 \equiv \boldsymbol{A}_1 + \boldsymbol{A}_2 = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right) + \frac{4\pi}{\sqrt{3}a}(0, 1) = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right).$$

Using the reciprocal primitive vectors $\widetilde{\boldsymbol{A}}_1$ and $\boldsymbol{A}_2$, the reciprocal lattice of a two-dimensional triangular lattice is again a two-dimensional Bravais lattice, with lattice constant $(4\pi)/(\sqrt{3}a)$, but rotated by 30° degrees relative to the directions of the $\boldsymbol{r}$-domain vectors $\boldsymbol{a}_i$ and $\boldsymbol{a}_j$. See *three* for picture.

3.5   The Geometric Structure Factor for a FCC Lattice

Definition

- The geometric structure factor is a dimensionless quantity encoding how a crystal lattice scatters indident x-rays. The geometric structure factor can be assigned to a generic (not necessarily Bravais) lattice defined with a set of primitive vectors $\boldsymbol{a}_i$ and N basis vectors $\boldsymbol{d}_n$, in which the lattice positions $\boldsymbol{R}$ are written in the general form

$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 + \boldsymbol{d}_n.$$

  For the purposes of our course, we will define the geometric structure factor as

$$S(\boldsymbol{K}) = \sum_n e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_n},$$

  where the sum runs over all of the lattice's N basis vectors $\boldsymbol{d}_1, \boldsymbol{d}_2, \ldots, \boldsymbol{d}_N$. The choice of $\boldsymbol{K}$ depends on the way we mathematically formulate the lattice's reciprocal vectors. Note that this expression for the GSF is not general—we have assumed an equal scattering amplitude from each basis atom $\boldsymbol{d}_i$.

- More theory:

- Divide structure factor into atomic structure and geometric structure factor. The atomic structure factor encodes the scattering of x-rays from a single atom in a lattice, while the geometric structure factor encodes scattering from the lattice as a whole. (is related to the positions of atoms within the lattice?)

- For monoatomic crystals (containing only a single species of atom), the the atomic structure factors out of the total structure factor, and we can consider only the geometric structure factor.

- For review, the GSF is defined as

$$S(\boldsymbol{K}) = \sum_n e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_n},$$

  where $\boldsymbol{d}_n$ are the basis vectors used to describe the lattice.

Geometric Structure Factor for the FCC Lattice

- We begin by giving four equivalent interpretations of a FCC lattice structure:

  1. a primitive unit cell (e.g. Wigner-Seitz or parallelepiped), or a non-primitive, cubic unit cell with lattice vectors $\boldsymbol{a}_i$ given in Equation 2.2.
     The key is the lack of a basis; the existance of a Bravais lattice, in which the $\boldsymbol{a}_i$ describe every point in the lattice.

  2. a simple-cubic unit cell, with the additional face-centered atoms represented by the four basis vectors

$$\boldsymbol{d}_1 = \boldsymbol{0} \qquad \boldsymbol{d}_2 = a\left(0, \tfrac{1}{2}, \tfrac{1}{2}\right) \qquad \boldsymbol{d}_3 = a\left(\tfrac{1}{2}, 0, \tfrac{1}{2}\right) \qquad \boldsymbol{d}_4 = a\left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right). \quad (3.6)$$

  See the figure *basis* for a picture.

26

3. a regular hexagonal unit cell (a three dimensional rhombous), together with the basis vectors

$$\boldsymbol{d}_A = \boldsymbol{0} \qquad \boldsymbol{d}_B = \frac{1}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + \frac{1}{3}\boldsymbol{a}_3 \qquad \boldsymbol{d}_C = \frac{2}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + \frac{2}{3}\boldsymbol{a}_3$$

This formulation is related to the $ABCABC$ cubic close-packed formulation of the FCC lattice discussed in [Exercise 2.1.3.]

4. a regular hexagonal lattice, together with the basis vectors $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ above. Supposedly, this is related to a $ABAB$ hexagonal close-packed structure.

3.5.1 Bravais Lattice Formulation

- For the first formulations of the FCC structure, using the Wigner-Seitz cell or the unit cell defined the lattice vectors $\boldsymbol{a}_i$, respectively, there is no basis (or alternatively a single trivial basis vector $\boldsymbol{d}_1 = (0,0,0)$), and the geometric structure factor is simply

$$S(\boldsymbol{K}) = e^{-i(K_x, K_y, K_z)\cdot(0,0,0)} = 1.$$

3.5.2 Simple Cubic with a Basis

- For review, the simple cubic primitive vectors read

$$\boldsymbol{a}_1 = a(1,0,0) \qquad \boldsymbol{a}_2 = a(0,1,0) \qquad \boldsymbol{a}_3 = a(0,0,1).$$

The additional basis vectors needed to fully describe the FCC lattice are

$$\boldsymbol{d}_1 = 0 \qquad \boldsymbol{d}_2 = a\left(0, \tfrac{1}{2}, \tfrac{1}{2}\right) \qquad \boldsymbol{d}_3 = a\left(\tfrac{1}{2}, 0, \tfrac{1}{2}\right) \qquad \boldsymbol{d}_4 = a\left(\tfrac{1}{2}, \tfrac{1}{2}, 0\right)$$

- From [Exercise 3.3.1,] the simple cubic reciprocal primitive vectors

$$\boldsymbol{A}_1 = \frac{2\pi}{a}(1,0,0) \qquad \boldsymbol{A}_2 = \frac{2\pi}{a}(0,1,0) \qquad \boldsymbol{A}_3 = \frac{2\pi}{a}(0,0,1).$$

Note that $\boldsymbol{A}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij}$, as required for a reciprocal lattice.

- For the SC + basis formulation,

$$S_{\boldsymbol{K}} = 1 + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_2} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3},$$

where we have used $\boldsymbol{d}_1 = \boldsymbol{0}$.

- When interpreting the FCC structure as a simple cubic Bravais lattice plus the basis vectors $\boldsymbol{d}_i$ in Equation 3.6, the GSF reads

$$S_{\boldsymbol{K}} = 1 + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_2} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_4}.$$

In this case

$$\boldsymbol{K} = \frac{2\pi}{a}(m_1, m_2, m_3) \tag{3.7}$$

- To compute the GSF, we need an expression for the reciprocal lattice vectors $\boldsymbol{K}$. In general, a reciprocal lattice vector is given by the linear combination

$$\boldsymbol{K} = m_1\boldsymbol{A}_1 + m_2\boldsymbol{A}_2 + m_3\boldsymbol{A}_3,$$

where $\boldsymbol{A}_i$ are the reciprocal primitive vectors. Subsituting these $\boldsymbol{A}_j$ into the expression for $\boldsymbol{K}$ produces

$$\boldsymbol{K} = \frac{2\pi}{a}\big[m_1 \cdot (1,0,0) + m_2 \cdot (0,1,0) + m_3 \cdot (0,0,1)\big] = \frac{2\pi}{a}(m_1, m_2, m_3).$$

GSF

- The geometric structure factor, using the known expression for $\boldsymbol{K}$ and $\boldsymbol{d}_i$, is thus

$$S(\boldsymbol{K}) = e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_1} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_2} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3}$$

$$= 1 + e^{-\frac{2\pi i}{a}(m_1,m_2,m_3)\cdot\frac{a}{2}(0,1,1)} + e^{-\frac{2\pi i}{a}(m_1,m_2,m_3)\cdot\frac{a}{2}(1,0,1)} + e^{-\frac{2\pi i}{a}(m_1,m_2,m_3)\cdot\frac{a}{2}(1,1,0)}$$

$$= 1 + e^{-i\pi(m_2+m_3)} + e^{-i\pi(m_1+m_3)} + e^{-i\pi(m_1+m_2)}. \tag{3.8}$$

Idea: can we find a combination of m_i such that $S_{\boldsymbol{K}} = 0$, which we could then observe in experiment as zero scattering?

Here are some possible cases for the value of $S(\boldsymbol{K})$, depending on the values of the Miller indeces m_i:

1. If the m_i are all even, then the sum $m_i + m_j$ of any two Miller indices is also even. In this case the GSF equals

$$S(\boldsymbol{K}) = 1 + e^{-i\pi\cdot\mathcal{E}} + e^{-i\pi\cdot\mathcal{E}} + e^{-i\pi\cdot\mathcal{E}} = 1 + 3e^{-2\pi i\cdot n} = 4, \qquad (m_i \text{ even}),$$

where $\mathcal{E}$ denotes an arbitrary even number, which we then wrote in the form $\mathcal{E} = 2n$, where $n \in \mathbb{N}$ is an integer and $e^{2\pi i n} = 1$.

2. Similarly, if all m_i are odd, then the sum $m_i + m_j$ of any two Miller indices is again even. By an identical argument to that above, the corresponding geometric structure factor is

$$S(\boldsymbol{K}) = 4 \qquad (m_i \text{ odd}).$$

3. If two Miller indeces are even and one is odd, one of the sums $m_i + m_j$ in Equation 3.8 is even, while the other two are odd. The resulting structure factor reads

$$S(\boldsymbol{K}) = 1 + e^{-i\pi\cdot\mathcal{E}} + 2e^{-i\pi\cdot\mathcal{O}} = 1 + e^{-2\pi i\cdot n} + e^{-i\pi(1+2n)}$$
$$= 1 + 1 + 2\cdot(-1) = 0,$$

where $\mathcal{E}$ and $\mathcal{O}$ denote an arbitrary even and odd number, respectively, and we have used $e^{2\pi i n} = 1$ and $e^{i(\pi+2\pi n)} = -1$.

4. Finally, if two Miller indeces are odd and one is even, then once again one of the sums $m_i + m_j$ in Equation 3.8 is even, while the other two are odd. The resulting structure factor reads, as in the previous case, is

$$S(\boldsymbol{K}) = 0 \qquad (\text{two } m_i \text{ odd, one } m_i \text{ even; or vice-versa}).$$

Physical interpreation: not all reciprocal lattice vectors $\boldsymbol{K}$ scatter x-ray light—only those for which the m_i are either all even or all odd.

Without proof, a reciprocal vector $\boldsymbol{K}$ is formed of either all odd or all even m_i exactly one-fourth of the time, leading to $S(\boldsymbol{K}) = 4$. The remaining three quarters of the possible $\boldsymbol{K}$ have a mixed number of odd and even Miller indexes and have $S(\boldsymbol{K}) = 0$.

- Next: imagine generating a a reciprocal; we then observe which reciprocal vectors within the reciprocal lattice have a non-zero geometric structure factor $S(\boldsymbol{K}) \neq 0$.

  Begin with a simple cubic structure (in RL space) and draw eight cells of this structure. Recall latice constant is $2\pi/a$.

  The parent cube's side lengths are thus $4\pi/a$. See *SC-basis-RL*

  We then draw the nonzero sites given nonzero $S_{\boldsymbol{K}}$, based on the values of the Miller indexes which we can deduce from looking at the picture. The even are on the vertices and the single all-odd is in the center and is $(1, 1, 1)$.

  Note that the nonzero points form a BCC Bravais lattice in RL space with lattice constant $4\pi/a$. This is precisely that reciprocal lattice of a FCC lattice in position space (recall we're working with a FCC lattice all along).

  Summary: (when treating FCC as SC and basis), the RL lattice sites give nonzero GSF occur only in the possitions of a BCC lattice, which is precisely the RL of a FCC cell. The reason we have zero contributions is because SC is not a primitive cell but bigger than FCC primitive cell, so of course there's extra unused lattice sites.

3.5.3   Regular Hexagonal Plus a Basis

- First, for review, the hexagonal primitive vectors are

$$\boldsymbol{a}_1 = a(1,0,0) \qquad \boldsymbol{a}_2 = a\left(\tfrac{1}{2}, \tfrac{\sqrt{3}}{2}, 0\right) \qquad \boldsymbol{a}_3 = a(0,0,\sqrt{6}).$$

  The vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are simply three-dimensional generalizations of the 2D hexagonal primitive vectors in Equation 3.5.

  Note that the height between layers is $h = \sqrt{2/3}$. The third vector simply points three layers up to the next A layer. The height is thus $3 \cdot \sqrt{2/3} = \sqrt{6}$.

- For a FCC lattice formulated as a regular hexagonal Bravais lattice plus a basis, the basis vectors are

$$\boldsymbol{d}_A = 0 \qquad \boldsymbol{d}_B = \frac{1}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + \frac{1}{3}\boldsymbol{a}_3 \qquad \boldsymbol{d}_C = \frac{2}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + \frac{2}{3}\boldsymbol{a}_3,$$

  and the general form of the geometric structure factor is

$$S_{\boldsymbol{K}} = 1 + e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_B} + e^{-i\boldsymbol{K}\cdot\boldsymbol{r}_C},$$

  where we have used $\boldsymbol{d}_A = \boldsymbol{0}$.

- The reciprocal lattice of a regular hexagaonal Bravais lattice is again a regular hexagonal lattice in reciprocal space.

  The reciprocal lattice is such that the reciprocal primitive vectors $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ form a 2D hexagonal lattice in reciprocal space (as derived in Exercise 3.4). Meanwhile, the third reciprocal primitive vector is given by,

$$\boldsymbol{A}_3 = \frac{2\pi}{|\boldsymbol{a}_3|}(0,0,1) = \frac{2\pi}{a}(0,0,1).$$

Safety calculation:

$$V_0 = |\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = \frac{3a^3}{\sqrt{2}} \qquad \boldsymbol{A}_3 = 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_3}{V_0} = 2\pi \frac{a^2(0,0,\sqrt{3}/2)}{a^3(3/\sqrt{2})}$$

The complete set of regular hexagonal reciprocal primitive vectors is thus

$$\boldsymbol{A}_1 = \frac{4\pi}{\sqrt{3}a}\left(\tfrac{\sqrt{3}}{2}, \tfrac{1}{2}, 0\right) \qquad \boldsymbol{A}_2 = \frac{4\pi}{\sqrt{3}a}(0,1,0) \qquad \boldsymbol{A}_3 = \sqrt{\frac{2}{3}}\frac{\pi}{a}(0,0,1).$$

Note that this choice of reciprocal vectors satisfies $\boldsymbol{a}_i \cdot \boldsymbol{A}_j = 2\pi\delta_{ij}$. Since $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ form a two-dimensional triangular lattice while $\boldsymbol{A}_3$ points directly out of the page, the reciprocal primitive vectors $\boldsymbol{A}_j$ form a regular hexagonal lattice in reciprocal space.

GSF

- Recall
$$S_{\boldsymbol{K}} = 1 + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_B} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_C},$$

- Next, we aim to write a general reciprocal lattice vector as the linear combination
$$\boldsymbol{K} = m_1\boldsymbol{A}_1 + m_2\boldsymbol{A}_2 + m_3\boldsymbol{A}_3.$$

When evaluating the dot products $\boldsymbol{K}\cdot\boldsymbol{d}_B$ and $\boldsymbol{K}\cdot\boldsymbol{d}_C$ in the GSF, we take advantage of the fact that the basis vectors $\boldsymbol{d}_B$ and $\boldsymbol{d}_C$ are written in terms of the primitive vectors $\boldsymbol{a}_i$. This allows us to use the identity $\boldsymbol{A}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij}$. We then get

$$\boldsymbol{K} \cdot \boldsymbol{d}_B = (m_1\boldsymbol{A}_1 + m_2\boldsymbol{A}_2 + m_3\boldsymbol{A}_3)\cdot\frac{1}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3) = \frac{2\pi}{3}(m_1 + m_2 + m_3)$$

$$\boldsymbol{K} \cdot \boldsymbol{d}_C = (m_1\boldsymbol{A}_1 + m_2\boldsymbol{A}_2 + m_3\boldsymbol{A}_3)\cdot\frac{2}{3}(\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3) = \frac{4\pi}{3}(m_1 + m_2 + m_3)$$

Obviously, since $\boldsymbol{d}_A = \boldsymbol{0}$, we have $\boldsymbol{K} \cdot \boldsymbol{d}_A$ for all $\boldsymbol{K}$.

- Anway $S_{\boldsymbol{K}}$ comes out to
$$S_{\boldsymbol{K}} = 1 + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_B} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_C} = 1 + e^{-\frac{2\pi i}{3}(m_1+m_2+m_3)} + e^{-\frac{4\pi i}{3}(m_1+m_2+m_3)}$$

- Consider three cases where $m_1 + m_2 + m_3 = 3N$ where $N \in \mathbb{Z}$. This gives $S_{\boldsymbol{K}} = 3$ (happens in 1/3 of all cases)

Where $m_1 + m_2 + m_3 = 3N + 1$ in this case we have
$$1 + e^{-i\frac{2\pi}{3}} + e^{-i\frac{4\pi}{3}} = 0$$

And finally where $m_1 + m_2 + m_3 = 3N + 2$ in this case we have
$$1 + e^{-i\frac{4\pi}{3}} + e^{-i\frac{8\pi}{3}} = 0$$

- Interpration: the last two zero cases occur 2/3 of the time. As before, we chose a lattice cell that was (3 times) bigger than the primitive FCC cell. The result is (3 times) more zero-scattering lattice sites in RL space.

The end result is that net x-ray scattering from the RL lattice is the same observable results: for example ITC $1/3 \cdot 3 = 1$ or for SC and basis $1/4 \cdot 4 = 1$.

- Main less: every choice of lattice for a given crystal structure gives the same observable result when it comes to scattering of x-rays in RL space (we just use x-ray example because x-rays are the easiest experimental way to observe crystal structures).

3.5.4 TODO: HCP ABAB

- This was left as an exercise—come back to it.

4 Fourth Exercise Set

4.1 TODO An X-Ray Scattering Experiment

Basically clean up from here forward.

We perform two experiments with a crystal, which we know can be represented as a simple cubic structure with an additionaly atom somewhere, at an unknown location, along the main body diagonal. The following experimental data is known:

- *When we expose the crystal, in powder form, to x-ray light with wavelength $\lambda = 2\,\text{Å}$ (angstrom), the first two Bragg peaks occur at scattering angles $\theta_1 = 83.6°$ and $\theta_2 = 141.1°$, respectively.*

- *When we rotate a single-crystal with large-scale structure, we observe that the two scattering peaks have different intensities, with a ratio of 1 to 4.*

Use the experimental data to determine the position of the unknown atom along the main body diagonal.

- We will represent the crystal as a simple cubic lattice plus a basis. The simple cubic basis vectors are

$$\boldsymbol{a}_1 = a(1,0,0) \qquad \boldsymbol{a}_2 = a(0,1,0) \qquad \boldsymbol{a}_3 = a(0,0,3),$$

  while the basis encoding the unknown diagonal atom is

$$\boldsymbol{d}_1 = \boldsymbol{0} \qquad \boldsymbol{d}_2 = x(1,1,1)$$

  The second basis vector $\boldsymbol{d}_2$, which lies along the cubic lattice's main body diagonal, represents the unknown atom. The parameter x encodes the atom's position along the diagonal.

- We begin by computing our crystal's geometric structure factor using the known basis vectors $\boldsymbol{d}_1$ and $\boldsymbol{d}_2$. This reads

$$S_{\boldsymbol{K}} = e^{i\boldsymbol{K}\cdot\boldsymbol{d}_1} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_2} = 1 + e^{-ix\boldsymbol{K}\cdot(1,1,1)}. \tag{4.1}$$

  From Equation 3.7, a reciprocal lattice vector for a simple cubic structure takes the general form

$$\boldsymbol{K} = \frac{2\pi}{a}(m_1, m_2, m_3),$$

  where m_1, m_2 and m_3 are the three Miller indeces parameterizing $\boldsymbol{K}$. Substituting the above expression for $\boldsymbol{K}$ into Equation 4.1 and evaluating the dot product produces

$$S_{\boldsymbol{K}} = 1 + e^{-2\pi i \frac{x}{a}(m_1 + m_2 + m_3)}.$$

- Next, we decompose our problem into two possible cases. These are:

  1. The unknown atom occurs exactly halfway along the body diagonal. In this case $x = a/2$, and the crystal has a BCC lattice structure.

  2. The unknown atom occurs anywhere along else along the main diagonal except for the midpoint, i.e. $x \neq a/2$.

We will use the given experimental data to determine which case is correct.

Notes on Case 1: If $x = a/2$

- If $x = a/2$, meaning the crystal has a BCC structure, we have two further options:

  1. First, we could simply continue reprsenting the crystal with a simple cubic lattice plus a basis $\boldsymbol{d}_1 = \boldsymbol{0}$ and $\boldsymbol{d}_2 = (a/2) \cdot (1,1,1)$. In this case, using $x = a/2$ in Equation 4.1, the crystal's GSF reads

$$S(\boldsymbol{K}) = 1 + e^{-\pi i (m_1 + m_2 + m_3)}.$$

  This geometric structure factor obeys

$$S(\boldsymbol{K}) = \begin{cases} 2 & m_1 + m_2 + m_3 \text{ is even} \\ 0 & m_1 + m_2 + m_3 \text{ is odd.} \end{cases}$$

  2. Alternatively, we could directly analyze the crystal in terms of BCC unit cell without using a basis, in which case $S(\boldsymbol{K}) = 1$. If we choose to represent the crystal with a BCC cell, we must perform our scattering analysis using the BCC reciprocal lattice, which, from Exercise 3.3.2, is a FCC with lattice constant $4\pi/a$ and reciprocal vectors

$$\boldsymbol{A}_1 = \frac{2\pi}{a}(0,1,1) \qquad \boldsymbol{A}_2 = \frac{2\pi}{a}(1,0,1) \qquad \boldsymbol{A}_3 = \frac{2\pi}{a}(1,1,0)$$

- Since we don't know *a priori* if $x = a/2$ or $x \neq a/2$, we will have to analyze both possibilities. In the case $x = a/2$, we have the two further options, number one and two above.

4.1.1 First Experiment: Analyzing Scattering Angles

- We begin with the first set of experimental data, which reports two scattering angles $\theta_1 = 86.6°$ and $\theta_2 = 141.1°$. From Bragg's law, the scattering angle θ is related to the distance d between lattice planes and wavelength λ of incident light according to

$$2d \sin \frac{\theta}{2} = n\lambda,$$

where the distance d between lattice planes is given by

$$d = \frac{2\pi}{|\boldsymbol{K}|},$$

where $\boldsymbol{K}$ is a vector in the reciprocal lattice.

Alternatively:

$$2\frac{2\pi}{|\boldsymbol{K}|} \sin \frac{\theta}{2} = \lambda$$

Simple Cubic

- We begin with the simple cubic plus basis representation. To apply Bragg's law, we must first compute the distance d between lattice planes, which in turn requires an expression for the reciprocal lattice vector $\boldsymbol{K}$. From Equation 3.7, the reciprocal lattice vector for a simple cubic lattice takes the general form

$$\boldsymbol{K} = \frac{2\pi}{a}(m_1, m_2, m_3) \implies d = \frac{2\pi}{|\boldsymbol{K}|} = \frac{a}{\sqrt{m_1^2 + m_2^2 + m_3^2}}.$$

We then substitute this lattice spacing d into Bragg's condition and assume $n = 1$, which results in

$$\frac{2a\sin(\theta/2)}{\sqrt{m_1^2 + m_2^2 + m_3^2}} = \lambda \tag{4.2}$$

Analyzing Scattering Angles

- First, we arrange Equation 4.2 to get

$$\sin\frac{\theta}{2} = \frac{\lambda}{2a}\sqrt{m_1^2 + m_2^2 + m_3^2}$$

Note that, since λ and a are constants, a smaller scattering angle θ corresponds to a smaller sum of the Miller indeces m_i.

The first scattering angle $\theta_1 = 86.6°$ occurs for the smallest possible non-zero combination of Miller indices, i.e.

$$m_1^2 + m_2^2 + m_3^2 = 1 \implies \sqrt{m_1^2 + m_2^2 + m_3^2} = 1.$$

The Miller indices satisfying this condition belong to the following set:

$$(m_1, m_2, m_3) \in \big\{(\pm 1, 0, 0), (0, \pm 1, 0), (0, 0, \pm 1)\big\}.$$

- Meanwhile, the second scattering angle $\theta_2 = 141.1°$ corresponds to the next-largest sum of scattering angles, i.e.

$$m_1^2 + m_2^2 + m_3^2 = 2 \implies \sqrt{m_1^2 + m_2^2 + m_3^2} = \sqrt{2}.$$

This condition is satisfied if two m_i are ± 1 and a single m_i is zero.

- The predicted lattice constants a for θ_1 and θ_2 are

$$a_1 = \frac{\lambda\sqrt{1}}{2\sin\frac{83.6°}{2}} \approx \frac{2\,\text{Å}}{2 \cdot (2/3)} = 1.5\,\text{Å}$$

$$a_2 = \frac{\lambda\sqrt{2}}{2\sin\frac{141.1°}{2}} \approx \frac{\sqrt{2} \cdot 2\,\text{Å}}{2 \cdot (2\sqrt{2}/3)} = 1.5\,\text{Å}.$$

Since the two predictions for a are consistent, the simple cubic plus basis model of the crystal is consistent with the experimental data

Body-Centered Cubic

- Using the BCC reciprocal primitive vectors $\boldsymbol{A}_i$ in Equation 3.4, a generic reciprocal lattice vector for a BCC lattice takes the form

$$\boldsymbol{K} = m_1\boldsymbol{A}_1 + m_2\boldsymbol{A}_2 + m_3\boldsymbol{A}_3 = \frac{2\pi}{a}(m_2 + m_3, m_1 + m_3, m_1 + m_2).$$

The corresponding spacing d between lattice planes is

$$d = \frac{2\pi}{|\boldsymbol{K}|} = \frac{a}{\sqrt{(m_2 + m_3)^2 + (m_1 + m_3)^2 + (m_1 + m_2)^2}}.$$

- We then substitute this expression for d into the Bragg's equation, which produces

$$\frac{2a\sin(\theta/2)}{\sqrt{(m_2 + m_3)^2 + (m_1 + m_3)^2 + (m_1 + m_2)^2}} = \lambda$$

The corresponding lattice constant a is

$$a = \frac{\lambda}{2}\frac{\sqrt{(m_2 + m_3)^2 + (m_1 + m_3)^2 + (m_1 + m_2)^2}}{\sin(\theta/2)}$$

Case Two

- We now consider the second case, in which we assume the unknown atom lies halfway along the body diagonal at $x = a/2$.

  Recall we have two further "sub-options" for this case, which for review are

  1. First, we could simply continue reprsenting the crystal with a simple cubic lattice plus a basis $\boldsymbol{d}_1 = \boldsymbol{0}$ and $\boldsymbol{d}_2 = (a/2)\cdot(1,1,1)$. In this case, using $x = a/2$ in Equation 4.1, the crystal's GSF reads

  $$S(\boldsymbol{K}) = 1 + e^{-\pi i(m_1 + m_2 + m_3)}.$$

  This geometric structure factor obeys

  $$S(\boldsymbol{K}) = \begin{cases} 2 & m_1 + m_2 + m_3 \text{ is even} \\ 0 & m_1 + m_2 + m_3 \text{ is odd.} \end{cases}$$

  2. Alternatively, we could directly analyze the crystal in terms of BCC unit cell without using a basis, in which case $S(\boldsymbol{K}) = 1$. If we choose to represent the crystal with a BCC cell, we must perform our scattering analysis using the BCC reciprocal lattice, which, from Exercise 3.3.2, is a FCC with lattice constant $4\pi/a$ and reciprocal vectors

  $$\boldsymbol{A}_1 = \frac{2\pi}{a}(0,1,1) \qquad \boldsymbol{A}_2 = \frac{2\pi}{a}(1,0,1) \qquad \boldsymbol{A}_3 = \frac{2\pi}{a}(1,1,0)$$

- We first consider the SC plus basis model, which we will analyze using the crystal's GSF. In this case, the scattering angle θ_1 corresponds to the smallest possible absolute-value combination of Miller indices m_i such that the sum of m_i is even. The smallest possible even number is two, and occurs for

$$m_1^2 + m_2^2 + m_3^2 = 2 \implies \sqrt{m_1^2 + m_1^2 + m_1^2} = \sqrt{2}.$$

The Miller indices satsifying the above condition are

$$(m_1, m_2, m_3) \in \Big\{(\pm 1, \pm 1, 0), (\pm 1, 0, \pm 1), (0, \pm 1, \pm 1),$$
$$(\pm 1, \mp 1, 0), (\pm 1, 0, \mp 1), (0, \pm 1, \mp 1)\Big\},$$

- Meanwhile, the scattering angle θ_2 corresponds to the next-largest possible even absolute-value combination of Miller indices m_i, i.e.

$$m_1^2 + m_1^2 + m_1^2 = 4 \implies \sqrt{m_1^2 + m_1^2 + m_1^2} = 2.$$

The m_i satisfying this requirement are

$$(m_1, m_2, m_3) \in \left\{ (\pm 2, 0, 0), (0, \pm 2, 0), (0, 0, \pm 2) \right\}.$$

- The lattice constants a for θ_1 and θ_2 corresponding to the above two possibilities of m_i are

$$a_1 = \frac{\lambda\sqrt{m_1^2 + m_1^2 + m_1^2}}{2\sin\frac{86.6°}{2}} \approx \frac{\sqrt{2} \cdot 2\,\text{Å}}{2 \cdot (2/3)} \approx 2.12\,\text{Å}$$

$$a_2 = \frac{\lambda\sqrt{m_1^2 + m_1^2 + m_1^2}}{2\sin\frac{141.1°}{2}} \approx \frac{2 \cdot 2\,\text{Å}}{2 \cdot (2\sqrt{2}/3)} \approx 2.12\,\text{Å}$$

Again, the two predictions for a are constistent, which means the assumption $x = a/2$ is also consistent with our experimental data.

In other words, so far we can't tell if $x = a/2$ or not—both options lead to lattice constant predictions consistent with our experimental data.

- *Note*: for lack of time, we left out the second $x = a/2$ subcase, in which we would represent the unknown crystal directly with a BCC lattice.

4.1.2 Second Experiment: Crystal Rotation

- Analyzing the scattering angles θ_1 and θ_2 alone was not enough to determine the position of the unknown diagonal atom, since both the options $x = a/2$ and $x \neq a/2$ produce consisten lattice constant.

We thus turn to the second set of experimental data to determine if $x = a/2$. The second experiment tells us that the relative intensities of the scattering peaks differ by a factor of four. Our first step is to find scattering intensity, which is proportional to the square of the GSF.

$$I \propto |S(\boldsymbol{K})|^2 = \left| 1 + e^{i\frac{2\pi x}{a}(m_1+m_2+m_3)} \right|^2 = 1 + 1 + 2\cos\left[\frac{2\pi x}{a}(m_1 + m_2 + m_3) \right]$$

$$= 2\left(1 + \cos\left[\frac{2\pi x}{a}(m_1 + m_2 + m_3) \right] \right)$$

Using the power-reducing identity $2\cos^2 x = 1 + \cos 2x$, this simplifies to

$$I \propto 4\cos^2\left[\frac{\pi x}{a}(m_1 + m_2 + m_3) \right]$$

- Recall from earlier if $x \neq a/2$ we have posibilites for m_i of like 01-1 (last one). The sum is either 2 or 0

Meanwhile if $x = a/2$ then we have 200 or 020 or 002. The sum is always 2

- We know from I that the intensity depends on sum of m_i. But for second option—$x = a/2$, we have sum of m_i is always two.

  The observed structure, however, showed that the intensity changed changed with sum of m_i or something.

  We thus conclude $x \neq a/2$.

- So for $x \neq a/2$ we have e.g.

$$\frac{1}{4} \equiv \frac{I_{110}}{I_{1-10}} = \frac{4\cos^2\left(\frac{2\pi x}{a}\right)}{4\cos^2(0)} = \cos^2\left(\frac{2\pi x}{a}\right).$$

  We chose 110 for above because its sum 2 and the same as equivalent 101 and 011. They key here is just to choose a sum 2 intensity on the top and the sum zero intensity on the bottom.

  Ah!!! the different peak intensities correspond to either sum of m_i for $x \neq a/2$ equal to zero or equal to two.

  That is why we rejected option of m_i sum being the same for $x = a/2$. Because same sum of m_i wouldn't give different peak intensities in the second experiment.

  The rotating method gives different intensities for different rotations of the cubic crystal cell—to get different intensities we would expect the center atom to be in an asymmetrical position. If $x = a/2$ and the center atoms is symmetric, rotating the crystal would give same intensities in any orientation.

- We now solve for the position x of the unknown atom.

$$\cos^2\left(\frac{2\pi x}{a}\right) = \frac{1}{4} \implies \cos\left(\frac{2\pi x}{a}\right) = \frac{1}{2} \implies \frac{2\pi x}{a} \in \left\{\frac{\pi}{3}, \frac{2\pi}{3}, \frac{4\pi}{3}, \frac{5\pi}{3}\right\}.$$

  The corresponding solutions for x are

$$x \in \left\{\frac{a}{6}, \frac{a}{3}, \frac{2a}{3}, \frac{5a}{6}\right\}.$$

  However, the last two results, i.e. $2a/3$ and $5a/6$, contain the same physical information as $x = a/6$ or $x = a/3$, respectively, just with the inside atom reflected across the main diagonal.

  We can thus conlude that the two possible positions of the center atom are either $x = a/6$ or $x = a/3/$

Summary

- Cubic crystal structure. Model as cubic unit cell. We found the lattice constant a from the given data.

- We knew we had two atoms—one along the body diagonal.

- Assuming a SC Bravais lattice plus a basis, we define the basis

$$\boldsymbol{d}_1 = \boldsymbol{0} \qquad \boldsymbol{d}_2 = x(1,1,1),$$

  where x parameterizes the poisiton along the body diagonal.

- We found from data that either

$$x = a/6 \quad \text{or} \quad x = a/3$$

- We write a simple cubic reciprocal lattice vector $\boldsymbol{K}$ as

$$\boldsymbol{K} = \frac{2\pi}{a}(m_1 + m_2 + m_3)$$

  The corresponding simple cubic geometric structure factor is

$$S(\boldsymbol{K}) = 1 + e^{-i\frac{2\pi x}{a}(m_1 + m_2 + m_3)}$$

- We use the above $\boldsymbol{K}$ for the Bragg condition for constructive interference of scattered x-rays.

  Bragg condition, for review, reads

$$2d\sin\frac{\theta}{2} = \lambda$$

  where d is directly related to $\boldsymbol{K}$ via

$$d = \frac{2\pi}{|\boldsymbol{K}|} = \frac{a}{\sqrt{m_1^2 + m_2^2 + m_3^2}}.$$

- Recall we detected reflection at two scattering angles, $\theta_1 = 86.6°$ with $100, 010, 001$ or $\theta_2 = 141.1°$ with $110, 101, 011, 1-10, 10-1, 01-1$.

- Plot the Bragg condition and detect underlying physical information. Try to plot lattice planes from which x-rays scatter.

  We have three lattice planes.

- Begin with plane 100 — this is analogous to 010 and 001, just for other Cartesian coordinates. (cubic symmetry)

  Recall from lecture that $\boldsymbol{K} = \frac{2\pi}{a}(1, 0, 0)$ is perpendicular to the lattice plane. Thus the planes for this $\boldsymbol{K}$ are perpendicular to the x axis.

  Supposedly also from lecture that $d = a$.

- Next we consider Miller index possibility 200 (this turned out to be impossible; corresponded to BCC; but we plot it now for sake of completeness).

  In this case $\boldsymbol{K} = \frac{2\pi}{a}(2, 0, 0)$ and $d = a/2$—same orientation of planes as before, but now twice as dense.

- Next the plane 110, with $K = \frac{2\pi}{a}(1, 1, 0)$ and $d = \frac{a}{\sqrt{2}}$.

  $\boldsymbol{K}$ points in the direction of the (x, y) bisector or $\phi = \pi/4$

- Next we have $1 - 10$ for which $K = \frac{2\pi}{a}(1, -1, 0)$ and $d = \frac{a}{\sqrt{2}}$.

  In this case the planes are *tangent* to $\phi = \pi/4$.

Next, Discussion

- X-ray scatters from electron distribution on atoms in the lattice.

  Sum scattering over contribution of all atoms in the lattice, and require the individual scattering rays interfere constructively.

  Model scattering from electron distribution on atoms in the lattice as scattering from lattice planes (easier to analyze). This leads to the condition that the distance between lattice planes d satisfies the Bragg condition.

- First case. Return to 100. Consider both SC black atoms and the green off-diagonal atom. The off-diagonal atoms (because they do not lie on the lattice planes, which are related to the Bragg condition) the off-diagonal atoms will not in general contribute to constructive interference.

  Limit case: if the off-diagonal is along the center of the main diagonal, then it is exactly half a plane distance between the black atom planes, and we have exactly destructive interference.

  We thus expect zero scattered intensity for 100. Compare to earlier BCC treatment!

  Keep in mind as many green atoms as black atoms net—just not drawn that way for one cell.

- Next case: 200. In this case (if we assume green atom is centered along main diagonal) because $d = a/2$ is half of that for 100, the center atom at $d = a/2$ between SC planes is exactly the wavelength, and we get complete constructive interference. Again compare earlier BCC.

- Case 110. If we assume a BCC structure for the green atom, between lattice planes, we get partial destructive interference. (distance between orange and green reflected rays is a partial multiple of wavelength).

- This was just for review...

5 Fifth Exercise Set

5.1 The Drude Model

5.1.1 Theory: Review of the Drude Model

- The Drude model is a simple microscopic model for electric conduction, which describes electrons as classical particles obeying Newton's second law. We consider two contributions to the net force:

  1. an accelerating electric field force $q\boldsymbol{E}$, and
  2. a dissipative force representing collisions of electrons with impurities in the conductor. We model this dissipative force as $\boldsymbol{p}/\tau$, where $\boldsymbol{p}$ is electron momentum and the parameter τ is the mean free time between collisions.

  Newton's second law for electrons in the Drude model thus reads

  $$m\ddot{\boldsymbol{r}} = q\boldsymbol{E} - \frac{\boldsymbol{p}}{\tau}. \tag{5.1}$$

- Assuming we can solve the equation for electron position $\boldsymbol{r}$, we can find current density $\boldsymbol{j}$ in a conductor with

  $$\boldsymbol{j} = n_{\mathrm{e}}q\boldsymbol{v} = n_{\mathrm{e}}q\dot{\boldsymbol{r}},$$

  where n_{e} is the number density of electrons in the conducting material.

5.1.2 Exercise: The Drude Model for an Alternating Electric Field

Find the current density $\boldsymbol{j}$ of electrons in a conductor exposed to an alternating electric field of the form

$$\boldsymbol{E} = \boldsymbol{E}_0 e^{-i\omega t},$$

where $\boldsymbol{E}_0$ is a constant. Derive and interpret the limit cases for small and large electric field frequencies ω.

- We first comment on the electric field: $\boldsymbol{E}$ is evidently homogeneous, but time-dependent due to the factor $e^{-i\omega t}$. Although the ansatz for $\boldsymbol{E}$ is complex, only the electric field's real component is physically relevant; in practice, we use the complex formulation above for mathematical simplicity, and take the real component of the final result to find the physical electric field.

- As for a static electric field, we base our analysis on Newton's law (Eq. 5.1), and substitute in the oscillating ansatz $\boldsymbol{E} = \boldsymbol{E}_0 e^{-i\omega t}$ to get

  $$m\ddot{\boldsymbol{r}} = q\boldsymbol{E} - \frac{m\dot{\boldsymbol{r}}}{\tau} = q\boldsymbol{E}_0 e^{-i\omega t} - \frac{m\dot{\boldsymbol{r}}}{\tau}.$$

  We then solve for position $\boldsymbol{r}$ with the oscillating ansatz $\boldsymbol{r}(t) = \boldsymbol{r}_0 e^{-i\omega t}$, where $\boldsymbol{r}_0$ is the amplitude of electron oscillation in the alternating electric field.

- Substituting the ansatz $\boldsymbol{r}(t) = \boldsymbol{r}_0 e^{-i\omega t}$ into Newton's law produces

  $$-m\omega^2 \boldsymbol{r}_0 e^{-i\omega t} q\boldsymbol{E}_0 e^{-i\omega t} - \frac{m}{\tau}(-i\omega)\boldsymbol{r}_0 e^{-i\omega t}.$$

We then cancel $e^{-i\omega t}$ and solve $\boldsymbol{r}_0$, which comes out to

$$\boldsymbol{r}_0 = \frac{q\boldsymbol{E}_0}{-m\omega^2 - \frac{im\omega}{\tau}}.$$

In other words, if we know the electric field amplitude $\boldsymbol{E}_0$ we can find $\boldsymbol{r}_0$—the amplitude of electron oscillation. Using the just-derived amplitude $\boldsymbol{r}_0$, an electron's motion in the conductor is thus given by

$$\boldsymbol{r}(t) = \boldsymbol{r}_0 e^{-i\omega t} = \frac{q\boldsymbol{E}_0}{-m\omega^2 - \frac{im\omega}{\tau}} e^{-i\omega t} = \frac{q\boldsymbol{E}(t)}{-m\omega^2 - \frac{im\omega}{\tau}},$$

where we have reintroduced the original electric field $\boldsymbol{E}(t) = \boldsymbol{E}_0 e^{-i\omega t}$.

- The corresponding current density $\boldsymbol{j}$ is

$$\boldsymbol{j} = n_\mathrm{e} q\dot{\boldsymbol{r}} = n_\mathrm{e} q(-i\omega)\boldsymbol{r}_0 e^{-i\omega t} = \frac{n_\mathrm{e} q^2}{m} \frac{-i\omega}{-\omega^2 - \frac{i\omega}{\tau}} \boldsymbol{E}_0 e^{-i\omega t}.$$

We then cancel ω, multiply through by τ and recognize $\boldsymbol{E}(t) = \boldsymbol{E}_0 e^{-i\omega t}$ to get

$$\boldsymbol{j} = \frac{n_\mathrm{e} q^2 \tau}{m} \frac{-i}{-\omega\tau - i} \boldsymbol{E}(t) = \frac{n_\mathrm{e} q^2 \tau}{m} \frac{1}{1 - i\omega\tau} \boldsymbol{E}(t).$$

Lesson: current density is linearly proportional to $\boldsymbol{E}$, which is the essence of Ohm's law. The proportionality coefficient between $\boldsymbol{j}$ and $\boldsymbol{E}$ is called material's *electric conductivity*, and for the Drude model equals

$$\sigma_\mathrm{E}(\omega) = \frac{n_\mathrm{e} q^2 \tau}{m} \frac{1}{1 - i\omega\tau}.$$

Limit Cases

- We now consider the behavior of electric conductivity in the high and low electric field frequency limits. First, we consider the low-frequency limit $\omega \ll \frac{1}{\tau}$, in which case σ_E reduces to

$$\sigma_\mathrm{E}(\omega) \approx \frac{n_\mathrm{e} e_0^2 \tau}{m}$$

This is simply the electric field corresponding to a static electric field with $\omega = 0$.

- Next, we consider the high-frequency limit $\omega \gg 1/\tau$. In this case $\omega\tau \gg 1$, and electrical conductivity reduces to

$$\sigma_\mathrm{E}(\omega) \approx \frac{n_\mathrm{e} e_0^2 \tau}{m} \frac{1}{-i\omega\tau} = \frac{i n_\mathrm{e} e_0^2}{m\omega}.$$

Note that the conductivity no longer depends on the mean free time τ between electron collisions. Interpreted physically, the electric field oscillates so rapidly that, during a given oscillation, an electron hardly ever collides with impurities in the conductor, and the parameter τ is thus negligible.

In other words, small ω corresponds to many electron collisions per electric field oscillation, while large ω corresponds to negligible collisions per oscillation.

Note also that the conductivity σ_E is purely imaginary quantity for large electric field frequencies ω, which means that current density $\boldsymbol{j}$ and electric field $\boldsymbol{E}$ are out of phase by $\pi/2$ in the high-frequency limit.

- Finally, recall from *EMP* that Ohmic losses in a conductor are given by

$$\boldsymbol{j} \cdot \boldsymbol{E}$$

In the high-frequency limit, in which case $\boldsymbol{j}$ and $\boldsymbol{E}$ are out of phase by $\pi/2$, the time-averaged Ohmic losses $\langle \boldsymbol{j} \cdot \boldsymbol{E} \rangle$ are zero. Meanwhile, for small ω we have non-zero Ohmic losses, and the conductor acts like an Ohmic resistor.

5.2   Theory: Review of Free Electrons in Crystals

- Formally, electrons moving in a crystal experience a periodic potential, with period identical to the period of the crystal's underlying lattice structure. In symbols, this periodic potential takes the form

$$V(\boldsymbol{r}) = V(\boldsymbol{r} + \boldsymbol{R}),$$

where $\boldsymbol{R}$ is any vector in the crystal's Bravais lattice. However, we will begin with a free electron approximation in which $V(\boldsymbol{r}) \approx 0$.

- Geometrically, we represent the crystal containing the electrons as a cuboid with side lengths L_x, L_y, and L_z, and model the cyrstal as a three-dimensional infinite potential well containg the electrons, inside of which the potential is $V = 0$.

- Importantly, we impose periodic boundary conditions on the electron wave wave functions in the crystal. These periodic boundary conditions read

$$\psi(x + L_x, y, z) = \psi(x, y, z), \tag{5.2}$$
$$\psi(x, y + L_y, z) = \psi(x, y, z), \tag{5.3}$$
$$\psi(x, y, z + L_z) = \psi(x, y, z). \tag{5.4}$$

We use periodic boundary conditions (as opposed to requiring, more realistically, that the electron wave functions vanish near the crystal edges), because periodic boundary conditions greatly simplify the analysis of electron dynamics while still giving an excellent description of electrons *inside* the crystal. In other words, we can only use periodic boundary conditions to describe electrons in the *interior* of the crystal, where surface effects are not important. Surface effects require more realistic boundary conditions, but these fall beyound the scope of our course.

- Periodic boundary conditions allow us to write the wave function of electron in the crystal in the form

$$\psi(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k} \cdot \boldsymbol{r}},$$

where $\boldsymbol{k}$ is the electron's wave vector and V is the crystal's volume. The periodic boundary conditions in Equations 5.2 to 5.4 then require

$$e^{ik_x L_x} = 1 \qquad e^{ik_y L_y} = 1 \qquad e^{ik_z L_z} = 1,$$

which implies the wave vector components are discretized according to

$$k_x = \frac{2\pi}{L_x} n_x \qquad k_y = \frac{2\pi}{L_y} n_y \qquad k_z = \frac{2\pi}{L_z} n_z, \qquad \text{where } n_x, n_y, n_z \in \mathbb{Z}. \tag{5.5}$$

- Finally, we note that, in the free electron model, the electron wavefunctions are eigenfunctions of the Hamiltonian $H = \frac{p^2}{2m}$, i.e.

$$H\psi_{\boldsymbol{k}}(\boldsymbol{r}) = E\psi_{\boldsymbol{k}}(\boldsymbol{r}), \qquad E_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m}, \qquad H = \frac{p^2}{2m}.$$

- The *density of states*, denoted by $g(E)$, is the number N of available electron states in the energy range $E, E + \mathrm{d}E$ per unit energy per unit volume. In symbols, this reads

$$g(E) = \frac{1}{V}\frac{\mathrm{d}N(E, E + \mathrm{d}E)}{\mathrm{d}E} \tag{5.6}$$

In practice, we will write only $N(E)$, with the implicit understanding that $N(E)$ formally means $N(E, E + \mathrm{d}E)$.

5.3 Density of States

Derive the free electron density of states $g(E)$ in three, two, and one dimensions.

5.3.1 Three Dimensions

- Our plan is to compute each of the expressions in Equation 5.6 term by term, and then assemble these pieces into the final expression for $g(E)$.

- First, we note that periodic boundary conditions require the electron wave vector components k_x, k_y, k_z are discretized as in Equation 5.5. Thus, the electron energy eigenstates are also discrete. We denote the volume of a *single* state in $\boldsymbol{k}$ space by

$$V_1^* = \frac{(2\pi)^3}{V},$$

where V is the crystal's volume (in position space). In terms of the single-state volume V_1^*, the total number of electron states in a crystal is

$$N = \frac{V^*}{V_1^*}, \tag{5.7}$$

where V^* denotes the total volume of the $\boldsymbol{k}$ space spanned by the electron's energy eigenstates.

- Next, we recall that a free electron's energy and wave vector are related by

$$E = \frac{\hbar^2 k^2}{2m}.$$

From $E = E(|\boldsymbol{k}|)$ (i.e. E depends only on wave vector magnitude k and not dirction), it follows that surfaces of constant energy are spheres of radius k in $\boldsymbol{k}$ space. Thus, every electron energy eigenvalue E_k may be associated with a corresponding sphere of radius k in $\boldsymbol{k}$ space.

- Next, we aim to find an expression for the number $\mathrm{d}N$ of electron states in the energy range $(E, E + \mathrm{d}E)$. In $\boldsymbol{k}$ space, these two energies correspond to spheres with radii

$$k(E) = \frac{2mE}{\hbar^2} \qquad \text{and} \qquad k(E + \mathrm{d}E) = \frac{2m(E + \mathrm{d}E)}{\hbar^2}.$$

The volume $\mathrm{d}V^*$ in $\boldsymbol{k}$ space between these two spheres is

$$\mathrm{d}V^* = 4\pi k^2 \, \mathrm{d}k,$$

from which we can find the desired number of states $\mathrm{d}N$ from Equation 5.7, i.e.

$$\mathrm{d}N(E) = 2 \cdot \frac{\mathrm{d}V^*}{V_1^*} = 2 \cdot \frac{4\pi k^2 \, \mathrm{d}k}{(2\pi)^3/V} = \frac{V k^2 \, \mathrm{d}k}{\pi^2}.$$

Important: the factor of two accounts for the electron's two possible spin states.

- Return to calculation of $g(E)$; we have so far found the numerator $\mathrm{d}N(E)$, and our current (incomplete) expression for density of states reads

$$g(E) = \frac{1}{V}\frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{1}{V}\cdot\left(\frac{V k^2}{\pi^2}\frac{\mathrm{d}k}{\mathrm{d}E}\right) = \frac{k^2}{\pi^2}\frac{\mathrm{d}k}{\mathrm{d}E}.$$

Next, using the free-electron dispersion relation $\frac{\mathrm{d}E}{\mathrm{d}k} = \frac{\hbar^2 k}{m}$, the density of states becomes

$$g(E) = \frac{k^2}{\pi^2}\cdot\frac{m}{\hbar^2 k} = \frac{m}{\pi^2\hbar^2}k = \frac{m}{\pi^2\hbar^2}\sqrt{\frac{2mE}{\hbar^2}} = \frac{\sqrt{2m^3}}{\pi^2\hbar^3}\sqrt{E}.$$

Note that (at least in three dimensions) the free electron density of states increases as $g(E) \sim \sqrt{E}$.

5.3.2 Two Dimensions

- In two dimensions, we model a crystal as a rectangle with side lengths L_x and L_y and area S. By analogy with the three-dimensional case, a free electron's energy and wave function read

$$E(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m} \qquad \text{and} \qquad \psi_\kappa = \frac{1}{\sqrt{S}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}},$$

while the two-dimensional density of states reads

$$g_{2\mathrm{D}}(E) = \frac{1}{S}\frac{\mathrm{d}N(E)}{\mathrm{d}E}.$$

- The volume of a single electron eigenstate in two-dimensional $\boldsymbol{k}$ space is now

$$V_1^* = \frac{(2\pi)^2}{S},$$

and the number of states N in a $\boldsymbol{k}$ space volume V^* is

$$N = \frac{V^*}{V_1^*} = \frac{V^*}{(2\pi)^2/S}.$$

- Next, as in the three dimensional case, we find the volume between two closely spaced energies E and $E + \mathrm{d}E$. In two dimensions, these energies correspond to circles with radii

$$k(E) = \frac{2mE}{\hbar^2} \qquad \text{and} \qquad k(E + \mathrm{d}E) = \frac{2m(E + \mathrm{d}E)}{\hbar^2}.$$

The volume V^* in $\boldsymbol{k}$ space between these circles is

$$\mathrm{d}V^* = 2\pi k\,\mathrm{d}k,$$

from which we find the desired number of states $\mathrm{d}N$ according to

$$\mathrm{d}N(E) = 2 \cdot \frac{\mathrm{d}V^*}{V_1^*} = 2 \cdot \frac{2\pi k\,\mathrm{d}k}{(2\pi)^2/S} = \frac{Sk}{\pi}\,\mathrm{d}k.$$

Using $\mathrm{d}N(E)$, the corresponding density of states $g(E)$ is

$$g(E) = \frac{1}{S}\frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{1}{S} \cdot \left(\frac{Sk}{\pi}\frac{\mathrm{d}k}{\mathrm{d}E} \right) = \frac{k}{\pi}\frac{\mathrm{d}k}{\mathrm{d}E}.$$

Finally, using $\mathrm{d}E = \hbar^2 k\,\mathrm{d}k/m$, the density of states reads

$$g(E) = \frac{k}{\pi} \cdot \frac{m}{\hbar^2 k} = \frac{m}{\pi\hbar^2} \tag{5.8}$$

We immediately note that the two-dimensional density of states is independent of energy. However, since the density of states is undefined for electrons with negative energy, a more complete expression would read

$$g_{2\mathrm{D}}(E) = \frac{m}{\pi\hbar^2}H(E),$$

where $H(E)$ is the Heaviside step function.

5.3.3   One Dimensional

- In one dimension, we model a crystal as a line of length L. In this case, two closely-spaced energies E and $E + \mathrm{d}E$ correspond to two closely spaced points in one-dimensional k states with wave vectors $k(E)$ and $k(E) + \mathrm{d}k$.

- The spacing between states in one-dimensional k space is

$$V_1^* = \frac{2\pi}{L}.$$

- Spacing k space between energies E and $E + \mathrm{d}E$ is

$$\mathrm{d}V^* = 2\,\mathrm{d}k.$$

The factor two arises because any two wave vectors $\pm k$ correspond to the same energy E.

- The number of electrons in the energy range E and $E + \mathrm{d}E$ is then

$$\mathrm{d}N = \frac{\mathrm{d}V^*}{V_1^*} = \frac{2\,\mathrm{d}k}{2\pi/L} = \frac{L}{\pi}\,\mathrm{d}k,$$

and the corresponding density of states is

$$g_{1\mathrm{D}}(E) = 2 \cdot \frac{1}{L}\frac{\mathrm{d}N(E)}{\mathrm{d}E} = \frac{2}{L} \cdot \left(\frac{L}{\pi}\frac{\mathrm{d}k}{\mathrm{d}E} \right) = \frac{2}{\pi}\frac{\mathrm{d}k}{\mathrm{d}E},$$

where we have again added a factor of two to account for the electron's two spin states. Finally, using $E(k) = \frac{\hbar^2 k^2}{2m}$, the density of states comes out to

$$g_{1\mathrm{D}}(E) = \frac{2}{\pi}\frac{\mathrm{d}k}{\mathrm{d}E} = \frac{2}{\pi}\frac{m}{\hbar^2 k} = \frac{2m}{\pi\hbar^2}\sqrt{\frac{\hbar^2}{2mE}} = \frac{\sqrt{2m}}{\pi\hbar}\frac{1}{\sqrt{E}}.$$

In other words, $g(E)$ diverges for small energies in one dimension.

- Finally, we note that density of states for free electron in arbitrary dimension d takes the general form

$$g_d(E) \propto E^{\frac{d-2}{2}} H(E), \tag{5.9}$$

where the Heaviside function ensures that the density of states is zero for negative energies.

5.4 Temperature Dependence of the Chemical Potential (For an Electron Gas)

- Once we know the density of states $g(E)$ for electrons in a conductor, we can use $g(E)$ to derive many other interesting quantities describing the electrons.

  For example, the number N of electrons in the crystal is given by

$$N = V \int_{-\infty}^{\infty} g(E) f(E) \, dE,$$

where $f(E)$ is the Fermi-Dirac distribution, and gives the number of occupied electron states at a given energy. Note that in the above expression $g(E)$ represents *available* states, which we then multiply by the number of actually *occupied* states, encoded by $f(E)$, to find total number of electrons N.

- For review, the Fermi-Dirac distribution reads

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

where μ is a parameter called the *chemical potential*. Note that $f(E) = 1/2$ when $E = \mu$. The chemical potential at zero temperature, is given a special name and symbol—the *Fermi energy* $E_{\mathrm{F}} \equiv \mu\big|_{T=0}$.

- At zero temperature, where $\beta \to \infty$, the Fermi-Dirac distribution approaches an inverted step function of the form

$$\lim_{T \to 0} f(E) = \begin{cases} 1 & E \in (0, E_{\mathrm{F}}) \\ 0 & E \in (E_{\mathrm{F}}, \infty). \end{cases}$$

Note that $f(E) = 0$ for $E < 0$ (at any temperature), which simply encodes the absence of non-physical electron states with negative energy. Frim the simplified zero-temperature Fermi-Dirac distribution, the number of electrons in the crystal at $T = 0\,\mathrm{K}$ is given by

$$N\big|_{T=0} = V \int_0^{E_{\mathrm{F}}} g(E) \, dE$$

Assuming the crystal is isolated from its surroundings, the number electrons in the crystal is conserved when the temperature increases—we cannot just "destroy" or "create" electrons by changing the temperature. As a result, the number $N(T > 0)$ for non-zero energy should equal $N\big|_{T=0}$, i.e.

$$N(T > 0) = V \int_0^{\infty} g(E) f(E) \, dE \equiv V \int_0^{E_{\mathrm{F}}} g(E) \, dE = N\big|_{T=0}. \tag{5.10}$$

From here, without derivation, we quote the lecture result

$$\mu(T) \approx E_{\mathrm{F}} - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_{\mathrm{F}})}{g(E_{\mathrm{F}})}, \tag{5.11}$$

which gives an (approximate) expression for the chemical potential as a function of temperature. The result is derived using the Sommerfeld expansion, which holds in the regime $k_B T \ll E_{\mathrm{F}}$.

- To find chemical potential, we thus need expressions for the ratio $g'(E_{\mathrm{F}})/g(E_{\mathrm{F}})$, which we find from the general d-dimensional formula in Equation 5.9.

$$g(E) = A_d E^{\frac{d-2}{2}} H(E) \qquad \text{and} \qquad g'(E) = A_d \frac{d-2}{2} E^{\frac{d-2}{2}} \cdot E^{-1} H(E)$$

The ratio $g'(E_{\mathrm{F}})/g(E_{\mathrm{F}})$ in d dimensions is thus

$$\frac{g'(E_{\mathrm{F}})}{g(E_{\mathrm{F}})} = \frac{d-2}{2} \frac{1}{E_{\mathrm{F}}},$$

while from Equation 5.11, the chemical potential in d dimensions reads

$$\mu(T) = E_{\mathrm{F}} - \frac{\pi^2}{6}(k_B T)^2 \frac{d-2}{2} \frac{1}{E_{\mathrm{F}}} = E_{\mathrm{F}} \left[1 - \frac{\pi^2}{6} \frac{d-2}{2} \left(\frac{k_B T}{E_{\mathrm{F}}} \right)^2 \right].$$

- Finally, in our problem's concrete one-, two- and three-dimensional cases, $\mu(T)$ reads

$$d = 3: \quad \mu(T) = E_{\mathrm{F}} \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_{\mathrm{F}}} \right)^2 \right]$$

$$d = 2: \quad \mu(T) = E_{\mathrm{F}}$$

$$d = 1: \quad \mu(T) = E_{\mathrm{F}} \left[1 + \frac{\pi^2}{12} \left(\frac{k_B T}{E_{\mathrm{F}}} \right)^2 \right].$$

Note the varied behavior behavior in different dimensions!

6   Sixth Exercise Set

6.1   Theory: Two-Dimensional Expansion of Chemical Potential

- In the previous exercise set, we found that the Sommerfeld expansion predicted a two-dimensional chemical potential

$$\mu(T) = E_{\text{F}} \qquad (2\text{D}, \ k_B T \ll E_{\text{F}}).$$

  This result is not fully correct. Although $\mu(T) = \text{constant} = E_{\text{F}}$ is a good low-temperature approximation, formally, even in two dimensions, the chemical potential is temperature dependent, i.e. $\mu = \mu(T)$.

- Quick note on why the Sommerfeld expansion predicts a constant 2D chemical potential: the Sommerfeld expansion involves a Taylor expansion of the density of states $g(E)$ about the chemical potential μ in the form

$$g(E) = g(\mu) + (E - \mu)g'(\mu) + \cdots .$$

  Because the two-dimensional density of states is constant, (i.e. $g_{2\text{D}}(E) = \text{constant}$; see Equation 5.8), the Sommerfeld expansion will read simply

$$g(E) = g(\mu)$$

  for all orders of expansion. Thus, by construction, the Sommerfeld expansion will always predict $g(E) = g(\mu)$ in 2D. Because $g(E)$ is constant, the term $\frac{g'(E_{\text{F}})}{g(E_{\text{F}})}$ in Equation 5.11 will always come out to zero, which leads to $\mu(T) = E_{\text{F}} = \text{constant}$.

A More Accurate Approximation for $\mu(T)$

- We begin our analysis with by requiring conservation of electron number in the crystal at both zero and not-zero temperature. Just like in Equation 5.10, this requirement reads

$$N(T)\big|_{T=0} = \int_0^{E_{\text{F}}} g(E)\,\mathrm{d}E = \int_0^\infty g(E)f(E)\,\mathrm{d}E = \int_0^\infty \frac{g(E)\,\mathrm{d}E}{e^{\beta(E-\mu)} + 1} = N(T)\big|_{T>0}.$$

  Since $g(E)$ is constant in two dimensions, we can cancel it from both sides and get

$$\int_0^{E_{\text{F}}} \mathrm{d}E = E_{\text{F}} = \int_0^\infty \frac{\mathrm{d}E}{e^{\beta(E-\mu)} + 1}.$$

- The integral is solved with the substitution $u = e^{\beta(E-\mu)} + 1$; the solution reads

$$E_{\text{F}} = \frac{1}{\beta} \int_{e^{-\beta\mu}+1}^\infty \frac{\mathrm{d}u}{u(u-1)} = \frac{1}{\beta} \int_{e^{-\beta\mu}+1}^\infty \left(-\frac{1}{u} + \frac{1}{u-1} \right) \mathrm{d}u = \frac{1}{\beta} \ln \frac{u-1}{u} \bigg|_{e^{-\beta\mu}+1}^\infty$$

$$= \frac{1}{\beta} \ln\left(1 + e^{\beta\mu} \right).$$

  We then solve this result for μ, which, after a few steps of algebra, comes out to

$$\mu = \frac{1}{\beta} \ln\left(e^{\beta E_{\text{F}}} - 1 \right).$$

- Next, a slight trick. First, using the logarithm identity $\ln(AB) = \ln A + \ln B$, we rearrange the result $\mu = \frac{1}{\beta} \ln(e^{\beta E_F} - 1)$ as follows:

$$\mu = \frac{1}{\beta} \ln \left[e^{\beta E_F} (1 - e^{-\beta E_F}) \right] = \frac{1}{\beta} \left[\beta E_F + \ln \left(1 - e^{-\beta E_F} \right) \right].$$

Under the assumption $k_B T \ll E_F$ the second term, using $\ln(1-x) \approx -x$ becomes

$$\mu \approx E_F - \frac{1}{\beta} e^{-\beta E_F} = E_F - k_B T e^{-\frac{E_F}{k_B T}}.$$

This is the desired, more accurate expression for $\mu(T)$ in two dimensions.

6.2 The Kronig-Penney Model

6.2.1 Introduction to the Kronig-Penney Model

- The Kronig-Penney model serves as our introduction to electrons in a periodic potential (so far we have considered only free electrons). The Kronig-Penney model is a one-dimensional toy model with an analytic solution. Although it is oversimplified, the model is useful in that it predicts an energy band structure.

- Consider a one-dimensional lattice with lattice constant a and periodic potential $V(x + a) = V(x)$. The Kronig-Penney model models the potential as a series of upward-point delta functions of height λ. In symbols, this potential reads

$$V(x) = \sum_n \lambda \delta(x - na).$$

Note that V is constant (and without loss of generality equal to zero) everywhere except at $x = na$ for $n \in \mathbb{Z}$.

- We will describe electrons in the lattice with wavefunction ψ_n, where ψ_n denotes the wavefunction for an electron on the n-th lattice site. Our goal is to solve the stationary Schrödinger equation

$$H\psi(x) = -\frac{\hbar^2}{2m} \psi''(x) + V(x)\psi(x) = E\psi(x)$$

for the electron's energy eigenvalues and eigenfunctions.

- Recall from the previous semester's course in quantum mechanics that neighboring wave functions must be continuous at lattice points $x = na$. In symbols, this boundary condition reads
$$\psi_{n-1}(na) = \psi_n(na). \tag{6.1}$$

Additionally, specific to a delta function potential, the wave function derivatives must satisfy the boundary condition

$$\psi'_n(na) = \psi'_{n-1}(na) = \frac{2m\lambda}{\hbar^2} \psi_n(na) \equiv 2Q\psi_n(na), \tag{6.2}$$

where we have defined the constant $Q = \frac{m\lambda}{\hbar^2}$, which has units of length^{-1}.

- Since the potential $V(x)$ is constant nearly everywhere along the real line, we will use the plane-wave ansatz

$$\psi_n(x) = A_n e^{iqx} + B_n e^{-iqx}, \quad \text{where } q = \sqrt{\frac{2mE}{\hbar^2}},$$

where the quantity q is just the electron wave number (the same quantity we have often denoted by k). Note that an electron wave function ψ_n has the same functional form at all lattice sites—only the plane wave amplitudes A_n and B_n change from site to site.

- Next, we substitute the ansatz ψ_n into the boundary conditions. The continuity condition in Equation 6.1 results in

$$A_{n-1}e^{-qna} + B_{n-1}e^{-iqna} = A_n e^{iqna} + B_n e^{-iqna}, \tag{6.3}$$

while the derivative condition in Equation 6.2 produces

$$iq(A_n e^{iqna} - B_n e^{-iqna}) - iq(A_{n-1}e^{iqna} - B_{n-1}e^{-iqna}) =$$
$$= 2Q(A_n e^{iqna} + B_n e^{-iqna}) \tag{6.4}$$

Letting N denote the number of crystal lattice sites, periodic boundary conditions require

$$\psi(x + Na) = \psi(x). \tag{6.5}$$

Together with this periodic boundary condition, Equations 6.3 and 6.4 represent coupled system of $2N$ linear equations with $2N$ amplitude terms A_n and B_n where $n = 1, \ldots, N$. Note that, in a macroscopic crystal, we have $N \sim 10^{26}$. That's a lot of equations! This trick is to take advantage of the crystal's translation symmetry; this is formalized by Bloch's theorem, which we now review.

6.2.2 Review of Bloch's Theorem

- We first define the translation operator T according to the relationship

$$T\psi(x) = \psi(x + a).$$

In other words, T translates a wavefunction by a distance a, which in our case is the crystal's lattice constant. Interpretted physically, T simply moves a wavefunction from one lattice point to the next.

- Applied to the periodic potential $V(x)$, the operator T produces

$$TV(x) = V(x + a)T \equiv V(x)T,$$

since $V(x + a) \equiv V(x)$ by the definition of a periodic potnetial. Meanwhile, when applied to an electron's kinetic energy, T gives

$$T\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}T.$$

The derivative is unchanged because a constant shift of x does not affect derivatives of x. Combining the kinetic and potential energy results, the translation operator's effecton on an electron's Hamiltonian is

$$TH = HT \implies [H, T] = 0,$$

i.e. T commutes with an electron's Hamiltonian in a periodic potential.

- Because H and T commute, we can find electron states that are eigenstates of both H and T. These states must satisfy the eigenvalue equation

$$T\psi(x) = \psi(x + a) = c\psi(x),$$

where we have used c for a translation operator eigenvalue to avoid conflict with the constant λ using the potential energy $V(x)$. If we apply T to an electron wavefunction ψ a total of N times, the result is

$$T^N\psi(x) = c^N\psi(x).$$

Meanwhile, from periodic boundary conditions $\psi(x + Na) = \psi(x)$ (Eq. 6.5), we have

$$T^N\psi(x) = \psi(x + Na) = \psi(x).$$

We can then conclude

$$c^N\psi(x) = \psi(x) \implies c^N = 1 \quad \text{and} \quad |c| = 1.$$

Note that the translation eigenvalue c is in general a complex quantity, which we will write in the form

$$c = e^{ika}, \quad k \in \mathbb{R}. \tag{6.6}$$

The formulation in terms of k is just an equivalent way of encoding the eignevalue c, which turns out to be more useful in practice.

Keep in mind that this k is used to defined the eigenvalues of the translation operator T, while the electron wave vectors—the eigenvalues of the momentum operator—are given by q.

- We now aim to find an expression for k. Using $c^N = 1$ we have

$$c^N = (e^{ika})^N = 1 \implies e^{iNka} = 1 \implies Nka = 2\pi n \implies k = \frac{2\pi}{Na}n,$$

where $n \in \mathbb{Z}$. Next, we imagine the transformation $ka \to ka + 2\pi m$, where $m \in \mathbb{Z}$. In this case, using $c = e^{ika}$, the eigenvalue c transforms as

$$c = e^{ika} \to e^{i(ka+2\pi m)} = e^{ika} = c,$$

since the complex exponential function has periodi 2π. It follows that, c is unchanged under a shift $ka \to ka + 2\pi m$. We can thus restrict our entire analysis of the translation operator the interval $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$. Since the eigenvalue c is unchanged under transformations $ka \to ka + 2\pi m$, the interval $k \in \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$ encodes all possible c, i.e. all possible eigenvalues of the operator T.

- For the purposes of our course, Bloch's theorem states that any electron wavefunction ψ that is both an eigenfunction of the translation operator T and Hamiltonian H takes the general form

$$T\psi(x) = \psi(x + a) = e^{ika}\psi(x).$$

6.2.3 Returning to the Kronig-Penney Model

- We now return to the electron wave function ansatz, which we write as

$$\psi_{n-1}(x) = A_{n-1}e^{iqx} + B_{n-1}e^{-iqx},$$

and apply Bloch's theorem $T\psi(x) = \psi(x+a) = e^{ika}\psi(x)$, to ψ_{n-1}, which produces

$$A_n e^{iq(x+a)} + B_n e^{-iq(x+a)} = e^{ika}\left(A_{n-1}e^{iqx} + B_{n-1}e^{-iqx}\right).$$

This equation must hold for all x in the region $[x, x+a]$. Since e^x and e^{-x} are linearly independent, we can separately equate coefficients of the A_n and B_n terms to get

$$A_n e^{iqa}e^{iqx} = A_{n-1}e^{ika}e^{iqx} \qquad \text{and} \qquad B_n e^{-iqa}e^{-iqx} = B_{n-1}e^{ika}e^{-iqx}.$$

After simplifying and rearranging, these two equalities imply

$$A_{n-1} = A_n e^{i(q-k)a} \qquad \text{and} \qquad B_{n-1} = B_n e^{-i(q+k)a}.$$

- We then substitute these expressions for A_{n-1} and B_{n-1} into the continuity condition in Equation 6.3, producing

$$A_n e^{i(q-k)a}e^{iqna} + B_n e^{-i(q+k)a}e^{-iqna} = A_n e^{iqna} + B_n e^{-iqna}. \tag{6.7}$$

Similarly, substituting the expressions for A_{n-1} and B_{n-1} into the derivative condition in Equation 6.4 produces

$$iq(A_n e^{iqna} - B_n e^{-iqna}) - iq(A_n e^{i(q-k)a}e^{iqna} - B_n e^{-i(q+k)a}e^{-iqna}) =$$
$$= 2Q(A_n e^{iqna} + B_n e^{-iqna}). \tag{6.8}$$

Note that these two equations contain only A_n and B_n (and not also A_{n-1} and B_{n-1} like Equations 6.3 and 6.4). In other words, using the recursive relationships between the amplitudes A_n and A_{n-1}, and between B_n and B_{n-1}, we reduced a system of $2N$ equations into a realistically solvable system of two equations with two unknowns.

- The system of equations for A_n and B_n is homogeneous, which means the system has a non-trivial solution if the corresponding determinant is zero. The next step in the analysis would be to write Equations 6.7 and 6.8 as a matrix system, and require the determinant equal zero. This involves a lot of tedious algebra, so we will only quote the result: without proof, the above requirement of zero determinant produces

$$\cos ka = \cos qa + \frac{Qa}{qa}\sin qa \tag{6.9}$$

Note that the above Kronig-Penney equation is not general, but relies on a Taylor expansion in the limit $Qa \ll 1$.

- With Equation 6.9 known, the subsequent analysis procedure reads:

  - Choose an energy E

– Use the value of E to compute the electron wave number q from

$$q = \sqrt{\frac{2mE}{\hbar^2}}$$

– Compute the RHS of Equation 6.9. Determine if the absolute value of the RHS is less than one by absolute value, since $\cos ka \in [-1, 1]$. If the RHS is in the range $[-1, 1]$, there exists and energy eigenstate at E. If the RHS is outside the range $[-1, 1]$, then no electron energy states exist at the energy E.

In other words, the Kronig-Penney model predicts an *energy band structure* for electron energy eigenstates in a one-dimensional crystal with a periodic potential— only certain energies, for which the RHS of Equation 6.9 falls in the range $[-1, 1]$, can correspond to electron eigenstates in the crystal, while forbidden energies fall in the so-called *band gap*.

7 Seventh Exercise Set

7.1 The Kronig-Penney Model for Nearly-Free Electrons

- In the nearly free-electron model, the electron energy is given by

$$E \approx \frac{\hbar^2 q^2}{2m} = \frac{\hbar^2 (qa)^2}{2ma^2},$$

where q denotes the electron's wave number and we have introduced the dimensionless variable qa instead of q in the second equality.

- As discussed at the end of the previous exercise set, energy band gaps occur for those values of qa for which the RHS of the Kronig-Penney equation (Eq. 6.9) is larger than one; these gaps occur for $qa \in (n\pi, \epsilon_n)$, where the ϵ_n are small, to-be-determined quantities encoding the width of the band gap.

  In general, the energy gap between the n-th and $(n+1)$-th energy bands is

$$\Delta E_n = E(qa)\big|_{n\pi+\epsilon_n} - E(qa)\big|_{n\pi} = \frac{\hbar^2}{2ma^2} \left[(n\pi + \epsilon_n)^2 - (n\pi)^2 \right]$$

$$= \frac{\hbar^2}{2ma^2} \left[(n\pi)^2 + 2n\pi\epsilon_n - (n\pi)^2 + \mathcal{O}(\epsilon_n^2) \right].$$

  We will ignore the higher-order terms of order $\mathcal{O}(\epsilon_n^2)$, in which case the band gap is simply

$$\Delta E_n \approx \frac{\hbar^2 n\pi\epsilon_n}{ma^2}$$

  In other words, if we know the dimensionless wave number spacing ϵ_n between band gaps, we can find the value of energy gaps ΔE_n.

  Note: the index n in the expression for ΔE_n indexes the band gap number, and is unrelated to the index $n = 1, 2, \ldots, N$ used in the previous exercise set to index the lattice sites in the one-dimensional crystal.

- We now aim to find the values of qa for which band gaps occur. The first step is to find those qa for which the RHS of the Kronig-Penney equation equals one or negative one. For review, the Kronig-Penney equation (Eq. 6.9), reads

$$\cos(ka) = \cos(qa) + \frac{Qa}{qa}\sin(qa), \qquad \text{where } Q = \frac{m\lambda}{\hbar^2}, \quad Qa \ll 1.$$

  We will find the desired qa by expanding the Kronig-Penney equation near the band gap borders where $qa = n\pi + \epsilon_n$. Approximating $\cos(ka)$ as $\cos(n\pi) = (-1)^n$, the expansion reads

$$(-1)^n = \cos(n\pi + \epsilon_n) + \frac{Qa}{n\pi + \epsilon_n}\sin(n\pi + \epsilon_n).$$

  Assuming $\epsilon_n \ll 1$, we then expand the sine and cosine terms about $n\pi$ to get

$$(-1)^n \approx (-1)^n \left(1 - \frac{\epsilon_n^2}{2} \right) + \frac{Qa}{n\pi + \epsilon_n}(-1)^n \epsilon_n + \mathcal{O}(\epsilon_n^3).$$

We then further expand the denominator of $\frac{Qa}{n\pi + \epsilon_n}$ in the limit $\epsilon_n \ll 1$, producing

$$(-1)^n \approx (-1)^n \left(1 - \frac{\epsilon_n^2}{2}\right) + \frac{Qa}{n\pi}(-1)^n \epsilon_n + \mathcal{O}(\epsilon_n^2 Qa) + \mathcal{O}(\epsilon_n^3).$$

Finally, we cancel $(-1)^n$ from both sides and drop the higher-order terms $\mathcal{O}(\epsilon_n^2 Qa)$ and $\mathcal{O}(\epsilon_n^3)$ to get

$$1 = 1 - \frac{\epsilon_n^2}{2} + \frac{Qa}{n\pi}\epsilon_n \implies \epsilon_n^2 - \frac{2Qa}{n\pi}\epsilon_n = 0.$$

The resulting quadratic equation has two solutions; these are

$$\epsilon_n = 0 \qquad \text{and} \qquad \epsilon_n = \frac{2Qa}{n\pi}.$$

The solution $\epsilon_n = 0$ represents the left boundary of the band gap at $qa = n\pi$, while the second solution represents the right boundary at $qa = n\pi + \epsilon_n$.

- Using the just-derived ϵ_n, the energy band gaps for nearly-free electrons in the Kronig-Penney model are thus

$$\Delta E_n = \frac{\hbar^2 n\pi}{ma^2} \cdot \frac{2Qa}{n\pi} = \frac{2\hbar^2 Q}{ma} = \frac{2\hbar^2 m\lambda}{ma\hbar^2} = \frac{2\lambda}{a}. \tag{7.1}$$

Note that all band gaps are the same size. This is a consequence of the Kronig-Penney model's assumption of identical delta function potentials at each lattice site. In general, a more complex model using different potentials at different lattice sites would result in different energy gaps between different electron energy bands.

7.2 Theory: Review of the Free Electron Model

7.2.1 Electron Wave Function in Three Dimensions

- In a three-dimensional crystal, the energy of a free electron with crystal momentum $\boldsymbol{k}$ is

$$E_{\boldsymbol{k}}^{(0)} = \frac{\hbar^2 \boldsymbol{k}^2}{2m} \tag{7.2}$$

In the nearly-free electron model, the wave function of an (nearly-free) electron with crystal momentum $\boldsymbol{k}$ reads

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{K}} c_{\boldsymbol{k}-\boldsymbol{K}} e^{i(\boldsymbol{k}-\boldsymbol{K})\cdot\boldsymbol{r}},$$

where $\boldsymbol{K}$ is an element of the crystal's reciprocal lattice and the $c_{\boldsymbol{k}-\boldsymbol{K}}$ are to-be-determined coefficients. Finding a nearly-free electron's wavefunction essentially reduces to computing the coefficients $c_{\boldsymbol{k}-\boldsymbol{K}}$.

- Next, we write the crystal's periodic potential $U(\boldsymbol{r})$—I am using U to avoid conflict with volume V—in the form

$$U(\boldsymbol{r}) = \sum_{\boldsymbol{K}} U_{\boldsymbol{K}} e^{i\boldsymbol{K}\cdot\boldsymbol{r}}, \quad \text{where } U_{\boldsymbol{K}} = \frac{1}{V_0} \iiint_{\text{uc}} U(\boldsymbol{r}) e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} \, dV, \tag{7.3}$$

and V_0 is the volume of single unit cell (in position space) and the triple integral runs over a single unit cell. We find the coefficients $c_{\boldsymbol{k}-\boldsymbol{K}}$, and thus the electron wave function, by solving the system of equations

$$\left(E^{(0)}_{\boldsymbol{k}-\boldsymbol{K}} - E\right) c_{\boldsymbol{k}-\boldsymbol{K}} + \sum_{\boldsymbol{K}'} c_{\boldsymbol{k}-\boldsymbol{K}'} U_{\boldsymbol{K}'-\boldsymbol{K}} = 0. \tag{7.4}$$

For weak potentials we can solve the system of equations perturbatively, which we will do in practice over the course of the next few exercise sets.

7.2.2 Band Gap in One Dimension

- We now consider how to find the band gap between two electron energy bands in a one-dimensional crystal.

- First, we need to decide which reciprocal lattice vectors K to sum over in equation 7.4. To do this, we first draw the parabolic $E(k)$ dispersion relation for free electrons, which are centered at reciprocal lattice vectors $K_n = \frac{2\pi}{a}n$ for $n \in \mathbb{Z}$.

  The intersections of difference K_n parabolas at the edges of the first Brillioun zone at $k = \pm\frac{\pi}{a}$ correspond to positions of band gaps when electrons are no long free.

  To determine the relevant reciprocal lattice vectors for the e.g. m-th band gap, find the two K_n the create the m-th intersection.

- For concreteness, we will consider the band gap between the ground state and first excited energy bands. The relevant $E(k)$ curves are those centered at $K_0 = 0$ (ground state band) and $K_1 = 2\pi/a$ (first excited band), which intersect at the edge of the Brillioun zone $k = \pi/a$. The energy at $E(\pi/a)$ is degenerate for free electrons.

  Thus, the relevant K_n for the first band gap are K_0 and K_1, and in Equation 7.4 we will sum over $K' \in \{K_0, K_1\}$.

- For the $E(k)$ curve centered at $K = K_0$, Equation 7.4 reads

$$\begin{aligned}
0 &= \left(E^{(0)}_{k-K_0} - E\right) c_{k-K_0} + \sum_{K' \in \{K_0, K_1\}} c_{k-K'} U_{K'-K_0} \\
&= \left(E^{(0)}_{k-K_0} - E\right) c_{k-K_0} + c_{k-K_0} U_{K_0-K_0} + c_{k-K_1} U_{K_1-K_0} = 0 \\
&= \left(E^{(0)}_{k-K_0} - E + U_0\right) c_{k-K_0} + c_{k-K_1} U_{K_1-K_0} = 0.
\end{aligned}$$

Meanwhile, for $K = K_1 = 2\pi/a$, Equation 7.4 reads

$$\begin{aligned}
0 &= \left(E^{(0)}_{k-K_1} - E\right) c_{k-K_1} + \sum_{K' \in \{K_0, K_1\}} c_{k-K'} U_{K'-K_1} \\
&= \left(E^{(0)}_{k-K_1} - E\right) c_{k-K_1} + c_{k-K_0} U_{K_0-K_1} + c_{k-K_1} U_{K_1-K_1} = 0 \\
&= \left(E^{(0)}_{k-K_1} - E + U_0\right) c_{k-K_1} + c_{k-K_0} U_{K_0-K_1} = 0.
\end{aligned}$$

We thus have a system of two equations for the two coefficients c_{k-K_0} and c_{k-K_1}. In one place, these are

$$\left(E^{(0)}_{k-K_0} - E + U_0\right) c_{k-K_0} + c_{k-K_1} U_{K_1-K_0} = 0 \tag{7.5}$$

$$\left(E^{(0)}_{k-K_1} - E + U_0\right) c_{k-K_1} + c_{k-K_0} U_{K_0-K_1} = 0. \tag{7.6}$$

- Next, we apply Equation 7.2 for free electron energy to the point of degeneracy $k = \pi/a$ and substitute in $K_0 = 0$ and $K_1 = 2\pi/a$ to get the equalities

$$E^{(0)}_{k-K_0} = E^{(0)}_{\pi/a} = \frac{\hbar^2(\pi/a)^2}{2m} \qquad \text{and} \qquad E^{(0)}_{k-K_1} = E^{(0)}_{-\pi/a} = \frac{\hbar^2(-\pi/a)^2}{2m} = E^{(0)}_{k-K_0}.$$

Because both energies are equal, we introduce the more compact notation

$$E^{(0)}_{k-K_0} = E^{(0)}_{k-K_1} \equiv E_0.$$

In terms of E_0, Equations 7.5 and 7.6 reduce to the simpler notation

$$(E_0 - E + U_0)c_{k-K_0} + U_{K_1-K_0}c_{k-K_1} = 0$$
$$(E_0 - E + U_0)c_{k-K_1} + U_{K_1-K_1}c_{k-K_0} = 0.$$

- In equivalent matrix form, the above system of equations reads

$$\begin{pmatrix} E_0 - E + U_0 & U_{K_1-K_0} \\ U_{K_0-K_1} & E_0 - E + U_0 \end{pmatrix} \begin{pmatrix} c_{k-K_0} \\ c_{k-K_1} \end{pmatrix} = 0.$$

This is a homogeneous system of equations, and thus has a non-trivial solution if the matrix's determinant equals zero; setting the determinant equal to zero and using the general identity $U_K = U^*_{-K}$ produces

$$(E^0 - E + U_0)^2 - U_{K_1-K_0}U^*_{-(K_1-K_0)} = (E^0 - E + U_0)^2 - |U_{K_1-K_0}|^2 = 0.$$

We then solve for the electron energy E, which comes out to

$$E_\pm = E_0 + U_0 \pm |U_{K_1-K_0}| \implies \Delta E = 2|U_{K_1-K_0}|. \tag{7.7}$$

In other words, finding the value of a band gap ΔE in general reduces to computing Fourier components U_K—we will do this in practice in the coming problems.

- Finally, note that we can set $U_0 = 0$ without loss of generality; doing so just corresponds to a constant shift of potential. In practice, the Fourier component U_0 is often left out for simplicity.

7.3 Kronig-Penney Model for Nearly-Free Electrons

Finding Band Gap

- From Equation 7.7, the energy gap between the ground state and first excited energy band in one-dimensional crystal is

$$\Delta E = 2|U_{K_1-K_0}|.$$

Finding band gap thus reduces to solving for the Fourier components U_K for a specific potential using Equation 7.3, which for review reads

$$U_{\boldsymbol{K}} = \frac{1}{V_0} \iiint_{\text{uc}} U(\boldsymbol{r})e^{-i\boldsymbol{K}\cdot\boldsymbol{r}} \, dV,$$

where V_0 is the volume of a unit cell.

- In the one-dimensional Kronig-Penney model the potential is $U(x) = \lambda\delta(x)$, while the volume of a unit cell is just the lattice constant a. In this case the Fourier components read

$$U_K = \frac{1}{a}\int_{0_-}^{a_-} U(x)e^{-iKx}\,\mathrm{d}x = \frac{1}{a}\int_{0_-}^{a_-} \lambda\delta(x)e^{-iKx} = \frac{\lambda}{a}, \qquad (7.8)$$

where the last equality follows from the integral definition of the delta function. From Equation 7.7, the band gap is then

$$\Delta E = 2|U_K| = \frac{2\lambda}{a}.$$

Note that this result agrees with the band gap $\Delta E_n = \frac{2\lambda}{a}$ found analytically in Equation 7.1, as we should expect.

Finding Wave Functions

- We now aim to find the wave functions associated with the electron energy eigenvalues E_+ and E_- in Equation 7.7. For review, we found these eigenvalues from the two equations

$$(E_0 - E + U_0)c_{k-K_0} + U_{K_1-K_0}c_{k-K_1} = 0$$
$$(E_0 - E + U_0)c_{k-K_1} + U_{K_1-K_1}c_{k-K_0} = 0,$$

or, in matrix form,

$$\begin{pmatrix} E_0 - E + U_0 & U_{K_1-K_0} \\ U_{K_0-K_1} & E_0 - E + U_0 \end{pmatrix} \begin{pmatrix} c_{k-K_0} \\ c_{k-K_1} \end{pmatrix} = 0. \qquad (7.9)$$

Again for review, the problem's relevant point of degeneracy occurrs at the edge of Brillioun zone $k = \pi/a$, and corresponds to an interesection of dispersion relations centered at the reciprocal lattice vectors $K_0 = 0$ and $K_1 = 2\pi/a$.

- From Equation 7.8, the Fourier components for the Kronig-Penney potential are simply $U_K = \lambda/a$ for all K in the reciprocal lattice, while from Equation 7.7, the eigenvalues $E_\pm$ are

$$E_\pm = E_0 + U_0 \pm |U_{K_1-K_0}| = E_0 + U_0 \pm \frac{\lambda}{a}.$$

- We first find the eigenvector for E_+. Substituting E_+ into Equation 7.9 produces

$$\begin{pmatrix} -\frac{\lambda}{a} & \frac{\lambda}{a} \\ - & - \end{pmatrix} \begin{pmatrix} c_{k-K_0} \\ c_{k-K_1} \end{pmatrix} = 0 \implies \begin{pmatrix} c_{k-K_0} \\ c_{k-K_1} \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}.$$

Meanwhile, substituting E_- into Equation 7.9 produces the eigenvector

$$\begin{pmatrix} \frac{\lambda}{a} & \frac{\lambda}{a} \\ - & - \end{pmatrix} \begin{pmatrix} c_{k-K_0} \\ c_{k-K_1} \end{pmatrix} = 0 \implies \begin{pmatrix} c_{k-K_0} \\ c_{k-K_1} \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}.$$

- Using the just-derived eigenvectors and the equation,

$$\psi_k(x) = \sum_{K\in\{K_0,K_1\}} c_{k-K}e^{i(k-K)x},$$

the wavefunctions corresponding to the eigenvalues E_+ and E_- are

$$\psi_+(x) \propto 1 \cdot e^{i(k-K_0)x} + 1 \cdot e^{i(k-K_1)x} = e^{i\frac{\pi}{a}x} + e^{-i\frac{\pi}{a}x} \propto \cos\frac{\pi x}{a}$$

$$\psi_-(x) \propto 1 \cdot e^{i(k-K_0)x} - 1 \cdot e^{i(k-K_1)x} = e^{i\frac{\pi}{a}x} - e^{-i\frac{\pi}{a}x} \propto \sin\frac{\pi x}{a}$$

The corresponding probability density functions are

$$\rho_+(x) \propto \cos^2\frac{\pi x}{a} \qquad \text{and} \qquad \rho_-(x) \propto \sin^2\frac{\pi x}{a}.$$

Note that, as should be expected, both functions have period a—the period of one-dimensional crystal lattice.

7.4   Band Gap in a FCC Crystal for Nearly-Free Electrons

Find the energy band gap at the vertex of a FCC crystal's first Brillioun zone.

- First, from Section 3.3.3, recall the FCC reciprocal lattice is a BCC lattice with lattice constant $4\pi/a$. Next, we aim to find the reciprocal lattice's first Brillioun zone—this is simply the reciprocal lattice's Wigner-Seitz cell, which we know from Section 2.4 to be a truncated octahedron.

- By convention, the vertices of an FCC lattice's first Brillioun zone's are denoted by the symbol W. We work in a coordinate system with the octahedron drawn in the plane of the page and k_x to the right, k_y into the page, and k_z vertically upward, and consider the vertex

$$\boldsymbol{W} = \frac{4\pi}{a}\left(\tfrac{1}{2}, 0, \tfrac{1}{4}\right).$$

We then identify the reciprocal lattice vectors $\boldsymbol{K}$ that are equidistant from the vertex $\boldsymbol{W}$; these are

$$\boldsymbol{K}_1 = \mathbf{0} \qquad \boldsymbol{K}_2 = \frac{4\pi}{a}(1,0,0) \qquad \boldsymbol{K}_3 = \frac{4\pi}{a}\left(\tfrac{1}{2}, -\tfrac{1}{2}, \tfrac{1}{2}\right) \qquad \boldsymbol{K}_4 = \frac{4\pi}{a}\left(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\right).$$

The origin is at $\boldsymbol{K}_1$—the center of the "first" BCC reciprocal lattice cell, $\boldsymbol{K}_2$ is the center site of the BCC cell immediately to the right, and $\boldsymbol{K}_3$ and $\boldsymbol{K}_4$ are two vertices of the BCC unit cell centered at the origin. By construction of the Wigner-Seitz cell as the set of points equidistant from the origin, the Brillioun zone vertex $\boldsymbol{W}$ must be equidistance from each of the four $\boldsymbol{K}$ points, i.e.

$$|\boldsymbol{W} - \boldsymbol{K}_1| = |\boldsymbol{W} - \boldsymbol{K}_2| = |\boldsymbol{W} - \boldsymbol{K}_3| = |\boldsymbol{W} - \boldsymbol{K}_4|.$$

- Recalling Equation 7.2, which for review reads

$$E_{\boldsymbol{k}}^{(0)} = \frac{\hbar^2 \boldsymbol{k}^2}{2m},$$

we see that the equality of the $|\boldsymbol{W} - \boldsymbol{K}_i|$ implies free electrons with wave vectors $\boldsymbol{W} - \boldsymbol{K}_i$ have equal energies, i.e.

$$E_{\boldsymbol{W}-\boldsymbol{K}_1}^{(0)} = E_{\boldsymbol{W}-\boldsymbol{K}_2}^{(0)} = E_{\boldsymbol{W}-\boldsymbol{K}_3}^{(0)} = E_{\boldsymbol{W}-\boldsymbol{K}_4}^{(0)} \equiv E_0.$$

From this we concluded that the point $\boldsymbol{W}$ is four-times degenerate, leading to the 4×4 eignevalue problem

$$
\begin{pmatrix}
E_0 + U_{\boldsymbol{K}_1 - \boldsymbol{K}_1} - E & U_{\boldsymbol{K}_2 - \boldsymbol{K}_1} & U_{\boldsymbol{K}_3 - \boldsymbol{K}_1} & U_{\boldsymbol{K}_4 - \boldsymbol{K}_1} \\
U_{\boldsymbol{K}_1 - \boldsymbol{K}_2} & E_0 + U_{\boldsymbol{K}_2 - \boldsymbol{K}_2} - E & U_{\boldsymbol{K}_3 - \boldsymbol{K}_2} & U_{\boldsymbol{K}_4 - \boldsymbol{K}_2} \\
U_{\boldsymbol{K}_1 - \boldsymbol{K}_3} & U_{\boldsymbol{K}_2 - \boldsymbol{K}_3} & E_0 + U_{\boldsymbol{K}_3 - \boldsymbol{K}_3} - E & U_{\boldsymbol{K}_4 - \boldsymbol{K}_3} \\
U_{\boldsymbol{K}_1 - \boldsymbol{K}_4} & U_{\boldsymbol{K}_2 - \boldsymbol{K}_4} & U_{\boldsymbol{K}_3 - \boldsymbol{K}_4} & E_0 + U_{\boldsymbol{K}_4 - \boldsymbol{K}_4} - E
\end{pmatrix}
\begin{pmatrix}
c_{\boldsymbol{W} - \boldsymbol{K}_1} \\
c_{\boldsymbol{W} - \boldsymbol{K}_2} \\
c_{\boldsymbol{W} - \boldsymbol{K}_3} \\
c_{\boldsymbol{W} - \boldsymbol{K}_4}
\end{pmatrix} = \mathbf{0}
$$

We will solve the problem for a general potential $U = U(\boldsymbol{r})$, and leverage the FCC reciprocal lattice's symmetry properties. More specifically, we will use that fact that for any symmetry operation $\mathbf{R}$ mapping the reciprocal lattice back into itself, the potential must obey

$$
U(\mathbf{R}\boldsymbol{r}) = U(\boldsymbol{r}). \tag{7.10}
$$

- Our first step is to find the Fourier components

$$
U_{\boldsymbol{K}} = \frac{1}{V_0} \iiint_{\text{uc}} U(\boldsymbol{r}) e^{-i\boldsymbol{K} \cdot \boldsymbol{r}} \, \mathrm{d}V,
$$

where V_0 is the volume of a single unit cell. For simplicity, we choose the global potential energy level such that $U_{\mathbf{0}} = 0$. Next, keeping in mind that the potential $U(\boldsymbol{r})$ is real (i.e. $U = U^*$), we note the complex conjugate identity

$$
U_{\boldsymbol{K}} = \left(U_{\boldsymbol{K}}^* \right)^* = \left(\frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{i\boldsymbol{K} \cdot \boldsymbol{r}} \, \mathrm{d}V \right)^* = U_{-\boldsymbol{K}}^*. \tag{7.11}
$$

Next, using the change of variables $\boldsymbol{r} \to -\boldsymbol{r}$, and keeping in mind that the potential $U(\boldsymbol{r})$ is invariant under spatial inversion (i.e. $U(-\boldsymbol{r}) = U(\boldsymbol{r})$) we note the identity

$$
U_{\boldsymbol{K}} = \frac{1}{V_0} \iiint U(-\boldsymbol{r}) e^{-i\boldsymbol{K} \cdot (-\boldsymbol{r})} \, \mathrm{d}V = \frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{i\boldsymbol{K} \cdot \boldsymbol{r}} \, \mathrm{d}V = U_{-\boldsymbol{K}}. \tag{7.12}
$$

Combining the results of Equations 7.11 and 7.12 produces

$$
U_{-\boldsymbol{K}} = U_{\boldsymbol{K}} = U_{-\boldsymbol{K}}^* \implies U_{-\boldsymbol{K}}, U_{\boldsymbol{K}} \in \mathbb{R}.
$$

In other words, the Fourier components $U_{\boldsymbol{K}}$ are real. From $U_{\boldsymbol{K}} = U_{-\boldsymbol{K}}$ and $U_{\boldsymbol{K}} \in \mathbb{R}$, the 4×4 perturbation matrix has only 6 independent components.

- In fact, we can simplify the 4×4 perturbation matrix further using by considering the effect of a rotation $\mathbf{R}$ on a reciprocal lattice vector $\boldsymbol{K}$. The Fourier component for a rotated vector $\mathbf{R}\boldsymbol{K}$ reads

$$
U_{\mathbf{R}\boldsymbol{K}} = \frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{i\mathbf{R}\boldsymbol{K} \cdot \boldsymbol{r}} \, \mathrm{d}V = \frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{-i\mathbf{R}\boldsymbol{K} \cdot \mathbf{R}\mathbf{R}^{-1}\boldsymbol{r}} \, \mathrm{d}V,
$$

where we have used $\boldsymbol{r} = \mathbf{I}\boldsymbol{r} = \mathbf{R}\mathbf{R}^{-1}$ in the last equality, where $\mathbf{I}$ is the identity operation. Note that we can be sure of the inverse $\mathbf{R}^{-1}$'s existence because, as found in Section 2.2, a BCC lattice's symmetry operations form a group, so all cubic lattice symmetry operations have inverses.

- Next, we note that rotations are orthogonal transformations and thus preserve the scalar product of two vectors, i.e. $(\mathbf{R}\boldsymbol{a})(\mathbf{R}\boldsymbol{b}) = \boldsymbol{a} \cdot \boldsymbol{b}$, from which we conclude

$$
\mathbf{R}\boldsymbol{K} \cdot \mathbf{R}(\mathbf{R}^{-1}\boldsymbol{r}) = \boldsymbol{K} \cdot \mathbf{R}^{-1}\boldsymbol{r} \implies U_{\mathbf{R}\boldsymbol{K}} = \frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{-i\boldsymbol{K} \cdot \mathbf{R}^{-1}\boldsymbol{r}} \, \mathrm{d}V.
$$

Finally, we introduce the new variable $\mathbf{R}^{-1}\boldsymbol{r} = \boldsymbol{u}$ or $\boldsymbol{r} = \boldsymbol{R}\boldsymbol{u}$. Because a rotation matrix has unit determinant, i.e. $|\det \mathbf{R}| = 1$, the integrals transform trivially under the change of variables as $\int \mathrm{d}\boldsymbol{r} = \int \mathrm{d}\boldsymbol{u}$, from which we have

$$
\begin{aligned}
U_{\mathbf{R}\boldsymbol{K}} &= \frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{-i\boldsymbol{K}\cdot\mathbf{R}^{-1}\boldsymbol{r}} \,\mathrm{d}^3\boldsymbol{r} = \frac{1}{V_0} \iiint U(\mathbf{R}\boldsymbol{u}) e^{-i\boldsymbol{K}\cdot\boldsymbol{u}} \,\mathrm{d}^3\boldsymbol{u} \\
&= \frac{1}{V_0} \iiint U(\boldsymbol{u}) e^{-i\boldsymbol{K}\cdot\boldsymbol{u}} \,\mathrm{d}^3\boldsymbol{u} = U_{\boldsymbol{K}},
\end{aligned}
$$

where we have used $V(\mathbf{R}\boldsymbol{u}) = V(\boldsymbol{u})$ in the last equality (i.e. the potential is invariant under symmetry operations; see Eq. 7.10).

- The six Fourier components of matrix will decompose into two categories. In each categories the corresponding $\boldsymbol{K}$ can be connected dependently with symmetry operations. Result is two independent Fourier components.

8 Eighth Exercise Set

8.1 Band Gap in a FCC Crystal for Nearly-Free Electrons (continued)

Review

- In the previous exercise, we investigated the energy bands in a crystal with a FCC Bravais lattice, and asked how energy bands split in nearly-free electron model?

- Analysis idea: begin with free electrons and treat periodic potential as a perturbation. This perturbation plays an important role at points at the boundaries of Brillioun zone, where multiple bands have equal energy for free electrons. The values of k at these points in the first Brillioun zone are points of degeneracy.

- We considered the Brillioun zone vertex point W, and found the four values of reciprocal lattice vectors K that were equidistant from W. These values of K correspond to degenerete energies (correspond to electron bands intersecting at W?).

- Our only assumption was a periodic potential, but we did not specify the potential's exact functional form. We found, and will continue to find, that the Fourier components in the matrix are largely dependent.

  In particular, we found that if there exists a symmetry operation $\mathbf{R}$ connecting reciprocal lattice vectors (**TODO:** what does connecting mean quantitatively?), then the Fourier components correponding to those K are real.

- Our next step is to find which Fourier components (or which K?) are related by symmetry operationrs

Begin New Material

- First, we note that rotation by 90° about the k_z axis maps $U_{K_2 - K_1}$ into $U_{K_4 - K_3}$, which motivates the more compact definition

$$U_{K_2 - K_1} = U_{K_4 - K_3} \equiv U_1 \in \mathbb{R}$$

  Second, we note that reflections about the three coordinate planes normal to k_x, k_y and k_z produce symmetry relations between $K_3 - K_1$, $K_4 - K_1$, $K_3 - K_2$ and $K_4 - K_2$, which motivates the definition of U_2 as

$$U_{K_3 - K_1} = U_{K_4 - K_1} = U_{K_3 - K_2} = U_{K_4 - K_2} \equiv U_2$$

  In other words, using symmetry considerations, we have reduced the original set of 64 Fourier components to only the two independent componets U_1 and U_2. In terms of U_1 and U_2, and setting $U_0 = 0$, the perturbation matrix equation simplifies to

$$\begin{pmatrix} E_0 - E & U_1 & U_2 & U_2 \\ U_1 & E_0 - E & U_2 & U_2 \\ U_2 & U_2 & E_0 - E & U_1 \\ U_2 & U_2 & U_1 & E_0 - E \end{pmatrix} \begin{pmatrix} c_{W - K_1} \\ c_{W - K_2} \\ c_{W - K_3} \\ c_{W - K_4} \end{pmatrix} = \mathbf{0} \qquad (8.1)$$

  Note that the matrix is symmetric, as it must be—this serves as a safety check that our analysis so far was correct.

- The homogeneous system in Equation 8.1 has a non-trivial solution only if the perturbation matrix's determinant is non-zero. We will actually evaluate this determinant by hand using elementary row and column operations. We first subtract the second row from the first row, and also the third row from the fourth rod to get

$$\begin{pmatrix} E_0 - E - U_1 & U_1 - E_0 + E & 0 & 0 \\ U_1 & E_0 - E & U_2 & U_2 \\ U_2 & U_2 & E_0 - E & U_1 \\ 0 & 0 & U_1 - E_0 + E & E_0 - E - U_1 \end{pmatrix}$$

We then add the first and second column and also the third and fourth column, producing

$$\mathbf{M} \equiv \begin{pmatrix} E_0 - E - U_1 & 0 & 0 & 0 \\ U_1 & E_0 - E + U_1 & 2U_2 & U_2 \\ U_2 & 2U_2 & E_0 - E + U_1 & U_1 \\ 0 & 0 & 0 & E_0 - E - U_1 \end{pmatrix}$$

Having introduced plenty of zeros, we now evaluate the matrix's determinant by expanding about the first row. To do this, we multiply the $(1,1)$ element $E_0 - E - U_1$ by principal minor obtained by deleting the first row and column, i.e. the determinant of the the lower-right 3×3 sub-matrix. We find this "sub-determinant" by expanding the lower-right 3×3 sub-matrix about its last row. The end result for the original 4×4 determinant is

$$\det \mathbf{M} = (E_0 - E - U_1) \cdot \Big[(E_0 - E - U_1) \cdot \big[(E_0 - E + U_1)^2 - (2U_2)^2 \big] \Big].$$

The perturbation matrix's eigenvalues are the solutions to the polynomial equation $\det \mathbf{M} = 0$; without full derivation, these are

$$E_{1,2} = E_0 - U_1 \qquad E_3 = E_0 + U_1 - 2U_2 \qquad E_4 = E_0 + U_1 + 2U_3.$$

These eigenvalues encode the energy band splitting at the FCC lattice's Brillioun zone vertex point $\boldsymbol{W}$. Note that the originally four-fold energy degeneracy at $\boldsymbol{W}$ for free electrons is not fully lifted by a periodic potential in the free electron model—the $E_{1,2}$ energy is still degenerate. Note that this result is completely general for a FCC structure for any a periodic potential in the free electron model, and is derived from FCC symmetry considerations only.

8.2 Kronig-Penney Model with the Tight Binding Model

Review: The Tight-Binding Model

- The tight-binding model is an alternate approach to analyzing electron energy bands in crystal lattices. Recall that in the nearly-free electron model, we begin an analysis with free electrons described by plane wave eigenfunctions and treat the crystal's periodic potential as a perturbation on these plane wave states.

- The tight-binding model begins with the opposite limit, of a very strong potential, in which electron wavefunctions are farm from plane waves. Instead, as a basis function we take the wave function of an electron in an isolated atom. We then treat the overlap of atomic electron wave functions as a perturbation on these atomic electron states.

63

8.2.1 Introduction

- For review from Exercise 6.2, the Kronig-Penney model uses a periodic potential consisting of a one-dimensional chain of delta functions. For the tight-binding model we require these delta functions point downward (and not upwards as in Exercise 6.2), we will lead to to localized atomic orbitals as required by the tight-binding model.

  Letting a denote the lattice constant, our problem's periodic potential then reads

  $$U(x) = \sum_n -\lambda\delta(x - na), \quad \lambda > 0,$$

  where $n \in \mathbb{Z}$ is an integer.

- The potential at a single atomic lattice site takes the form

  $$U(x) = -\lambda\delta(x).$$

  Recall from the previous semester's course in quantum mechanics. that this potential leads to a single bound state with energy

  $$E_{\mathrm{at}} = -\frac{m\lambda^2}{2\hbar^2},$$

  while the corresponding wave function is

  $$\psi_{\mathrm{at}}(x) = \sqrt{\kappa_0}e^{-\kappa_0|x|}, \qquad \kappa_0 = \frac{m\lambda}{\hbar^2},$$

  where we have used "at" as shorthand for "atomic", since these quantities apply to a single atom. Once we consider multiple atoms and thus multiple potentials at multiple lattice sites, the exponential tails of the atomic wave functions on each lattice site will overlap for large enough values of the paratmeter λ.

  If atoms are very far away, all electron states will still have the same energy E_{at} as for isolated individual atoms. After overlap, however, the electron energies will spread out into an energy band centered around E_{at}.

8.2.2 Analytic Solution

- We begin with the Kronig-Penney equation (Eq. 6.9) from Exercise 6.2, which for review reads

  $$\cos ka = \cos qa + Qa\frac{\sin qa}{qa}; \quad Q = \frac{m\lambda}{\hbar^2},$$

  where k is a Bloch wave vector from the first Brillioun zone $k \in [-\pi/a, \pi/a]$ and

  $$q = \sqrt{\frac{2mE}{\hbar^2}}$$

  is the wave vector of a free electron energy with energy E. Note also that Q is equivalent to κ_0 from quantum mechanics; we use Q because this notation is more conventional in the context of the Kronig-Penney model. We now adapt this general analytic solution to our problem involving the tight-binding model. In

particular, the above solution applied to upward-pointing delta potentials $U(x) = \lambda\delta(x)$, while the tight-binding model uses $U(x) = -\lambda\delta(x)$.

TODO: change every λ above to $\widetilde{\lambda}$, but not the one in the definition of Q, so from the review of delta function.

Define

$$\widetilde{Q} = \frac{m\widetilde{\lambda}}{\hbar^2} \implies Q = -\widetilde{Q} \tag{8.2}$$

- Then note that E_{at} is a negative energy, being bound. We thus change q to not be imaginary by defining

$$\widetilde{q} \equiv \sqrt{\frac{2m(-E)}{\hbar^2}} = i\sqrt{\frac{2mE}{\hbar^2}} = iq. \tag{8.3}$$

But **TODO:** resolve we worked with $q = i\widetilde{q}$. Dude figure this out:

$$i\sqrt{-c} = \sqrt{-1}\sqrt{-c} = \sqrt{c} \qquad \text{and} \qquad i\sqrt{-c} = i\sqrt{-1}\sqrt{c} = i^2\sqrt{c} = -\sqrt{c}$$

- In terms of the quantities $\widetilde{q}$ and $\widetilde{Q}$, the Kronig-Penney equation, adapted to a downward delta function, reads

$$\cos ka = \cos(i\widetilde{q}a) - \widetilde{Q}a\frac{\sin(i\widetilde{q}a)}{i\widetilde{q}a}.$$

In terms of the hyperbolic functions $\cos ix = \cosh x$ and $\sin ix = i\sinh x$, this reads

$$\cos ka = \cosh(\widetilde{q}a) - \widetilde{Q}a\frac{\sinh(\widetilde{q}a)}{\widetilde{q}a}$$

Note that $\widetilde{q}a$ still encodes electron energy, and the larger the value of $\widetilde{q}a$, the more negative the energy (corresponding to a more tightly bound electron).

- We will try to solve the equation graphically. First, we note that the LHS, i.e. $\cos ka$, is bound in in the range $[-1, 1]$. Or goal is to find the values of $\widetilde{q}a$ for which the RHS also falls in the allowed range $[-1, 1]$.

We won't find this solution generally, but only in the limit $\widetilde{Q}a = \frac{m\widetilde{\lambda}a}{\hbar^2} \gg 1$, i.e. for large $\widetilde{\lambda}$; this corresponds physically to strong potentials and tightly-bound electrons.

Note that $\widetilde{Q}a$ controls exponential attenuation of atomic electron wave function tails, and the limit $\widetilde{Q}a \gg 1$ means the atomic wavefunctions have small tails and thus little overlap, which is just the tight-binding model.

- We now consider two limit cases of electron energy $\widetilde{q}a$. For small electron energies $\widetilde{q}a \to 0$ the RHS of the Kronig-Penney equation becomes

$$\cosh\widetilde{q}a - \widetilde{Q}a\frac{\sinh\widetilde{q}a}{\widetilde{q}a} \to 1 - \widetilde{Q}a.$$

Meanwhile, in the opposite limit case for large electron energies $\widetilde{q}a \gg 1$ we have

$$\cosh\widetilde{q}a - \widetilde{Q}a\frac{\sinh\widetilde{q}a}{\widetilde{q}a} \to \infty.$$

- We now consider the behavior of the RHS for moderate electron energies $\widetilde{q}a$ in between the extreme cases $\widetilde{q}a \to 0$ and $\widetilde{q}a \to \infty$.

  Claim: in the tight-binding limit $\widetilde{Q}a \gg 1$, the RHS equals zero (intersects the $\widetilde{q}a$ axis) at roughly $\widetilde{q}a \sim \widetilde{Q}a$.

  Justification: noting that $\cosh x \approx \sinh x$ for $x \gg 1$, we note that for $\widetilde{Q}a \gg 1$ we have $\cosh \widetilde{Q}a \approx \sinh \widetilde{Q}a$ and thus

  $$\cosh \widetilde{Q}a - \widetilde{Q}a \frac{\sinh \widetilde{Q}a}{\widetilde{Q}a} = \cosh \widetilde{Q}a - \sinh \widetilde{Q}a \approx 0.$$

  In other words, the RHS is indeed (approximately) zero when $\widetilde{q}a \approx \widetilde{Q}a$ (in the tight-binding limit $\widetilde{Q}a \gg 1$).

- Next, we model the electron wave vector with the ansatz

  $$\widetilde{q}a = \widetilde{Q}a + \epsilon, \tag{8.4}$$

  in terms of which the Kronig-Penney equation reads

  $$\cos ka = \cosh\left(\widetilde{Q}a + \epsilon\right) - \widetilde{Q}a \frac{\sinh\left(\widetilde{Q}a + \epsilon\right)}{\widetilde{Q}a + \epsilon}.$$

  For small ϵ and $\widetilde{Q}a \gg 1$ (using the approximations $\cosh(x + \delta x) \approx \sinh(x + \delta x) \approx \frac{1}{2}e^x$ for $x \gg 1$ and $\delta x \ll 1$), the equation simplifies to

  $$\cos ka \approx \frac{e^{\widetilde{Q}a+\epsilon}}{2} - \frac{\widetilde{Q}a}{\widetilde{Q}a + \epsilon} \frac{e^{\widetilde{Q}a+\epsilon}}{2} = \frac{e^{\widetilde{Q}a+\epsilon}}{2} \left(1 - \frac{1}{1 + \epsilon/(\widetilde{Q}a)}\right).$$

  Finally, noting that $\epsilon/(\widetilde{Q}a) \ll 1$ and using $\frac{1}{1+x} \approx 1 - x$ for $x \ll 1$, we have

  $$\cos ka \approx \frac{e^{\widetilde{Q}a+\epsilon}}{2} \cdot \frac{\epsilon}{\widetilde{Q}a} = \frac{e^{\widetilde{Q}a}}{2} \cdot \frac{e^{\epsilon}\epsilon}{\widetilde{Q}a}$$

  Finally, we make the expansion

  $$e^{\epsilon}\epsilon \approx \left(1 + \epsilon + \frac{\epsilon^2}{2} + \cdots\right) \cdot \epsilon = \epsilon + \epsilon^2 + \frac{\epsilon^2}{3} + \cdots \approx \epsilon,$$

  where we have rejected higher-order terms in ϵ under the assumption $\epsilon \ll 1$. We then have

  $$\cos ka \approx \frac{e^{\widetilde{Q}a}}{2} \cdot \frac{e^{\epsilon}\epsilon}{\widetilde{Q}a} \approx \frac{e^{\widetilde{Q}a}}{2} \cdot \frac{\epsilon}{\widetilde{Q}a} \implies \epsilon \approx 2\widetilde{Q}a e^{-\widetilde{Q}a} \cos ka.$$

- Returning to the ansatz for electron wave vector $\widetilde{q}a$ in Equation 8.4, and using the just-derived expression for ϵ we have

  $$\widetilde{q}a = \widetilde{Q}a + \epsilon = \widetilde{Q}a \left(1 + 2e^{-\widetilde{Q}a} \cos ka\right).$$

In terms of this expression for $\widetilde{q}a$, the energy of a tightly-bound electron (from Eq. 8.3) reads

$$E = -\frac{\hbar^2}{2m}(\widetilde{q})^2 = -\frac{\hbar^2}{2ma^2}(\widetilde{q}a)^2 \approx -\frac{\hbar^2(\widetilde{Q}a)^2}{2ma^2}\left(1 + 4e^{-\widetilde{Q}a}\cos ka\right),$$

where we have dropped the $\propto e^{-2\widetilde{Q}a}$ term under the assumption $\widetilde{Q}a \gg 1$. After simplifying, the tightly-bound electron energy reads

$$E \approx -\frac{\hbar^2\widetilde{Q}^2}{2m}\left(1 + 4e^{-\widetilde{Q}a}\cos ka\right)$$

We then recall the single-atom energy E_{at} and define the *overlap term* γ according

$$E_{\mathrm{at}} = \frac{\hbar^2\widetilde{Q}^2}{2m} \qquad \text{and} \qquad \gamma \equiv -\frac{\hbar^2}{m}\widetilde{Q}^2 e^{-\widetilde{Q}a},$$

in terms of which the tightly-bound electron energy reads

$$E(k) = E_{\mathrm{at}} - 2\gamma\cos(ka). \tag{8.5}$$

Lesson: electron energies in the tight-binding model, instead all having the same energy E_{at} as for isolated atoms, spread out into an energy band centered around E_{at} with a band gap of 4γ. Note that γ is exponential in $\widetilde{Q}a$, which we assumed to be large, so that γ is small compared to E_{at}.

8.2.3 Using the Tight-Binding Model

Review of TB Model

- In three dimensions, the energy of an electron in the tight-binding model is

$$E(\boldsymbol{k}) = E_{\mathrm{at}} - \frac{\beta + \sum_{\boldsymbol{R}\neq\boldsymbol{0}}\gamma(\boldsymbol{R})e^{i\boldsymbol{k}\cdot\boldsymbol{R}}}{1 + \sum_{\boldsymbol{R}\neq\boldsymbol{0}}\alpha(\boldsymbol{R})e^{i\boldsymbol{k}\cdot\boldsymbol{R}}},$$

where E_{at} is the energy of an electron bound to an isolated atom with no overlap with its neighbors. The sums run over all Bravais lattice points except the origin—essentially all neighboring lattice sites to the lattice site holding the electron of interest.

- The integral β is given by

$$\beta = -\iiint_V \psi_{\mathrm{at}}^*\Delta U(\boldsymbol{r})\psi_{\mathrm{at}}(\boldsymbol{r})\,\mathrm{d}V, \tag{8.6}$$

where ψ_{at} is the wave function of an electron on an isolated atom, while the term ΔU is defined as

$$\Delta U(\boldsymbol{r}) = \sum_{\boldsymbol{R}\neq\boldsymbol{0}} U_{\mathrm{at}}(\boldsymbol{r} - \boldsymbol{R}).$$

- The overlap of orbitals on different atoms is encoded by γ and α; these are given by

$$\gamma(\boldsymbol{R}) = -\iiint_V \psi_{\mathrm{at}}^*(\boldsymbol{r})\Delta U(\boldsymbol{r})\psi_{\mathrm{at}}(\boldsymbol{r} - \boldsymbol{R})\,\mathrm{d}V \tag{8.7}$$

$$\alpha(\boldsymbol{R}) = \iiint_V \psi_{\mathrm{at}}^*(\boldsymbol{r})\psi_{\mathrm{at}}(\boldsymbol{r} - \boldsymbol{R})\,\mathrm{d}V. \tag{8.8}$$

- *Important*: these expressions for α, β and γ hold only under the assumption of one orbital per lattice site (primitive cell) in the Bravais lattice. This assumption is satisfied for Kronig-Penney model potential, which leads to only a single bound state per lattice site, but in general does not hold for arbitrary potentials.

8.2.4   Kronig-Penney Model Using the Tight-Binding Model

- We begin by defining the atomic energy and wave function for a Kronig-Penney model lattice site; these are

$$E_{\text{at}} = -\frac{\hbar^2 \widetilde{Q}}{2m} \qquad \psi_{\text{at}} = \sqrt{\widetilde{Q}} e^{-\widetilde{Q}|x|},$$

where $\widetilde{Q}$ is defined as in Equation 8.2 as

$$\widetilde{Q} = \frac{m\widetilde{\lambda}}{\hbar^2} = -\frac{m\lambda}{\hbar^2}.$$

- We then compute overlap integrals, beginning with β (Eq. 8.6). For the lattice site at the origin, this reads

$$\beta = -\int \psi_{\text{at}}^*(x)\Delta U(x)\psi_{\text{at}}(x)\,\mathrm{d}x$$

$$= -\int \sqrt{\widetilde{Q}} e^{-\widetilde{Q}|x|} \cdot \left(\sum_{n\neq 0} -\widetilde{\lambda}\delta(x - na)\right) \cdot \sqrt{\widetilde{Q}} e^{-\widetilde{Q}|x|}\,\mathrm{d}x$$

$$= \widetilde{Q}\widetilde{\lambda} \int e^{-2\widetilde{Q}|x|} \cdot \left(\sum_{n\neq 0} \delta(x - na)\right)\mathrm{d}x.$$

Since we are working in the tigh-binding model, we assume that wave functions at far-away lattice sites won't contribute appreciably to the origin's overlap integral β, so we consider only the two nearest neighbors to the origin lattice site, which occur at $x = \pm a$. From this train of thought, considering only $n = 1$, we have

$$\beta \sim \mathcal{O}\left(\widetilde{Q}\widetilde{\lambda} \int e^{-2\widetilde{Q}|x|} \cdot \delta(x - a)\,\mathrm{d}x\right) = \mathcal{O}\left(\widetilde{Q}\widetilde{\lambda} e^{-2\widetilde{Q}a}\right).$$

- We continue with γ (Eq. 8.7), which for $X = Na$ where $N \in \mathbb{Z}; N \neq 0$ reads

$$\gamma(Na) = -\int \psi_{\text{at}}^*(x)\Delta U(x)\psi_{\text{at}}(x - Na)\,\mathrm{d}x$$

$$= -\int \sqrt{\widetilde{Q}} e^{-\widetilde{Q}|x|}\left(\sum_{n\neq 0} -\widetilde{\lambda}\delta(x - na)\right)\sqrt{\widetilde{Q}} e^{-\widetilde{Q}|x-Na|}\,\mathrm{d}x$$

$$= \widetilde{Q}\widetilde{\lambda} \int e^{-\widetilde{Q}(|x|+|x-Na|)}\left(\sum_{n\neq 0} \delta(x - na)\right)\mathrm{d}x.$$

For the tight-binding model's localized wavefunctions, the γ term for $|N| > 1$ will be exponentially smaller than for $|N| = 1$, so to leading order we consider only

$\gamma(\pm a)$ for which $|N| = 1$. In this case we have

$$\gamma(\pm a) = \underbrace{\widetilde{Q}\widetilde{\lambda}e^{-\widetilde{Q}a}}_{\text{from } n=\pm 1} + \mathcal{O}\left(\widetilde{Q}\widetilde{\lambda}e^{-2\widetilde{Q}a}\right), \tag{8.9}$$

where the first term comes from $n = \pm 1$ in the sum over δ functions, while the second term represents the higher-order contributions for $|n| > 2$.

- Finally, we compute the α overlap integral (Eq. 8.6), which in one dimension for $N \in \mathbb{Z}$ reads

$$\alpha(Na) = \int \psi_{\text{at}}^*(x)\psi_{\text{at}}(x - Na)\,\mathrm{d}x = \int \sqrt{\widetilde{Q}}e^{-\widetilde{Q}|x|}\sqrt{\widetilde{Q}}e^{-\widetilde{Q}|x-Na|}\,\mathrm{d}x$$

$$= \widetilde{Q}\int e^{-\widetilde{Q}(|x|+|x-Na|)}\,\mathrm{d}x.$$

Considering only the $|N| = 1$ terms, the α integral becomes

$$\alpha(\pm a) \sim \mathcal{O}\left(\widetilde{Q}e^{-\widetilde{Q}a} \cdot a\right)$$

where we multiply by a which is the interval over which we have appreciable integral contribution?

- We now return to the expression for the energy of an electron in the tight-binding model, which in one dimension, and considering only the contributions of nearest-neighbor lattice sites, reads

$$E(k) = E_{\text{at}} - \frac{\beta + \gamma(a)e^{ika} + \gamma(-a)e^{-ika}}{1 + \alpha(a)e^{ika} + \alpha(-a)e^{-ika}}.$$

Recall β is of order $e^{-2\widetilde{Q}a}$ in its leading term and is thus negligible compared to α and γ. Neglecting γ and defining $\alpha(a) = \alpha(-a) \equiv \alpha$ and $\gamma(a) = \gamma(-a) \equiv \gamma$ we have

$$E(k) \approx E_{\text{at}} - \frac{\gamma \cdot (e^{ika} + e^{-ika})}{1 + \alpha \cdot (e^{ika} + e^{-ika})} = E_{\text{at}} - \frac{2\gamma\cos ka}{1 + 2\alpha\cos ka}.$$

Finally, neglecting α relative to γ we have

$$E(k) \approx E_{\text{at}} - 2\gamma\cos ka,$$

which agrees with the expression found analytically in Equation 8.5.

9   Ninth Exercise Set

9.1   FCC in Tight-Binding Model

- Assume overlap integrals are small. In practice we can neglect the overlap integral α, because it will be multiplied by other overlap integrals after a Taylor expansion or something.

  So we only keep the $\gamma(\boldsymbol{R})$ integral, and consider only those $\gamma(\boldsymbol{R})$ for which $\boldsymbol{R}$ is a nearest neighbor to the origin. (Well, to the lattice site holding the electron for which we are computing the energy E).

- Consider a FCC crystal. And consider the electron band, formed of s orbitals on each atom. Each atom has an s orbital (which are spherically symmetric).

  Thus overlap integrals only depend on radial distance between atoms. Useful!

- Energy is

$$E(\boldsymbol{k}) = \sum_{\boldsymbol{R}\,\in\{\text{nn}\}} \gamma(\boldsymbol{R})e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$$

  Sum over all vectors in Bravais lattice that are nearest neighbors of origin.

- The nearest neighbors (if origin is e.g. circled atoms in blue, origin in red.) There are 12 total nearest neighbors

$$a\left(0, \pm\tfrac{1}{2}, \pm\tfrac{1}{2}\right) \qquad a\left(\pm\tfrac{1}{2}, 0, \pm\tfrac{1}{2}\right) \qquad a\left(\pm\tfrac{1}{2}, \pm\tfrac{1}{2}, 0\right)$$

- Energy is then (each neighbors has a pair on the other side of the origin at $\boldsymbol{R} \to -\boldsymbol{R}$. Use $e^{i\boldsymbol{k}\cdot\boldsymbol{R}} + e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} = 2\cos\boldsymbol{k}\cdot\boldsymbol{R}$ and consider only six terms instead of 12)

$$E(\boldsymbol{k}) = -2\gamma\left[\cos\frac{k_y + k_z}{2}a + \cos\frac{k_y - k_z}{2}a + \cos\frac{k_x + k_z}{2}a + \cos\frac{k_x - k_z}{2}a\right.$$
$$\left. + \cos\frac{k_x + k_y}{2}a + \cos\frac{k_x - k_y}{2}a\right]$$

  In practice:

  - γ is considered only for nearest neighbors
  - β is only a shift of the entire energy band and depends on choice of potential.
  - α is neglected because its small relative to γ and β

- Next, using the identity $\cos(x \pm y) = \cos x \cos y \mp \sin x \sin y$ we rewrite the first cosine term, which we will call C_{yz}, to get

$$C_{yz} \equiv \cos\frac{k_y + k_z}{2}a + \cos\frac{k_y - k_z}{2}a$$
$$= \cos\frac{k_y a}{2}\cos\frac{k_z a}{2} - \sin\frac{k_y a}{2}\sin\frac{k_z a}{2} + \cos\frac{k_y a}{2}\cos\frac{k_z a}{2} + \sin\frac{k_y a}{2}\sin\frac{k_z a}{2}$$
$$2\cos\frac{k_y a}{2}\cos\frac{k_z a}{2}.$$

Similarly, for the other two sets of cosine terms we have

$$C_{xz} \equiv \cos \frac{k_x + k_z}{2}a + \cos \frac{k_x - k_z}{2}a = 2\cos \frac{k_x a}{2} \cos \frac{k_z a}{2}$$
$$C_{xy} \equiv \cos \frac{k_x + k_y}{2}a + \cos \frac{k_x - k_y}{2}a = 2\cos \frac{k_x a}{2} \cos \frac{k_y a}{2}.$$

Combining the expressions for C_{yz}, C_{xz}, and C_{yx} produces

$$E(\boldsymbol{k}) = -4\gamma \left[\cos \frac{k_y a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \right] \qquad (9.1)$$

The conclusion is: this $E(\boldsymbol{k})$ relation describes the electron energy band for s orbitals in the tight-binding model approximation of electrons in a FCC lattice. Or, s orbital electrons in a FCC crystal have the following energy band dispersion relation when analyzed with the tight-binding model.

9.1.1   Dispersion Relation Along Symmetry Points

- Note that this cannot be drawn easily, since $\boldsymbol{k} \in \mathbb{R}^3$.

  We have a trick for view 3D dispersion relations though.

  First recall $\boldsymbol{k}$ above in $E(\boldsymbol{k})$ is in the first Brillioun zone.

  Then recall the RL of a FCC lattice is a BCC lattice with lattice constant $4\pi/a$.

- Solution to viewing dispersion:

  Choose a one-dimensional path through the three-dimesional first Brillioun zone that passes through as many interesting symmetry points as possible.

  We will start this path in the Brillioun zone's center, which is conventionally denoted by Γ and has coordinates $\Gamma = (0, 0, 0)$.

  We then move to the center of the (square) right face, which is conventionally called X and has coordinates $X = (\frac{2\pi}{a}, 0, 0)$.

  From X move to the vertex point W, which, as in Exercise 7.4, has coordinates $W = (\frac{2\pi}{a}, 0, \frac{\pi}{a})$.

  Then center of hexagonal face, which is denoted by L and has coordinates $L = (\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$.

  From here we return to Γ, the center of the first Brillioun zone.

- Next: plot $E(\boldsymbol{k})$ on the ordinate and the above letter points as points on the abscissa.

  We introduce the variable q to parameterize the path between each of the above neighboring points.

- Define q as parameter for each path segment between two subsequent points. We then write $E(q)$ for each segment along the path using Equation 9.1 and the parameterized expressions for $\boldsymbol{k} = (k_x, k_y, k_z)$ in terms of q.

- For the path segment $\Gamma \to X$ the energy relation $E(q)$ reads

$$E(q) = -4\gamma \left(1 \cdot 1 + \cos \frac{qa}{2} \cdot 1 + \cos \frac{qa}{2} \cdot 1 \right) = -4\gamma - 8\gamma \cos \frac{qa}{2}$$

Energy ranges from -12γ to 4γ along this segment.

point	coordinates	segment	wave vector $\boldsymbol{k}$	parameter range
Γ	$(0,0,0)$	$\Gamma \to X$	$\boldsymbol{k} = (q,0,0)$	$q \in [0, \frac{2\pi}{a}]$
X	$\left(\frac{2\pi}{a},0,0\right)$	$X \to W$	$\boldsymbol{k} = \left(\frac{2\pi}{a},0,q\right)$	$q \in [0, \frac{\pi}{a}]$
W	$\left(\frac{2\pi}{a},0,\frac{\pi}{a}\right)$	$W \to L$	$\boldsymbol{k} = \left(\frac{2\pi}{a} - q, q, 0\right)$	$q \in [0, \frac{\pi}{a}]$
L	$\left(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a}\right)$	$L \to \Gamma$	$\boldsymbol{k} = \left(\frac{\pi}{a} - q, \frac{\pi}{a} - q, \frac{\pi}{a} - q\right)$	$q \in [0, \frac{\pi}{a}]$

- Next, for $X \to W$, $E(q)$ is

$$E(q) = -4\gamma \left(1 \cdot \cos\frac{qa}{2} + (-1)\cdot\cos\frac{qa}{2} + (-1)\cdot 1\right) = 4\gamma$$

Energy is, clearly, constant and equal to 4γ along this segment.

- Next, for $W \to L$, $E(q)$ is

$$E(q) = -4\gamma\left(\cos\frac{qa}{2}\cdot 1 + (-1)\cdot\cos\frac{qa}{2}\cdot 1 + (-1)\cdot\cos\frac{qa}{2}\cos\frac{qa}{2}\right) = 4\gamma\cos^2\frac{qa}{2}$$

Energy ranges from 4γ to 0 along this segement.

- Finally, for $L \to \Gamma$, since $k_x = k_y = k_z = q - \frac{\pi}{a}$ we have

$$E(q) = -3 \cdot 4\gamma\cos^2\left(\frac{qa}{2} - \frac{\pi}{2}\right) = -12\gamma\sin^2\frac{qa}{2}$$

Energy ranges from 0 to -12γ along this segment.

- Along the entire path, $E(q)$ changes from a maximum of $E = 4\gamma$ along the $X \to W$ segment to a minimum of -12γ along the $L \to \Gamma$ segment; the corresponding band gap for the entire path is thus $4\gamma - (-12\gamma) = 16\gamma$. Without proof, we note that the first Brillioun zone's characteristic symmetry points (like Γ, X, W and L) usually span the maximum band gap for the entire crystal; in other words, the energy band gaph for a path between symmetry points usually agrees with the entire three-dimensional crystal's band gap.

  For orientation, this analysis applies only to the energy band arising from electrons in s orbitals in a FCC crystal using the tight-binding model.

9.1.2   Taylor Approximation Near Central Point Γ

- We now aim to analyze the three-dimensional dispersion relation's behavior around the symmetry point Γ—the center of the first Brillioun zone. We use the ansatz

$$\boldsymbol{k} = \Gamma + \boldsymbol{q} = \boldsymbol{0} + \boldsymbol{q} = \boldsymbol{q}, \qquad |\boldsymbol{q}| \ll \frac{\pi}{a},$$

where $|\boldsymbol{q}| \ll \frac{\pi}{a}$ ensures $\boldsymbol{k}$ remains near the center of the first Brillioun zone. From Equation 9.1, we then recall the three-dimensional FCC dispersion relation

$$E(\boldsymbol{k}) = -4\gamma\left[\cos\frac{k_y a}{2}\cos\frac{k_z a}{2} + \cos\frac{k_x a}{2}\cos\frac{k_z a}{2} + \cos\frac{k_x a}{2}\cos\frac{k_y a}{2}\right]$$

We then substitute in the ansatz $\boldsymbol{k} = \boldsymbol{q}$ and Taylor-expand the cosine terms to second order in the regime $|\boldsymbol{q}| \ll \pi/a$ to get

$$E(\boldsymbol{q}) = -4\gamma\left[\left(1 - \frac{1}{2}\left(\frac{q_y a}{2}\right)^2\right)\left(1 - \frac{1}{2}\left(\frac{q_z a}{2}\right)^2\right) + \cdots \right.$$
$$+ \left(1 - \frac{1}{2}\left(\frac{q_x a}{2}\right)^2\right)\left(1 - \frac{1}{2}\left(\frac{q_z a}{2}\right)^2\right) + \cdots$$
$$\left. + \left(1 - \frac{1}{2}\left(\frac{q_x a}{2}\right)^2\right)\left(1 - \frac{1}{2}\left(\frac{q_y a}{2}\right)^2\right) + \cdots \right].$$

We then multiply out and neglect fourth-order terms in $q_y q_z$ to get

$$E(\boldsymbol{q}) \approx -4\gamma\left[3 - \frac{a^2}{8}\left(q_y^2 + q_z^2\right) - \frac{a^2}{8}\left(q_x^2 + q_z^2\right) - \frac{a^2}{8}\left(q_x^2 + q_y^2\right)\right]$$
$$= -4\gamma\left[3 - \frac{a^2}{4}(q_x^2 + q_y^2 + q_z^2)\right] = -12\gamma + \gamma a^2 q^2.$$

Minimum value of $E(\boldsymbol{q})$ is -12γ (best seen from full dispersion relation for $E(\boldsymbol{k})$, since maximum of cosine terms is one, maximum of the three cosine termsin square bracket is thus three, and maximum of $E(\boldsymbol{k})$ is then $-3 \cdot 4\gamma$).

- Finally, by convention, we write the final expression for $E(\boldsymbol{q})$ in terms of an *effective mass* m^* in the form

$$E(\boldsymbol{q}) \equiv -12\gamma + \frac{\hbar^2 q^2}{2m^*}, \quad \text{where } m^* \equiv \frac{\hbar^2}{2\gamma a^2}.$$

Note that m^* depends only on the overlap integral γ and is unrelated to the physical electron mass.

- We now consider the density of states $g(E)$ near the center point Γ. We begin with the expression

$$E(\boldsymbol{q}) = -12\gamma + \frac{\hbar^2 q^2}{2m^*}$$

for the dispersion relation near the Brillioun zone's center Γ. This expression, aside from the constant -12γ shift, resembles a quadratic free electron dispersion relation in the wave vector q.

- Following the free electron analogy, we thus heuristically expect the dispersion relation near Γ to obey $g(E) \propto \sqrt{E}$, as for free electrons. However, because of the constant energy shift by -12γ, we have the modified expression

$$g(E) \approx \sqrt{E + 12\gamma}$$

for the eleectron density of states near the center Γ of the FCC first Brillioun zone.

9.1.3   Taylor Approximation Near Hexagonal Face Center L

- We now analyze the dispersion relation near the point $L = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$—the center of the first Brillioun zone's hexagonal face. We again write the reciprocal vector $\boldsymbol{k}$ with an ansatz of the form

$$\boldsymbol{k} = L + \boldsymbol{q} = \left(\frac{\pi}{a} + q_x, \frac{\pi}{a} + q_y, \frac{\pi}{a} + q_z\right); \qquad |\boldsymbol{q}| \ll \frac{\pi}{a}.$$

Begin with the general dispersion relation from Equation 9.1, which reads

$$E(\boldsymbol{k}) = -4\gamma \left(\cos \frac{k_y a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \right)$$

We then substitute in the ansatz $\boldsymbol{k} = L + \boldsymbol{q}$. Because of the additional π/a term, the cosines change to sines, and the dispersion relation reads

$$E(\boldsymbol{q}) = -4\gamma \left(\sin \frac{q_y a}{2} \sin \frac{q_z a}{2} + \sin \frac{q_x a}{2} \sin \frac{q_z a}{2} + \sin \frac{q_x a}{2} \sin \frac{q_y a}{2} \right)$$

We then Taylor-expand the sine terms to first order in the regime $|\boldsymbol{q}| \ll \pi/a$ to get

$$\begin{aligned} E(\boldsymbol{q}) &\approx -4\gamma \left(\frac{q_y q_z a^2}{4} + \frac{q_x q_z a^2}{4} + \frac{q_x q_y a^2}{4} \right). \\ &= -\gamma a^2 (q_y q_z + q_x q_z + q_x q_y). \end{aligned}$$

- The above expression for $E(\boldsymbol{q})$ is a quadratic form in $\boldsymbol{q}$, which may be written in matrix form as

$$E(\boldsymbol{q}) = -\frac{\gamma a^2}{2} (q_x, q_y, q_z) \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix}.$$

We now aim to find the above matrix's eigenvalues. We first compute the characteristic polynomial, which, without full derivation, comes out to

$$-\lambda^3 + 2 + 3\lambda = 0.$$

After factoring, this polynomial may be written

$$(\lambda - 2)(\lambda + 1)^2 = 0,$$

so the quadratic form's eigenvalues are $\lambda \in \{-1, -1, 2\}$. The important conclusion here is that the eigenvalues have different signs. Since the quadratic form is symmetric, we can rotate the coordinate system to align with the quadratic form's eigenvectors, in which case $E(\boldsymbol{q})$ increases in the direction of the negative eigenvalue's eigenvectors and decreases in the direction of the positive eigenvalue's eigenvectors. Because $E(\boldsymbol{q})$ increases in the neighborhood of L in two spatial directions and decreases in the other spatial direction, we conclude the point L is a saddle point in the electron dispersion relation $E(\boldsymbol{k})$.

9.1.4 Taylor Approximation Near Square Face Center X

- Finally, we analyze the dispersion relation near the point $X = \left(\frac{2\pi}{a}, 0, 0 \right)$—the center of the first Brillioun zone's square face. We again write the reciprocal vector $\boldsymbol{k}$ with an ansatz of the form

$$\boldsymbol{k} = X + \boldsymbol{q} = \left(\frac{2\pi}{a} + q_x, q_y, q_z \right); \qquad |\boldsymbol{q}| \ll \frac{\pi}{a}.$$

As for the points Γ and L, we begin with the general FCC dispersion relation

$$E(\boldsymbol{k}) = -4\gamma \left(\cos \frac{k_y a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \right)$$

Because of the $k_x = \frac{2\pi}{a} + q_x$ component, terms containing $\cos \frac{k_x a}{2}$ get an extra minus sign, and the dispersion relation for $\boldsymbol{q}$ reads

$$E(\boldsymbol{q}) = -4\gamma \left(\cos \frac{q_y a}{2} \cos \frac{q_z a}{2} - \cos \frac{q_x a}{2} \cos \frac{q_z a}{2} - \cos \frac{q_x a}{2} \cos \frac{q_z a}{2} \right).$$

Just as in Section 9.1.2, we expand the cosine terms to second order in $\boldsymbol{q}$ to get

$$\begin{aligned}
E(\boldsymbol{q}) = -4\gamma \Bigg[&\left(1 - \frac{1}{2}\left(\frac{q_y a}{2}\right)^2\right)\left(1 - \frac{1}{2}\left(\frac{q_z a}{2}\right)^2\right) + \cdots \\
&- \left(1 - \frac{1}{2}\left(\frac{q_x a}{2}\right)^2\right)\left(1 - \frac{1}{2}\left(\frac{q_z a}{2}\right)^2\right) + \cdots \\
&- \left(1 - \frac{1}{2}\left(\frac{q_x a}{2}\right)^2\right)\left(1 - \frac{1}{2}\left(\frac{q_y a}{2}\right)^2\right) + \cdots \Bigg].
\end{aligned}$$

We then multiply out and neglect fourth-order terms in $q_y q_z$ to get

$$\begin{aligned}
E(\boldsymbol{q}) &\approx -4\gamma \left[1 - \frac{a^2}{8}\left(q_y^2 + q_z^2\right) - 1 + \frac{a^2}{8}\left(q_x^2 + q_z^2\right) - 1 + \frac{a^2}{8}\left(q_x^2 + q_y^2\right) \right] \\
&= -4\gamma \left(-1 + \frac{a^2 q_x^2}{4} \right) = 4\gamma - \gamma a^2 q_x^2.
\end{aligned}$$

In other words, (up to a second-order Taylor approximation in q) $E(\boldsymbol{q})$ is parabolic around X, but only in the component q_x.

- Next, we write the expression for $E(\boldsymbol{q})$ about X in terms of effective mass in the form
$$E(\boldsymbol{q}) \equiv 4\gamma - \frac{\hbar^2 q_x^2}{2m^*}, \quad \text{where } m^* \equiv \frac{\hbar^2}{2\gamma a^2}$$

Similarly to the discussion in the context of the point Γ, we note that $E(\boldsymbol{q})$ is quadratic in q, like for the dispersion of free electrons, except for the constant energy shift by 4γ and the minus sign in front of the q_x^2 term.

- Finally, we consider the electron density of states near X. We will reuse free electron analogy, but adapted to the 4γ energy shift and negative dispersion relation. The result is
$$g(E) \propto \frac{1}{\sqrt{4\gamma - E}}$$

TODO: we have written $\sqrt{E}$ in the denominator. Because of negative dispersion?

9.2 Tight-Binding Model for a 2D Square Bravais Lattice

- Consider a two-dimensional square Bravais lattice, and consider only the electron band formed of s orbitals.

- Begin with

$$E(\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}},$$

where the sum runs over the lattice sites $\boldsymbol{R}$ that are nearest neighbors to the origin. For a square Bravais lattice, these nearest-neighbor sites are

$$\boldsymbol{R} = (\pm a, 0) \qquad \text{and} \qquad \boldsymbol{R} = (0, \pm a),$$

in terms of which the square lattice dispersion relation reads

$$E(\boldsymbol{k}) = -\gamma \left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} \right) = -2\gamma(\cos k_x a + \cos k_y a). \quad (9.2)$$

- We now consider the reciprocal lattice. A square Bravais lattice's reciprocal lattice is again a square lattice with lattice constant $2\pi/a$, and the first Brillioun zone is given by

$$\left\{ (k_x, k_y) \,\big|\, k_x \in \left(-\tfrac{\pi}{a}, \tfrac{\pi}{a} \right) \text{ and } k_y \in \left(-\tfrac{\pi}{a}, \tfrac{\pi}{a} \right) \right\}.$$

- We consider a path from the Brillioun zone's center $\Gamma = (0,0)$ to the center of the right edge $X = (\pi/a, 0)$ to the vertex point $M = \left(\tfrac{\pi}{a}, \tfrac{\pi}{a} \right)$ back to the center Γ.

9.2.1 Deriving Band Gap

- First, we parameterize the paths in $\boldsymbol{k}$ space between the Brillioun zone symmetry points using the parameter q.

point	coordinates	segment	wave vector $\boldsymbol{k}$	parameter range
Γ	$(0,0)$	$\Gamma \to X$	$\boldsymbol{k} = (q, 0)$	$q \in [0, \tfrac{\pi}{a}]$
X	$\left(\tfrac{\pi}{a}, 0 \right)$	$X \to M$	$\boldsymbol{k} = \left(\tfrac{\pi}{a}, q \right)$	$q \in [0, \tfrac{\pi}{a}]$
M	$\left(\tfrac{\pi}{a}, \tfrac{\pi}{a} \right)$	$M \to \Gamma$	$\boldsymbol{k} = \left(\tfrac{\pi}{a} - q, \tfrac{\pi}{a} - q \right)$	$q \in [0, \tfrac{\pi}{a}]$

- Begin with general dispersion relation

$$E(\boldsymbol{k}) = -2\gamma(\cos k_x a + \cos k_y a)$$

- For the first semgent from Γ to X, substitute in $\boldsymbol{k} = (q, 0)$ to get

$$E(q) = -2\gamma(\cos qa + 1)$$

Energy ranges from $E = -4\gamma$ to $E = 0$ on this segment.

- For the second segment from X to M substitute in $\boldsymbol{k} = (\pi/a, q)$ to get

$$E(q) = -2\gamma(-1 + \cos qa)$$

Energy ranges from $E = 0$ to $E = 4\gamma$ on this segment.

- For the final segment from M to Γ substitute in $\boldsymbol{k} = \left(\tfrac{\pi}{a} - q, \tfrac{\pi}{a} - q \right)$

$$E(q) = -2\gamma \cdot 2\cos \left[\left(\tfrac{\pi}{a} - q \right) a \right] = -4\gamma \cos(\pi - qa) = -4\gamma \cos(qa - \pi)$$
$$= +4\gamma \cos qa$$

Energy ranges from $E = +4\gamma$ to $E = -4\gamma$ on this segment.

- Over the entire path, the electron energy ranges from a minimum of -4γ to a maximum of $+4\gamma$, so the entire path's band gap is 8γ

9.2.2 Symmetry Considerations

- Our next step is to find the electron density of states $g(E)$ near each Brillioun zone symmetry point.

- To simplify later calculations, we first consider the square lattice's symmetries. Symmetry operations include: (i) a four-fold rotation about an axis perpendicular to the plane of the lattice and through the lattice's center; and (ii) reflection about the lines $y = x$ and $y = -x$.

- We then return to the general expression

$$E(\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}},$$

  and consider the effect of a generic symmetry operation $\mathbf{S}$ that maps a square lattice back into itself. The dispersion for a transformed vector $\mathbf{S}\boldsymbol{k}$ is then

$$E(\mathbf{S}\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\mathbf{S}\boldsymbol{k}\cdot\boldsymbol{R}} = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\mathbf{S}\boldsymbol{k}\cdot(\mathbf{S}\mathbf{S}^{-1})\boldsymbol{R}},$$

  where in the last equality we have simply introduced $\boldsymbol{R} = \mathbf{I}\boldsymbol{R} = (\mathbf{S}\mathbf{S}^{-1})\mathbf{R}$—we can be sure the inverse exists because a square lattice's symmetry operations form a group. We then apply the scalar product's invariance to reflections and rotations, i.e.

$$\mathbf{S}\boldsymbol{k} \cdot \mathbf{S}(\mathbf{S}^{-1}\mathbf{R}) = \boldsymbol{k} \cdot (\mathbf{S}^{-1}\mathbf{R}),$$

  to get

$$E(\mathbf{S}\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\boldsymbol{k}\cdot(\mathbf{S}^{-1}\boldsymbol{R})}.$$

  Since the symmetry operation $\mathbf{S}$ maps a square lattice back into itself, and the sum runs over only the origin's nearest neighbors (i.e. a single square unit cell), the total sum over the transformed nearest neighbor sites $\mathbf{S}^{-1}\boldsymbol{R}$ will equal the sum over the original sites $\boldsymbol{R}$ (individual terms may be rearranged, but the total sum is the same). This consideration gives

$$E(\mathbf{S}\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\boldsymbol{k}\cdot(\mathbf{S}^{-1}\boldsymbol{R})} = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = E(\boldsymbol{k})$$

  In other words, as might be expected, the dispersion relation is invariant to square lattice symmetry operations $\mathbf{S}$.

- Next, we note that the square reciporcal lattice's four quadrants are mapped into each other by four-fold rotations (e.g. rotation by $\pi/2$ maps quadrant I into quadrant II). Because all quadrants are related by symmetry operations, the dispersion relation must be the same in each quadrant. In other words, we only need to find $E(\boldsymbol{k})$ in a single quadrant.

- Next, because of the square lattice's reflection symmetry about the lines $y = x$ and $y = -x$, we only need to find $E(\boldsymbol{k})$ in one half of a single quadrant, e.g. below the line $y = x$ in quadrant I.

- Next, without detailed proof, we note one more symmetry, which applies to the density of states $g(E)$. Basically, we aim to show that every point $\boldsymbol{k}$ in the first Brillioun zone with positive energy is uniquely matched to a different point the first Brillioun zone with negative energy; recalling the expression for $E(\boldsymbol{k})$ in Equation 9.2, this follows (supposedly) from the relationship

$$
\begin{aligned}
E\left(\frac{\pi}{a} - k_x, \frac{\pi}{a} - k_y\right) &= -2\gamma\left[\cos\left(\pi - k_x a\right) + \cos\left(\pi - k_y a\right)\right] \\
&= +2\gamma\left(\cos k_x a + \cos k_y a\right) \\
&= -E(k_x, k_y),
\end{aligned}
$$

where I assume the point k_x, k_y are mapped to $\left(\frac{\pi}{a} - k_x, \frac{\pi}{a} - k_y\right)$, which evidently has opposite sign because of the functional for of $E(\boldsymbol{k})$. In any case, the end conclusion is that $g(E) = g(-E)$, i.e. that the density of states is an even function. As a result, we only need to find density of states on one half of the E axis.

  TODO: could we have just noted that $E(\boldsymbol{k})$ is even?

- Putting results together: instead of computing $E(\boldsymbol{k})$ on the entire square Brillioun zone, it is enough, because of the lattice's symmetry, to compute $E(\boldsymbol{k})$ on only one half of one quadrant, and $g(E)$ on only one half of the E axis.

9.2.3 Computing Density of States

Density of States Near the Center Point Γ

- We first expand the dispersion relation about the central Brillioun zone points Γ, where, like in **TODO:** reference FCC, we will use the ansatz

$$
\boldsymbol{k} = \Gamma + \boldsymbol{q}, = \boldsymbol{0} + \boldsymbol{q} = \boldsymbol{q}, \qquad |\boldsymbol{q}| \ll \frac{\pi}{a}.
$$

For review, the full dispersion relation $E(\boldsymbol{k})$ (Eq. 9.2) reads

$$
E(\boldsymbol{k}) = -2\gamma(\cos k_x a + \cos k_y a),
$$

and so the corresponding expression for $\boldsymbol{k} = \Gamma + \boldsymbol{q}$ is

$$
\begin{aligned}
E(\boldsymbol{q}) = -2\gamma\left[\cos(q_x a) + \cos(q_y a)\right] &\approx -2\gamma\left(1 - \frac{q_x^2 a^2}{2} + 1 - \frac{q_y^2 a^2}{2}\right) \\
&= -4\gamma + \gamma a^2 q^2,
\end{aligned}
$$

where we have expanded the cosine terms to second order in q. Finally, in terms of an effective mass, the dispersion relation reads

$$
E(\boldsymbol{q}) = -4\gamma + \frac{\hbar^2 q^2}{2m^*}, \quad \text{where } m^* \equiv \frac{\hbar^2}{2\gamma a^2}.
$$

The dispersion relation near Γ is quadratic in q, just like for a free electron dispersion. Continuing the free electron analogy, we then write density of states near Γ as

$$
g(E) \propto \Theta(E + 4\gamma),
$$

where Θ is the Heaviside step function, which ensures $g(E) = 0$ for $E < -4\gamma$, which falls outside the allowed energy band found in **TODO:** reference.

- Next, (this was done rather in passing) we drew curves of constant energy—these are circles of radius q—centered around Γ in $\boldsymbol{k}$ space. Next, we map these circles into the vertex point $M = \left(\frac{\pi}{a}, \frac{\pi}{a}\right)$ by reflecting about the first quadrant's center $\frac{\pi}{2a}, \frac{\pi}{2a}$. The conclusion is that the dispersion relation must be the same about both Γ and M, i.e. M also has a quadratic dispersion relation with density of states

$$g(E) \propto \Theta(E + 4\gamma).$$

Density of States Near the Edge Point X

- We first expand $E(\boldsymbol{k})$ about the right edge point $X = (\pi/a, 0)$ using the ansatz

$$\boldsymbol{k} = X + \boldsymbol{q} = \left(\frac{\pi}{a} + q_x, q_y\right), \qquad |\boldsymbol{q}| \ll \frac{\pi}{a}$$

The corresponding energy near X is then

$$
\begin{aligned}
E(\boldsymbol{q}) &= -2\gamma(\cos k_x a + \cos k_y a) = -2\gamma\big[\cos(\pi + q_x a) + \cos q_y a\big] \\
&= -2\gamma\big[-\cos q_x a + \cos q_y a\big],
\end{aligned}
$$

where the phase shift by π flips the sign of the $\cos q_x a$ term. Expanding the cosine terms to second order in q produces

$$E(\boldsymbol{q}) \approx -2\gamma \left[-1 + \frac{q_x^2 a^2}{2} + 1 - \frac{q_y^2 a^2}{2}\right] = \gamma a^2(-q_x^2 + q_y^2).$$

As for the FCC L point in **TODO:** reference this dispersion relation is a quadratic form in $\boldsymbol{q}$. As for the FCC L point, we could diagonalize this quadratic form, which would have eigenvalues of opposite sign and thus reveal that X is a saddle point in the disperion relation.

10 Tenth Exercise Set

10.1 Tight-Binding Model for a Square Bravais Lattice (continued)

Review Given 2D Bravais lattice. One atom per primitive cell. Properties of energy band formed from s orbitals. Make approximation. Instead of whole Hilbert zpace of all orbitals, consider only one s orbital per atom. We then analyzed the electron energy band that forms under the condition that the s orbitals overlap weakly. (i.e. TB model). We found the s orbital energy band spans the values -4γ to 4γ.
We found dispersion relation was quadratic in q at the symmetry points Γ and M and a saddle point at X. Our goal is to compute the density of states at the saddle point X.

- Now point X was a saddle point. We can't use free electron results at a saddle point—free electrons apply only to parabolic dispersion relation.

- Instead turn to formal definition of density of states

$$g(E) = \frac{1}{S}\frac{\mathrm{d}N}{\mathrm{d}E} = \frac{1}{L^2}\frac{\mathrm{d}N}{\mathrm{d}E},$$

  where $\mathrm{d}N$ is number of states between energies E and $E + \mathrm{d}E$ and $S = L^2$ is the crystal's area. Our goal is to find an expression for a generic point on the dispersion relation at energy E and then find number of states $\mathrm{d}N$ between E and $E + \mathrm{d}E$.

- Easier: define function $N(E)$ giving number of energies between $E = 0$ and E. We can find density of states by differentiated $N(E)$ by energy

$$g(E) = \frac{1}{S}\frac{\mathrm{d}}{\mathrm{d}E}\big[N(E)\big].$$

  Note subtle difference (which will have equivalent end results)—instead of dividing two differentials $\mathrm{d}N$ and $\mathrm{d}E$, we differentiate the function $N(E)$ with respect to E.

- Define coordinate system with origin at point X and let the q_x axis point from X to Γ. Note that the choice of sign for the q_x is arbitrary for our problem because q_x is squared to compute energy.

  Recall **TODO:** reference that near X, the dispersion relation reads

$$E(\boldsymbol{q}) = \gamma a^2(-q_x^2 + q_y^2),$$

  where indicates $E(q)$ has a saddle point near X. For the neighborhood of X for which $E > 0$, we can solve for q_y to get

$$q_y = \sqrt{q_x^2 + \frac{E}{\gamma a^2}}.$$

  However, recall from **TODO:** reference that $g(E)$ is an even function, so it is enough to consider only $g(E)$'s behavior for $E > 0$, since $g(E) = g(-E)$.

- **TODO:** where the integrand comes from. Like, why does integrating $\boldsymbol{k}$ produce electron number? The expression for $N(E)$ is then

$$N(E) = 2 \cdot 8 \cdot \left(\frac{2\pi}{L}\right)^{-2} \int_0^{q_c} \left(\sqrt{q_x^2 + \frac{E}{\gamma a^2}} - q_x\right) \mathrm{d}q_x,$$

where we subtract q_x to subtract off a "line of constant energy". Now integration limits are tricky because expression for q_y relies on a Taylor approximation of $E(\boldsymbol{q})$ which is value only for a limited range of $\boldsymbol{q}$. We use q_c for the time being but it turns out the value of this limit won't matter.

Anyway we then have

$$N(E) = \frac{4L^2}{\pi^2} \int_0^{q_c} \left(\sqrt{q_x^2 + \frac{E}{\gamma a^2}} - q_x\right) \mathrm{d}q_x.$$

- Okay, we have an expression for $N(E)$. Substitute this into

$$g(E) = \frac{1}{S} \frac{\mathrm{d}}{\mathrm{d}E} \big[N(E)\big]$$

(and change the order of integration and differentiation?) to get

$$g(E) = \frac{1}{L^2} \frac{4L^2}{\pi^2} \int_0^{q_c} \frac{\frac{1}{\gamma a^2}}{2\sqrt{q_x^2 + \frac{E}{\gamma a^2}}} \, \mathrm{d}q_x = \frac{2}{\pi^2 \gamma a^2} \left[\sinh^{-1} \frac{q_x}{\sqrt{E/(\gamma a^2)}}\right]_0^{q_c},$$

where we have used the integral

$$\int \frac{\mathrm{d}x}{\sqrt{x^2 + a^2}} = \sinh^{-1} \frac{x}{a}.$$

The end result is

$$g(E) = \frac{2}{\pi^2 \gamma a^2} \sinh^{-1} \frac{q_c}{\sqrt{E/(\gamma a^2)}}$$

- For small energies $E \ll \gamma$, argument of $\sinh^{-1}$ function will grow large. Recall behavior of $\sinh^{-1} x = y$ for $x \gg y$ and note that

$$x = \sinh y \approx \frac{e^y}{2} \implies y \approx \ln(2x)$$

For $E \ll \gamma$ the density of states near X then reads

$$g(E) \approx \frac{2}{\pi^2 \gamma a^2} \ln \frac{2q_c}{\sqrt{E/(\gamma a^2)}}.$$

Next, we split logarithm using the identity $\ln(A/B) = \ln A - \ln B$ to split the logarithm into an energy-dependent term and and a constant term (and note power $1/2$ cancelling with the factor 2). The result is

$$g(E) = \frac{1}{\pi^2 \gamma a^2} (-\ln E) + \frac{2}{\pi^2 \gamma a^2} \ln\left(2q_c \sqrt{\gamma a^2}\right)$$

For $E \ll \gamma$ we can neglect the second logarithm of constant terms to get

$$g(E) \approx -\frac{\ln E}{\pi^2 \gamma a^2}$$

Note that units are off because the logarithm's argument is not dimensionless (because of dropping constants) but that's okay—the lesson here is that the density of states behaves logarithmically near the Brillioun zone symmetry point X for $E \ll \gamma$, i.e. as $E \to 0$.

10.2   Graphene Using the Tight-Binding Model

- Up to now using the TB model we always considered only one atomic orbital per primitive cell. This prevents us from analyzing energy bands that arise from orbitals that are not of type s. Example: when p and d bands are important, OR for basis structures with multiple atomic orbitals per primitive cell.

- Review graphene: it has a honey-comb lattice, which is not a Bravais lattice. We will describe graphene with a triangular Bravais lattice together with a basis. The lattice's primitive vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ **TODO:** reference are equally long and have angle 60° degrees between them.

  Define conventional points A and B and basis vectors (assuming A is the origin)

  $$\boldsymbol{d}_A = \boldsymbol{0} \qquad \text{and} \qquad \boldsymbol{d}_B = \frac{\boldsymbol{a}_1 + \boldsymbol{a}_2}{3}$$

  We consider only nearest neighbors (as in tight-binding model with localized orbitals). Both the A and B points have three nearest neighbors, drawn in Figure *graphene-nearest-neighbor.*

- For better understanding, we consider orbital structure of carbon: $1s^2 2s^2 2p^2$. Now the 1s are "frozen" deep below the Fermi energy (or so localized around the atomic nucleus that their is no overlap with neighbors). Thus the 1s do not contribute to energy bands. Now the remaining two orbitals hybridize to form $2sp_2^3 2p_z$, where the z axis points out of the page in our sketch. Quoted: near the Fermi energy only the $2p_z$ contribute appreciably to energy band formation; the $2sp_2^3$ are frozen below Fermi energy or localized around nucleus.

  We consider only contribution of $2p_z$ to energy band formation.

- Review: Two atoms A and B per unit cell of graphene. Each has three nearest neighbors. We consider only one p_z atom per atom. Or $2p_z$ oritals per unit cell. We can't use lecture formula (for what) because there we consider only one orbital per unit cell. We need to perform a derivation.

Derivation

- Form basis of Hilbert space in which we will work. This basis consists of orbitals specified by a vector in the Bravais lattice $\boldsymbol{R}$ and in index α denoting which orbital. Orbital states are labelled by $|\boldsymbol{R}_\alpha\rangle$. In our case $\alpha \in \{A, B\}$ where $\alpha = A$ means the orbital p_z around the A atom.

- In coordinate representation, the basis functions read

$$\phi_\alpha(\boldsymbol{r} - \boldsymbol{R} - \boldsymbol{r}_\alpha),$$

  where ϕ_α is the orbital's wave function and, I believe, $\boldsymbol{R} - \boldsymbol{r}_\alpha$ gives the position of the relevant atom (I suppose A or B).

- The following derivation using $|\boldsymbol{R}_\alpha\rangle$ allows for an arbitrary number of indeces α. Note: we consider only a small number of orbitals per unit cell, (not a continuum of orbitals or high-energy excited orbitals?), so the derivation is an approximation.

- We aim to solve the stationary Schrödinger equation

$$H |\psi\rangle = E |\psi\rangle,$$

  where we write $|\psi\rangle$ using the ansatz

$$|\psi\rangle = \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left|\boldsymbol{R}'_{\alpha'}\right\rangle.$$

  Substituting this ansatz into the Schrödinger equation produces

$$H \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left|\boldsymbol{R}'_{\alpha'}\right\rangle = \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} H \left|\boldsymbol{R}'_{\alpha'}\right\rangle = E \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left|\boldsymbol{R}'_{\alpha'}\right\rangle$$

  We then project the state $\langle \boldsymbol{R}_\alpha|$ onto this equation, which produces

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| H \middle| \boldsymbol{R}'_{\alpha'}\right\rangle = E \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle$$

  Note that the basis of $|\boldsymbol{R}_\alpha\rangle$ states is not orthonormal, so that $\left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle \neq \delta_{\alpha\alpha'}$.

- Next, we write the Hamiltonian H as the sum of an isolated atomic Hamiltonian and a potential term in the form

$$H = H^{\text{atom}}_{\boldsymbol{R}_\alpha} + \Delta U_{\boldsymbol{R}_\alpha},$$

  where the atomic Hamiltonian obeys the eigenvalue relation

$$H^{\text{atom}}_{\boldsymbol{R}_\alpha} |\boldsymbol{R}_\alpha\rangle = E_\alpha |\boldsymbol{R}_\alpha\rangle.$$

  Substituting this ansatz for H into Equation **TODO: reference** produces

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left(E^{\text{atom}}_\alpha \left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle + \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'}\right\rangle\right) = E \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle$$

  We then combine the like $\left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle$ terms, which produces

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'}\right\rangle = \left(E - E^{\text{atom}}_\alpha\right) \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle$$

  We then decompose the sum on the RHS and apply $\langle \boldsymbol{R}_\alpha | \boldsymbol{R}_\alpha \rangle = 1$ to get

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'}\right\rangle = \left(E - E^{\text{atom}}_\alpha\right) \left(c_{\boldsymbol{R}_\alpha} + \sum_{\boldsymbol{R}'_{\alpha'} \neq \boldsymbol{R}_\alpha} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'}\right\rangle\right)$$

  Note the LHS matrix element $\left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'}\right\rangle$ plays the same role as the β and γ overlap integral in the tight-binding model, while the RHS plays the same role as the α overlap integrals.

- Next, we introduce the shorthand notation

$$A_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} \equiv \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'} \right\rangle \qquad \text{and} \qquad B_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} \equiv \left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'} \right\rangle,$$

in terms of which the equation **TODO:** reference two up becomes

$$\sum_{\boldsymbol{R}'_{\alpha'}} A_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} = \left(E - E_\alpha^{\mathrm{atom}} \right) \sum_{\boldsymbol{R}'_{\alpha'}} B_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}}.$$

In equivalent matrix form, the above equation reads

$$\mathbf{A}\boldsymbol{c} = \left(E - E_\alpha^{\mathrm{atom}} \right) \mathbf{B}\boldsymbol{c},$$

which is a generalized eigenvalue problem. Note that if the RHS were just a scalar times $\boldsymbol{c}$ this would be an regular eigenvalue problem; the matrix $\mathbf{B}$ on the RHS (which arises because of a non-orthogonal basis in which $\left\langle \boldsymbol{R}_\alpha \middle| \boldsymbol{R}'_{\alpha'} \right\rangle \neq \delta_{\alpha\alpha'}$) make it a generalized eigenvalue problem.

- We solve Equation **TODO:** reference with the ansatz

$$\mathbf{B} = \mathbf{I} + \delta\mathbf{B}$$

which we substitute into Equation **TODO:** reference, then invert, to get

$$\mathbf{B}^{-1}\mathbf{A}\boldsymbol{c} = \left(E - E_\alpha^{\mathrm{atom}} \right) \boldsymbol{c}$$

where $\mathbf{B}^{-1} = \mathbf{I} + \delta\widetilde{\mathbf{B}}$. We then neglect $\widetilde{\mathbf{B}}$ term, because **TODO:** for the same reason we neglected α and β integrals in the tight-binding model.

We then end up with regular eigenvalue problem

$$\mathbf{A}\boldsymbol{c} = \left(E - E_\alpha^{\mathrm{atom}} \right) \boldsymbol{c}.$$

Written out in braket from, this reads

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'} \right\rangle = \left(E - E_\alpha^{\mathrm{atom}} \right) c_{\boldsymbol{R}_\alpha}$$

Finally, we decompose the sum on the RHS into diagonal and off-diagonal terms, which gives the final expression

$$\left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}_\alpha \right\rangle c_{\boldsymbol{R}_\alpha} + \sum_{\boldsymbol{R}'_{\alpha'} \neq \boldsymbol{R}_\alpha} \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'} \right\rangle c_{\boldsymbol{R}'_{\alpha'}} = \left(E - E_\alpha^{\mathrm{atom}} \right) c_{\boldsymbol{R}_\alpha}$$

10.2.1   One Orbital Per Unit Cell

- As an exercise, we first analyze the the simple case of one electron orbital per unit cell, which is essentially the tight-binding model from previous problems. We no longer need the index α, and introduce the tight-binding model overlap integrals β and γ according to

$$\left\langle \boldsymbol{R} \middle| \Delta U_{\boldsymbol{R}} \middle| \boldsymbol{R} \right\rangle = -\beta \qquad \text{and} \qquad \left\langle \boldsymbol{R} \middle| \Delta U_{\boldsymbol{R}} \middle| \boldsymbol{R}' \right\rangle = -\gamma(\boldsymbol{R}' - \boldsymbol{R}),$$

in terms of which the energy eigenvalue problem reads

$$\beta c_{\boldsymbol{R}} - \sum_{\boldsymbol{R}' \neq \boldsymbol{R}} \gamma(\boldsymbol{R}' - \boldsymbol{R}) c_{\boldsymbol{R}'} = \left(E - E^{\text{atom}} \right) c_{\boldsymbol{R}}.$$

We then rearrange this expression to get

$$- \sum_{\boldsymbol{R}' \neq \boldsymbol{R}} \gamma(\boldsymbol{R}' - \boldsymbol{R}) c_{\boldsymbol{R}'} = \left[E - \left(E^{\text{atom}} - \beta \right) \right] c_{\boldsymbol{R}}$$

Lesson: from $E^{\text{atom}} - \beta$ we see energy of atomic orbitals shifts by β, while the $\gamma(\boldsymbol{R}' - \boldsymbol{R})$ term on the RHS gives the energy required for an electron to jump from an atom at position $\boldsymbol{R}$ to an atom at position $\boldsymbol{R}'$.

- Next, we use Bloch's theorem to write coefficients in the form

$$c_{\boldsymbol{R}} = c_0 e^{i \boldsymbol{k} \cdot \boldsymbol{R}},$$

in terms of which energy eigenvalue equation becomes

$$- \sum_{\boldsymbol{R}' \neq \boldsymbol{R}} \gamma(\boldsymbol{R}' - \boldsymbol{R}) c_0 e^{i \boldsymbol{k} \cdot \boldsymbol{R}'} = \left[E - \left(E^{\text{atom}} - \beta \right) \right] c_0 e^{i \boldsymbol{k} \cdot \boldsymbol{R}}.$$

We then multiply through by $e^{-i \boldsymbol{k} \cdot \boldsymbol{R}}$ to and cancel c_0 to get

$$- \sum_{\boldsymbol{R}' \neq \boldsymbol{R}} \gamma(\boldsymbol{R}' - \boldsymbol{R}) e^{i \boldsymbol{k} \cdot (\boldsymbol{R}' - \boldsymbol{R})} = E - \left(E^{\text{atom}} - \beta \right),$$

which we then solve for E to get the dispersion relation

$$E(\boldsymbol{k}) = E^{\text{atom}} - \beta - \sum_{\boldsymbol{R}' \neq \boldsymbol{R}} \gamma(\boldsymbol{R}' - \boldsymbol{R}) e^{i \boldsymbol{k} \cdot (\boldsymbol{R}' - \boldsymbol{R})} \quad = E^{\text{atom}} - \beta - \sum_{\boldsymbol{R} \neq \boldsymbol{0}} \gamma(\boldsymbol{R}) e^{i \boldsymbol{k} \cdot \boldsymbol{R}}.$$

The takeaway here is that we have reproduced the tight-binding model result for the dispersion relation $E(\boldsymbol{k})$ in terms of the overlap integrals β and γ. **TODO:** reference equation.

10.2.2 Graphene—Two Orbitals Per Lattice Site

- Above was for practice and we just considered one orbital per unit cell. We now consider two orbitals per unit cell, which is a more realisitic model for graphene.

- Recall we consider only the contribution of $2p_z$ orbitals to electron energy bands, and that these orbitals are perpendicular to the plane of graphene.

  Consider B atom: we can write all nearest-neighbor orbitals (for A atoms) with a single real orbital (single because they're symmetric with $C3$ axis).

- Begin with the relationship from Equation **TODO:** reference.

$$\langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}_\alpha \rangle c_{\boldsymbol{R}_\alpha} + \sum_{\boldsymbol{R}'_{\alpha'} \neq \boldsymbol{R}_\alpha} \langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle c_{\boldsymbol{R}'_{\alpha'}} = \left(E - E_\alpha^{\text{atom}} \right) c_{\boldsymbol{R}_\alpha},$$

and define

$$\langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}_\alpha \rangle \equiv -\beta_\alpha \quad \text{and} \quad \langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle \equiv -\gamma_\alpha (\boldsymbol{R}' - \boldsymbol{R})$$

- Next, we note the equalities

$$E_A^{\text{atom}} = E_B^{\text{atom}} \equiv E^{\text{atom}} \qquad \text{and} \qquad \beta_A = \beta_B \equiv \beta.$$

We then have for $\boldsymbol{R}_{\text{B}}$

$$-\gamma c_{\boldsymbol{R}_A} - \gamma c_{\boldsymbol{R}+\boldsymbol{a}_{1_A}} - \gamma c_{\boldsymbol{R}+\boldsymbol{a}_{2_A}} = E - E^{\text{atom}} = \left[E - (E^{\text{atom}} - \beta) \right] c_{\boldsymbol{R}_B}$$

And for $\boldsymbol{R}_A$ we have

$$-\gamma c_{\boldsymbol{R}_B} - \gamma c_{\boldsymbol{R}-\boldsymbol{a}_{1_B}} - \gamma c_{\boldsymbol{R}-\boldsymbol{a}_{2_B}} = E - E^{\text{atom}} = \left[E - (E^{\text{atom}} - \beta) \right] c_{\boldsymbol{R}_A}$$

- We solve these equations with the Bloch ansatz

$$c_{\boldsymbol{R}_A} = c_A e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \qquad \text{and} \qquad c_{\boldsymbol{R}_B} = c_B e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$$

which we substitute into the above equations to get

$$-\gamma c_A e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - \gamma c_A e^{i\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{a}_1)} - \gamma c_A e^{i\boldsymbol{k}\cdot(\boldsymbol{R}+\boldsymbol{a}_2)} = \left[E - \left(E^{\text{atom}} - \beta \right) \right] c_B$$

$$-\gamma c_B e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - \gamma c_B e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{a}_1)} - \gamma c_B e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{a}_2)} = \left[E - \left(E^{\text{atom}} - \beta \right) \right] c_A$$

We end up with a set of only two equations because of the Bloch ansatz because the $e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$ terms cancelled. In matrix form, the above system of equations reads

$$\begin{pmatrix} E^{\text{atom}} - \beta - E & -\gamma \left(1 + e^{-i\boldsymbol{k}\cdot\boldsymbol{a}_1} + e^{-i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right) \\ -\gamma \left(1 + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right) & E^{\text{atom}} - \beta - E \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = \boldsymbol{0}$$

We then require the matrix's determinant equals zero, so that the homogeneous system has a nontrivial solution. Without derivation, the requirement of zero determinant produces

$$E(\boldsymbol{k}) = E^{\text{atom}} - \beta \pm \gamma \left| 1 + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right|$$

Lesson: the dispersion relation has two branches, and the two p_z orbitals thus contribute two electron energy bands. Without proof, considering N orbitals per unit cell in a problem's Hilbert space leads to N energy bands, one for each orbital.

11 Eleventh Exercise Set

11.1 Graphene Tight-Binding Model (continued)

- We left off in the last exercise set with the dispersion relation

$$E(\boldsymbol{k}) = E^{\text{atom}} - \beta \pm \gamma \left| 1 + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right|$$

from the two p_z orbitals in a two-dimensional graphene lattice. We drop the constant terms E^{atom} and β to get

$$E(\boldsymbol{k}) = \pm\gamma \left| 1 - e^{i\kappa\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right|$$

- Next, we will analyze dispersion relation at points of high symmetry in graphene's first Brillioun zone. For review, we describe graphene as a triangular lattice (see Exercise 3.4) with primitive vectors

$$\boldsymbol{a}_1 = a(1,0) \qquad \text{and} \qquad \boldsymbol{a}_2 = a\left(\tfrac{1}{2}, \tfrac{\sqrt{3}}{2}\right)$$

and the two basis vectors

$$\boldsymbol{d}_A = \boldsymbol{0} \qquad \text{and} \qquad \boldsymbol{d}_B = \frac{\boldsymbol{a}_1 + \boldsymbol{a}_2}{3}.$$

From Exercise 3.4, the triangular lattice's reciprocal lattice is again a triangular lattice with reciprocal vectors

$$\boldsymbol{b}_1 = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right) \qquad \text{and} \qquad \boldsymbol{b}_2 = \frac{4\pi}{\sqrt{3}a}(0,1).$$

Having identified the reciprocal lattice, we now construct the first Brillioun zone, which is the Wigner-Seitz of the reciprocal lattice. Following the standard Wigner-Seitz construction procedue, we draw lines form the origin to the six closest reciprocal lattice sites. The region bounded by the lines' perpendicular bisectors is the first Brillioun zone—in our triangular case this is a regular hexagon.

- Without formal derivation, we note that the most "interesting" physics occurs near the vertices of the hexagonal first Brillioun zone, conventionally denoted by K. We will consider the K vertex point lying on the positive portion of the k_x axis.

  We then expand a generic wave vector $\boldsymbol{k}$ about the vertex point K using the ansatz

$$\boldsymbol{k} = K + \boldsymbol{q}, \qquad |\boldsymbol{q}| \ll \frac{\pi}{a}.$$

  To find K's coordinates, we note that K is the centroid of the triangle formed by $\boldsymbol{b}_1 + \boldsymbol{b}_2$ and $\boldsymbol{b}_1$, and is thus (quoting from an e.g. introductory geometry course) given by

$$K = \frac{2}{3}\frac{\boldsymbol{b}_1 + (\boldsymbol{b}_1 + \boldsymbol{b}_2)}{2} = \frac{2\boldsymbol{b}_1 + \boldsymbol{b}_2}{3} = \frac{1}{3}\frac{4\pi}{\sqrt{3}a}(\sqrt{3}, 0) = \frac{4\pi}{3a}(1,0).$$

- We now find the energy near K. We begin with the general dispersion relation

$$E(\boldsymbol{k}) = \pm\gamma \left| 1 - e^{i\kappa\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right|$$

and substitute in the ansatz $\boldsymbol{k} = K + \boldsymbol{q}$ to get

$$E(\boldsymbol{q}) = \pm\gamma\left|1 + e^{i(K+\boldsymbol{q})\cdot\boldsymbol{a}_1} + e^{i(K+\boldsymbol{q})\cdot\boldsymbol{a}_2}\right|.$$

The dot products of K with $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ come out to

$$K \cdot \boldsymbol{a}_1 = \frac{4\pi}{3a}(1,0) \cdot a(1,0) = \frac{4\pi}{3}$$

$$K \cdot \boldsymbol{a}_2 = \frac{4\pi}{3a}(1,0) \cdot a\left(\tfrac{1}{2}, \tfrac{\sqrt{3}}{2}\right) = \frac{2\pi}{3},$$

in terms of which the dispersion relation $E(\boldsymbol{q})$ reads

$$E(\boldsymbol{q}) = \pm\gamma\left|1 + \exp\left[i\left(\frac{4\pi}{3} + \boldsymbol{q}\cdot\boldsymbol{a}_1\right)\right] + \exp\left[i\left(\frac{2\pi}{3} + \boldsymbol{q}\cdot\boldsymbol{a}_2\right)\right]\right|.$$

Written more compactly, and noting that $e^{i\frac{4\pi}{3}} = e^{-i\frac{2\pi}{3}}$, we have

$$E(\boldsymbol{q}) = \pm\gamma\left|1 + e^{-i\frac{2\pi}{3}}e^{i\boldsymbol{q}\cdot\boldsymbol{a}_1} + e^{i\frac{2\pi}{3}}e^{i\boldsymbol{q}\cdot\boldsymbol{a}_2}\right|.$$

We then Taylor expand the exponents to first order in $\boldsymbol{q}\cdot\boldsymbol{a}_1$ and $\boldsymbol{q}\cdot\boldsymbol{a}_2$ to get

$$E(\boldsymbol{q}) = \pm\left|1 + e^{-i\frac{2\pi}{3}}(1 + i\boldsymbol{q}\cdot\boldsymbol{a}_1) + e^{i\frac{2\pi}{3}}(1 + i\boldsymbol{q}\cdot\boldsymbol{a}_2)\right|$$

$$= \pm\gamma\left|1 + e^{-i\frac{2\pi}{3}} + e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}}i\boldsymbol{q}\cdot\boldsymbol{a}_1 + e^{i\frac{2\pi}{3}}i\boldsymbol{q}\cdot\boldsymbol{a}_2\right|.$$

We then note that $1 + e^{i\frac{2\pi}{3}} + e^{-i\frac{2\pi}{3}} = 0$ to get

$$E(\boldsymbol{q}) = \pm\gamma\left|e^{-i\frac{2\pi}{3}}i\boldsymbol{q}\cdot\boldsymbol{a}_1 + e^{i\frac{2\pi}{3}}i\boldsymbol{q}\cdot\boldsymbol{a}_2\right|$$

- Then some trigonometric acrobatics to get

$$E(\boldsymbol{q}) = \pm\gamma\left|\cos\left(\frac{2\pi}{3}\right)i\boldsymbol{q}(\boldsymbol{a}_1 + \boldsymbol{a}_2) + i\sin\left(\frac{2\pi}{3}\right)i\boldsymbol{q}(\boldsymbol{a}_2 - \boldsymbol{a}_1)\right|.$$

Noting that

$$\boldsymbol{a}_1 + \boldsymbol{a}_2 = a\left(\tfrac{3}{2}, \tfrac{\sqrt{3}}{2}\right) \qquad \text{and} \qquad \boldsymbol{a}_2 - \boldsymbol{a}_1 = \tfrac{a}{2}(-1, \sqrt{3}),$$

we then evaluate the dot products to get

$$E(\boldsymbol{q}) = \pm\gamma\left|-\frac{i}{2}a\left(\frac{3}{2}q_x + \frac{\sqrt{3}}{2}q_y\right) + \frac{\sqrt{3}i^2}{2}a\left(-\frac{1}{2}q_x + \frac{\sqrt{3}}{2}q_y\right)\right|$$

We then simplfy and factor out the common a term to get

$$E(\boldsymbol{q}) = \pm\gamma a\left|-\frac{3}{4}iq_x - \frac{\sqrt{3}}{4}iq_y + \frac{\sqrt{3}}{4}q_x - \frac{3}{4}q_y\right|.$$

Next, we evaluate the absolute value (which is the square of the real and imaginary terms) to get

$$E(\boldsymbol{q}) = \pm\gamma a \sqrt{\left(\frac{\sqrt{3}}{4}q_x - \frac{3}{4}q_y\right)^2 + \left(\frac{3}{4}q_x + \frac{\sqrt{3}}{4}q_y\right)^2}$$

$$= \pm\gamma a \sqrt{\frac{3}{16}q_x^2 + \frac{9}{16}q_y^2 + \frac{9}{16}q_x^2 + \frac{3}{16}q_y^2} = \pm\frac{\sqrt{3}}{2}\gamma a \sqrt{q_x^2 + q_y^2}$$

$$= \pm\frac{\sqrt{3}}{2}\gamma a |\boldsymbol{q}|.$$

This is the desired dispersion relation for graphene near the Brillioun zone vertex point K. We can actually plot the expression for $E(\boldsymbol{q})$ in three dimensions—the result is two cones centered at K with longitudinal axes normal to the q_x, q_y plane; one cone points upward and one downward.

11.2 Cyclotron Effective Mass

- We consider electrons near the minimum of an energy band with a quadratic dispersion relation of the form

$$E(\boldsymbol{k}) = \frac{\hbar^2}{2}\boldsymbol{k} \cdot \left(\mathsf{m}^*\right)^{-1}\boldsymbol{k} + E_0$$

  m^* is the effective mass tensor and $E_0 = E(\boldsymbol{k} = \boldsymbol{0})$. Because we assume the electrons occur near a minimum, the effective mass tensor must have all positive eigenvalues, so that energy increases in all $\boldsymbol{k}$ directions away from the minimum. We note also that the effective mass tensor is symmetric (or can be made so without loss of generality).

- We choose our coordinate system such that the external magnetic field aligns with the z axis, i.e. $\boldsymbol{B} = (0, 0, B)$, and describe the electron's dynamics in the magnetic with an "effective Newton's law" of the form

$$\hbar\dot{\boldsymbol{k}} = q\boldsymbol{v} \times \boldsymbol{B},$$

  where we have replaced classical acceleration with $\hbar\dot{\boldsymbol{k}}$. Our second expression relates electron velocity $\boldsymbol{v}$ and energy E, and reads

$$\boldsymbol{v} = \frac{1}{\hbar}\frac{\partial E}{\partial \boldsymbol{k}} \tag{11.1}$$

- Using the summation with α as a dummy index, we begin our analysis by substituting E into Equation 11.1 to get

$$v_\alpha = \frac{1}{\hbar}\frac{\partial E}{\partial k_\alpha} = \frac{1}{\hbar}\frac{\hbar^2}{2}\frac{\partial}{\partial k_\alpha}\left(k_i\left(\mathsf{m}^*\right)^{-1}_{ij}k_j\right) = \frac{\hbar}{2}\left[\delta_{i\alpha}\left(\mathsf{m}^*\right)^{-1}_{ij}k_j + k_i\left(\mathsf{m}^*\right)^{-1}_{ij}\delta_{j\alpha}\right]$$

$$= \frac{\hbar}{2}\left[\left(\mathsf{m}^*\right)^{-1}_{\alpha j}k_j + k_i\left(\mathsf{m}^*\right)^{-1}_{i\alpha}\right]$$

$$= \frac{\hbar}{2}\left[\left(\mathsf{m}^*\right)^{-1}_{\alpha j}k_j + k_i\left(\mathsf{m}^*\right)^{-1}_{\alpha i}\right],$$

where we have used the mass tensor's symmetry $\mathsf{m}^*_{i\alpha} = \mathsf{m}^*_{\alpha i}$ in the last equality. Since j is a dummy index, we can rewrite v_α more compactly as

$$v_\alpha = \frac{\hbar}{2}\left[2(\mathsf{m}^*)^{-1}_{\alpha i}k_i\right] = \hbar\left[(\mathsf{m}^*)^{-1}\boldsymbol{k}\right]_\alpha.$$

We then invert the last expression to get

$$\boldsymbol{v} = \hbar\left(\mathsf{m}^*\right)^{-1}\boldsymbol{k} \implies \mathsf{m}^*\boldsymbol{v} = \hbar\boldsymbol{k},$$

which we substitute into the $\hbar\dot{\boldsymbol{k}}$ Newton's law equation to get

$$\mathsf{m}^*\dot{\boldsymbol{v}} = q\boldsymbol{v} \times \boldsymbol{B}.$$

This expression resembles Newton's law for a classical charged particle in a magnetic field, except that mass is now a tensor and not a scalar. The above vector equation represents a homogeneous system of first-order linear differential equations in the componens v_α. We will solve the equations with the ansatz,

$$\boldsymbol{v} = \boldsymbol{v}_0 e^{-i\omega t} \implies \dot{\boldsymbol{v}} = -i\omega\boldsymbol{v}$$

which we substitute into Equation **TODO:** reference and divide out $e^{-i\omega t}$ to get

$$-i\omega\mathsf{m}^*\boldsymbol{v}_0 = q\boldsymbol{v}_0 \times \boldsymbol{B}.$$

We then evaluate the cross product $\boldsymbol{v}_0 \times \boldsymbol{B}$ by components, recalling $\boldsymbol{B} = (0, 0, B)$, to get

$$-i\omega\mathsf{m}^*\boldsymbol{v_0} = qB\begin{pmatrix} v_{0_y} \\ -v_{0_x} \\ 0 \end{pmatrix} \implies \mathsf{m}^*\boldsymbol{v_0} = \frac{iqB}{\omega}\begin{pmatrix} v_{0_y} \\ -v_{0_x} \\ 0 \end{pmatrix}$$

Written out in matrix form, this system of equations reads

$$\begin{pmatrix} m_{xx} & m_{xy} - \frac{qB}{i\omega} & m_{xz} \\ m_{yx} + \frac{qB}{i\omega} & m_{yy} & m_{yz} \\ m_{zx} & m_{zy} & m_{zz} \end{pmatrix}\begin{pmatrix} v_{0_x} \\ v_{0_y} \\ v_{0_z} \end{pmatrix} \equiv \mathsf{m}^*_{\boldsymbol{B}}\boldsymbol{v}_0 = \boldsymbol{0},$$

where I have written the mass tensor components without a * superscript for compactness. We then require the matrix's determinant equal zero so that the homogenous equation has a nontrivial solution.

- We write the determinant with a slight trick: we consider the determinant of a "pure" effective mass tensor m^* without B terms, and then add corrections because of $\mathsf{m}^*_{\boldsymbol{B}}$'s two magnetic field components. The result is

$$0 \equiv \det\mathsf{m}^*_{\boldsymbol{B}} = \det\mathsf{m}^* - \frac{iqB}{\omega}m_{yz}m_{zx} + \frac{iqB}{\omega}m_{zy}m_{xz} + \left[m_{zz}\left(\frac{iqB}{\omega}\right)^2\right].$$

But the two middle terms cancel because m^* is symmetric, leaving only

$$0 = \det\mathsf{m}^* - \left(\frac{qB\sqrt{m_{zz}}}{\omega}\right)^2$$

We then solve for electron oscillation frequency ω to get

$$\omega = \frac{|q|B\sqrt{m_{zz}}}{\sqrt{\det \mathsf{m}^*}} = |q|B\sqrt{\frac{m_{zz}}{\det \mathsf{m}^*}} \equiv \frac{|q|B}{m_c^*},$$

where we have defined the cyclotron effective mass m_c^*.

$$m_c^* = \sqrt{\frac{\det \mathsf{m}^*}{m_{zz}^*}} = \sqrt{\frac{\det \mathsf{m}^*}{\hat{\mathbf{e}}_B \cdot \mathsf{m}^* \cdot \hat{\mathbf{e}}_B}},$$

where we have defined the coordinate free expression $\boldsymbol{B} = \hat{\mathbf{e}}_B B$.

- Note resemblance to classical electron cyclotron frequency result

$$\omega_c = \frac{|q|B}{m}$$

- We find from ω_c and initial conditions the solution

$$\boldsymbol{v}(t) = \boldsymbol{v}_0 e^{-i\omega_c t}.$$

We would then find $\boldsymbol{r}$ from $\dot{\boldsymbol{r}} = \boldsymbol{v}$. Aha so finding dynamics is basically finding ω in ansatz.

- Non-isotropic dispersion relation (requiring effective mass tensor) leads to common physical quantities expressed with various effective quandities using determinant of m^*. For example

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

But near bottom of our dispersion band we would have

$$g(E) = \frac{\sqrt{2m^*}}{\pi^2 \hbar^3}\sqrt{E - E_0}, \quad \text{where } \mathsf{m}^* \equiv \sqrt[3]{\det \mathsf{m}^*}.$$

Lesson is that classical masses are replaced by different functions of the effective mass tensor.

11.3 Chemical Potential in a Doped Semiconductor

- In the context of SC we consider two energy bands—the conduction band and valence band. We denote the energy at the top of the valence band by E_v and energy at the bottom of the conduction band by E_c. Additionally, we define the *band gap* $E_g = E_c - E_v$, which is just the energy difference between the top of the valence band and bottom of the conduction band.

- The density of state of electrons near the bottom of the conduction band is

$$g_c = \frac{\sqrt{2m_c^*}}{\pi^2 \hbar^3}\sqrt{E - E_c}, \quad \text{where } m_c^* \equiv \sqrt[3]{\det \mathsf{m}_c^*},$$

while the density of state for holes near the top of the valence band is

$$g_v = \frac{\sqrt{2m_v^*}}{\pi^2 \hbar^3}\sqrt{E_v - E}, \quad \text{where } m_v^* \equiv \sqrt[3]{\det \mathsf{m}_v^*}.$$

In practice, the effective mass tensor m^* would be known for a given material; in principle m^* would be found from a Taylor expansion of the dispersion relation near the extremum of the relevant band.

- Doped semiconductors contain acceptors and donors—so called *dopants*—in addition to intrinsic charge carriers. We will consider a n-type semiconductor with only donors. The donors add a donor energy level with energy E_{d} just below the bottom of the conduction band E_{c}. Typically $E_{\mathrm{c}} - E_{\mathrm{d}} \sim 1\,\mathrm{meV}$ while $E_{\mathrm{g}} \sim 1\,\mathrm{eV}$.

  We characterize donors by their donor energy level E_{d} and their concentration N_{d}, which is the number of donors per unit volume in the semiconductor.

- In a semiconductor at temperature $T = 0\,\mathrm{K}$ the valence band is fully occupied, the donor energy levels are also fully occupied, and the conduction band is empty.

  At non-zero temperatures, because of thermal fluctuations, some electrons will be excited into the conduction band. A common quantity of interest is thus the number of electrons in the conduction band as a function of temperature.

- We define three quantities:

  1. n_{c} is the concentration of electrons in the conduction band
  2. p_{v} is the concentration of holes in the valence band
  3. p_{d} is the concentration of holes in donor energy levels

  At $T = 0\,\mathrm{K}$ we have $n_{\mathrm{c}} = p_{\mathrm{v}} = p_{\mathrm{d}} = 0$. Interpretation: valence band is fully occupied (with electrons) so no holes in valence band nor electrons in conduction band; similarly all donor levels are fully occupied (with electrons) so no holes in donor levels.

  At $T > 0\,\mathrm{K}$ we have $n_{\mathrm{c}} = n_{\mathrm{c}}(T)$, $p_{\mathrm{v}} = p_{\mathrm{v}}(T)$, $p_{\mathrm{d}} = p_{\mathrm{d}}(T)$, and in practice we are interested in the number of free charge carriers (of interest because free charge carriers can contribute to electric current), and these free charge carriers are electrons in conduction band or holes in valence band, given by $n_{\mathrm{c}}(T)$ and $p_{\mathrm{v}}(T)$.

- Our goal in this problem is effectively to find the number of free charge carriers in a doped semiconductor as a function of temperature. To do this, we need to know the location of the chemical potential as a function of temperature.

  This is because chemical potential will give us the Fermi function for the semiconductor, from which we can find n_{c} and p_{v} and other temperature-dependent quantities.

  So we will first find $\mu(T)$, then $n_{\mathrm{c}}(T)$ and $p_{\mathrm{v}}(T)$.

More Review from Lecture

- Concentration of electrons in conduction band is found from integrating over the conduction band

  $$n_{\mathrm{c}} = \int_{E_{\mathrm{c}}}^{\infty} g_{\mathrm{c}}(E) f(E)\, \mathrm{d}E.$$

  Since $f(E)$ depends on μ, we need to know $\mu(T)$ to find n_{c}. Without derivation, quote from lecture that, for a non-degenerate semiconductor, the conduction band electron density n_{c} is well-approxited by

  $$n_{\mathrm{c}} = N_{\mathrm{c}} e^{-\beta(E_{\mathrm{c}} - \mu)}, \quad \text{where } N_{\mathrm{c}} = \frac{1}{4}\left(\frac{2 m_{\mathrm{c}}^* k_B T}{\pi \hbar^2}\right)^{3/2}.$$

Note that n_c is the product of N_c (a weakly temperature-dependent quantity) and $e^{-\beta}$ (a very strongly temperature-dependent quantityjk.)

- Similarly, the exact expression for the number of holes in the valence band is

$$p_v = \int_{-\infty}^{E_v} g_v(E)\big[1 - f(E)\big]\,\mathrm{d}E,$$

which is well approximated for a non-degenerate semiconductor by

$$p_v = P_v e^{-\beta(\mu - E_v)}, \quad \text{where } P_v = \frac{1}{4}\left(\frac{2m_v^* k_B T}{\pi\hbar^2}\right)^{3/2}.$$

- Important: deriving the expression for n_c and p_v in Equation **TODO:** reference from the exact integral expressions in **TODO:** reference involves the approximation that $E_c - \mu$ and $\mu - E_v$, which we corresponds to a so-called non-degenerate semiconductor. In other words, we require the shifts of chemical potential from the edges of the band gap are much larger than the thermal energy $k_B T$.

  In practice, this approximation holds in many situations. As a safety check, however, after computing μ using a non-degenerate semiconductor approximation, we should ensure that the conditions $E_c - \mu \gg k_B T$ and $\mu - E_v \gg k_B T$ holds for the thus-computed results. If the conditions $E_c - \mu \gg k_B T$ and $\mu - E_v \gg k_B T$ are not fulfilled, the use of the non-degenerate semiconductor approximation was not justified.

- Finally, we write concentration of holes on donor levels as

$$p_d = N_d \frac{1}{1 + 2e^{-\beta(E_d - \mu)}}$$

  Discussion: a donor energy level may be occupied by no electrons, one electron (with spin up or down), or two electrons (one with spin up and one with down). The corresponding energies are $E = 0$, $E = E_d$, $E = E_d$ and $E = 2E_d + U$, where U arises from electrostatic repulsion, and is why double electron occupation on a single donor level is energetically unfavorable. This extra repulsion (after derivation via grand canonical ensemble) is the result for the extra factor of 2 in the denominator of p_d.

- We also consider conservation of charge: every electron excited into the conduction band (from valence band or donor levels) leaves behind a hole in the corresponding band. We write this as

$$n_c = p_v + p_d$$

  We then substitute in above expressions for n_c, p_v and p_d to get an equation for chemical potential as a function of temperature.

12 Twelfth Exercise Set

12.1 Chemical Potential in a Doped Semiconductor (continued)

- Begin by reviewing equations. Conservation of charge

$$n_c = p_v + p_d$$

$$n_c = N_c e^{-\beta(E_c - \mu)}$$

$$N_c = \frac{1}{4} \left(\frac{2m_c^* k_B T}{\pi \hbar^2} \right)^{3/2}$$

We can treat N_c as almost temperature constant

$$p_v = P_v e^{-\beta(\mu - E_v)}$$

$$P_v = \frac{1}{4} \left(\frac{2m_v^* k_B T}{\pi \hbar^2} \right)^{3/2}$$

and

$$p_d = N_d \frac{1}{1 + 2e^{-\beta(E_d - \mu)}}$$

12.1.1 Finding Chemical Potential

- First step to find $\mu(T)$. Find from conservation of charge. Leads to polynomial of third degree. To avoid this, note negligible donor gap ($T_F \sim 10\,\text{K}$) compared to band gap ($T_F \sim 10^4\,\text{K}$).

  We will consider temperatures low enough such that no appreciable number of electrons jumping from valence to conduction band. Thus $n_c \approx p_d$. We then check back later for validity.

  Using $n_c = p_d$ we have

$$N_c e^{-\beta(E_c - \mu)} = N_d \frac{1}{1 + 2e^{-\beta(E_d - \mu)}}$$

  Multiply through by denominator and get

$$N_c e^{-\beta E_c} e^{\beta \mu} + 2N_c e^{-\beta(E_c + E_d)} e^{2\beta \mu} - N_d = 0.$$

  Use $2^{\beta \mu} \equiv x$ and solve quadratic equation. Also set x^2 coefficient to one

$$e^{2\beta \mu} + \frac{1}{2} e^{\beta E_d} e^{\beta \mu} - \frac{N_d}{2N_c} e^{\beta(E_c + E_d)} = 0$$

  Solution is

$$e^{\beta \mu} = -\frac{1}{4} e^{\beta E_d} \pm \sqrt{ \left(\frac{1}{4} e^{\beta E_d} \right)^2 + \frac{N_d}{2N_c} e^{\beta(E_c + E_d)} }$$

$$= \frac{1}{4} e^{\beta E_d} \left[-1 \pm \sqrt{ 1 + \frac{8N_d}{N_c} e^{\beta(E_d - E_d)} } \right]$$

  Take logarithm to find μ. Only plus sign solution is physical btw.

Limit Cases

- We consider only two limit cases. Taylor expand square root when second term is gg or ll one.

- First

$$\frac{8N_\mathrm{d}}{N_\mathrm{c}} e^{\beta(E_\mathrm{d}-E_\mathrm{d})} \gg 1$$

  First note

$$N_\mathrm{c} \propto T^{3/2} \qquad \text{and} \qquad \beta \propto T^{-1}$$

  This limit case is physicaly the low temperature regime. Note that $E_\mathrm{c} - E_\mathrm{d} > 0$, so exponent is positive.

- Very roughly in this regime $k_B T \ll E_\mathrm{c} - E_\mathrm{d}$.

- We have

$$e^{\beta\mu} \approx \frac{1}{4} e^{\beta E_\mathrm{d}} \sqrt{\frac{8N_\mathrm{d}}{N_\mathrm{c}}} e^{\beta\frac{1}{2}(E_\mathrm{c}-E_\mathrm{d})} = \sqrt{\frac{N_\mathrm{d}}{2N_\mathrm{c}}} e^{\beta\frac{E_\mathrm{c} + \mathrm{Esdd}}{2}}$$

  From neglecting some ones.

  Then

$$\mu = \frac{1}{\beta} \ln e^{\beta\mu} = \frac{1}{\beta}\left(\ln\sqrt{\frac{N_\mathrm{d}}{2N_\mathrm{c}}} + \beta\frac{E_\mathrm{c}+E_\mathrm{d}}{2}\right) = \frac{E_\mathrm{c}+E_\mathrm{d}}{2} + k_B T \ln\sqrt{\frac{N_\mathrm{d}}{2N_\mathrm{c}}}$$

  As temperature to zero, we consider only leading logarithm term. Result is

$$e^{\beta\mu} \approx \frac{E_\mathrm{c}-E_\mathrm{d}}{2} - \frac{3}{4}k_B T \ln T$$

  At $T = 0\,\mathrm{K}$ we have $\mu = \frac{E_\mathrm{c}+E_\mathrm{d}}{2}$—between bands. Chemical potential then increases towards E_c with increasing temperature (for a bit, in the low-temperature regime).

High-Temperature Limit

- In this case

$$\frac{8N_\mathrm{d}}{N_\mathrm{c}} e^{\beta(E_\mathrm{d}-E_\mathrm{d})} \ll 1$$

  Recall

$$e^{\beta\mu} = \frac{1}{4} e^{\beta E_\mathrm{d}}\left[-1 \pm \sqrt{1 + \frac{8N_\mathrm{d}}{N_\mathrm{c}} e^{\beta(E_\mathrm{d}-E_\mathrm{d})}}\right]$$

  Taylor expand and get

$$e^{\beta\mu} = \frac{1}{4} e^{\beta E_\mathrm{d}} \cdot \left(\frac{1}{2}\frac{*N_\mathrm{d}}{N_\mathrm{c}} e^{\beta(E_\mathrm{c}-E_\mathrm{d})}\right) = \frac{N_\mathrm{d}}{N_\mathrm{c}} e^{\beta E_\mathrm{c}}$$

  Solve for μ to get

$$\mu = E_\mathrm{c} + k_B T \ln\frac{N_\mathrm{d}}{N_\mathrm{c}}$$

  Consider only leading logarithm term to get

$$\mu \approx E_\mathrm{c} - \frac{3}{2}k_B T \ln T$$

  We see μ is a decreasing function of temperature. Thus in the high-temperature regime μ falls with T, so there must be a maximum of $\mu(T)$ somewhere in between the low- and high-temperature regime.

Analysis

- Problem: we should know taht chemical potential cannot approach too close to edge of band gap to use non-degenerate semiconductor equations. Is the $\mu(T)$ maximum near the bottom of conduction band?

- Another problem: $\mu(T)$ cannot fall infinitely with temperature—once μ is near valence band, then electrons will jump from valence band to conduction band, and our approximation $n_c \approx p_d$. So "high-temperature" regime is high temperature in the regime $n_c \approx p_d$ but so long as $p_v \ll n_c, p_d$.

- At high enough temperatures when easy energetically for valence band electrons to conduction band, since many more lattice sites than dopants the valence electrons overwhelm dopants and we have again a simpler case $n_c \approx p_v$

12.1.2 Carrier Concentration as a Function of Temperature

Electron Concentration in Conduction Band

- Begin with low-temperature limit

$$e^{\beta\mu} = \sqrt{\frac{N_d}{2N_c}} e^{\beta\frac{E_c+E_d}{2}}$$

And

$$n_c = N_c e^{-\beta(E_c-\mu)} = N_c e^{-\beta E_c} e^{\beta\mu}$$

Substitute in expression for $e^{\beta\mu}$ to get

$$= N_c e^{-\beta E_c} \sqrt{\frac{N_d}{2N_c}} e^{\beta\frac{E_c+E_d}{2}} = \sqrt{\frac{N_d N_c}{2}} e^{-\beta\frac{E_c-E_d}{2}} \propto T^{3/4} e^{-\frac{E_c-E_d}{2k_B T}}$$

Intially $n_c = 0$, then increases exponentially

- High=temerperature

$$e^{\beta\mu} = \frac{N_d}{N_c} e^{\beta E_c}$$

As before begin with n_c and substitute in $e^{\beta\mu}$ to get

$$n_c = N_c e^{-\beta(E_c-\mu)} = N_d$$

So high-temperature $n_c(T)$ is constant. Sensible physical interpretation: temperature still low enough that no conduction band electron contribution, but all donors are excited into CB.

- We do not consider p_v because by construction we assumed $p_v \ll n_c, p_d$.

12.2 Lattice Oscillations with Alternating Spring Constants

A one-dimensional lattice consists of atoms of mass M connected, alternatively, by springs of spring constant K and Q. Find the dispersion of the dispersion relation describing the lattice oscillations.

- As primitive cell choose two-atom cell. With one of each spring constant. E.g. M, a K spring, another M atom, and the Q spring just up to the next M atom.

- Let u_n denote the displacement from equilibrium of the n-th QMK atom and v_n denote the displacement from equilibrium of the n-th KMQ atom, and let the positive x axis point in the direction of increasing n. In this notation, Newton's law for the n-th QMK atom reads

$$M\ddot{u}_n = K(v_n - u_n) - Q(u_n - v_{n-1}).$$

Note that if $v_n > u_n$, the term $K(v_n - u_n)$ contributes a force to the right on the chosen QMK atom via the K spring. Similarly, if $u_n - v_{n-1}$, the term $-Q(u_n - v_{n-1})$ (note the minus sign!) contributes a force to the left on the chosen QMK atom via the Q spring.

Analogously, Newton's law for the n-th KMQ atom reads

$$M\ddot{v}_n = Q(u_{n+1} - v_n) - K(v_n - u_n).$$

- Currently, Equations **TODO:** reference are a coupled system of $2N$ equations, N being the number of lattice sites. Such a large system is not practically solvable, so we will decouple the equations by levaraging the lattice's translational symmetry.

We begin with the oscillatory ansatzes

$$u_n = u_0 e^{i(kna - \omega t)} \qquad \text{and} \qquad v_n = v_0 e^{i(kna - \omega t)}$$

where the lattice constant a spans the entire two-atom unit cell. We first substitute these ansatzes into Equation **TODO:** reference to get

$$-\omega^2 M u_0 e^{i(kna - \omega t)} = K\left[(v_0 e^{i(kna - \omega t)}) - u_0 e^{i(kna - \omega t)} \right]$$
$$- Q\left[u_0 e^{i(kna - \omega t)} - v_0 e^{i(k(n-1)a) - \omega t} \right]$$

We then cancel the plane wave term to get the decoupled expression

$$-\omega^2 M u_0 = K(v_0 - u_0) - Q(u_0 - v_0 e^{-ika})$$

- Following an analogous procedure, we substitute the ansatzes into Equation **TODO:** reference to get

$$-\omega^2 M v_0 e^{i(kna - \omega t)} = Q\left[(u_0 e^{i(k(n+1)a - \omega t)}) - v_0 e^{i(kna - \omega t)} \right]$$
$$- K\left[v_0 e^{i(kna - \omega t)} - u_0 e^{ikna - \omega t} \right]$$

After canceling plane wave terms, we have

$$-\omega^2 M v_0 = Q(u_0 e^{ika} - v_0) - K(v_0 - v_0).$$

In matrix form, Equations **TODO:** reference and result in eigenvalue problem

$$\begin{pmatrix} K + Q - \omega^2 M & -K - Qe^{-ika} \\ -K - Qe^{ika} & K + Q - \omega^2 M \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}$$

for the amplitudes u_0 and v_0. We require the matrix's determinat equal zero for a non-trivial solution, which produces

$$0 \equiv (K + Q - \omega^2 M)^2 - \left| K + Qe^{ika} \right|^2.$$

We then solve rearrange and solve for oscillation frequency, which reads

$$\omega^2 M = K + Q \pm \left| K + Q e^{ika} \right|$$

Two by two system because two atoms per unit cell (this holds in one dimension with one degree of freedom).

- Solve for ω to get (skipping a few steps)

$$\omega^2 = \frac{K + Q}{M} \pm \frac{1}{M} \sqrt{K^2 + Q^2 + \underbrace{2KQ \cos ka}_{2KQ + 2KQ(-1 + \cos ka)}}$$

and use $-1 + \cos ka = -2 \sin^2 \frac{ka}{2}$ to get the complete square

$$\omega^2 = \frac{K + Q}{M} \pm \frac{1}{M} \sqrt{(K + Q)^2 - 4KQ \sin^2 \frac{ka}{2}}.$$

Final step: factor out to get

$$\omega^2 = \frac{K + Q}{M} \left[1 \pm \sqrt{1 - \frac{4KQ}{(K + Q)^2} \sin^2 \frac{ka}{2}} \right]$$

This is our final form for $\omega(k)$.

Analyze $\omega(k)$

- Analyze dispersion relation. Graph with $\omega(k)$. As for electron states, two avoid couting the same state multiple times, we restrict ourselves to the first Brillioun zone $|k| < \frac{\pi}{a}$.

- Consider first center of first Brillioun zone at $k = 0$.

  Use equation

$$\omega^2 M = K + Q \pm \left| K + Q e^{ika} \right|$$

  At $k = 0$ we get

$$\omega^2 = \frac{K + Q}{M} \pm \frac{|K + Q|}{M} = \begin{cases} \frac{2(K + Q)}{M} \\ 0 \end{cases}$$

  So two eigenvalues (instead of E eigenvalues we have ω eigenvalues).

- Now consider $k = \frac{\pi}{a}$ to get (I think same equation)

$$\omega^2 = \frac{K + Q}{M} \pm \frac{|K - Q|}{M}$$

  Consider picture of crystal again. Note that spring constant fully contained in unit cell is K and the spring connecting cells is Q. However this choice is arbitrary, we could just shift unit cell by an atom.

  We can thus, without loss of generality, shift our unit cell so that $K > Q$. Basically translational symmetry—the physics here is independent of the choice of unit cell.

  With this in mind

$$\omega^2 = \frac{K + Q}{M} \pm \frac{|K - Q|}{M} = \begin{cases} \frac{2K}{M} \\ \frac{2Q}{M} \end{cases}.$$

  We drew both of these eigenvalues as positive frequencies. Actually looks like we are plotting $\omega^2(k)$.

Dispersion Near Center of First Brillioun Zone

- Now consider the neighborhood of first Brillioun zone where $|k| \ll \frac{\pi}{a}$.

  Use the last ω^2 expression with sine and expand the sine Taylor to get

$$\omega^2 \approx \frac{K+Q}{M} \left[1 \pm \sqrt{1 - \frac{4KQ}{(K+Q)^2} \frac{(ka)^2}{4}} \right]$$

  Then expand the square root to get

$$\omega^2 \approx \frac{K+Q}{M} \left[1 \pm \left(1 - \frac{KQ}{2(K+Q)^2}(ka)^2 \right) \right]$$

- Consider the plus sign branch, which gives

$$\omega^2 = \frac{2(K+Q)}{M} - \mathcal{O}\big((ka)^2\big)$$

  Then consdier the minus sign branch, which gives

$$\omega^2 = \frac{K+Q}{M} \frac{KQ}{2(K+Q)^2}(ka)^2 = \frac{KQ}{2(K+Q)M}(ka)^2$$

  We square root to get

$$\omega = \sqrt{\frac{KQa^2}{2(K+Q)}M}|k| \equiv c|k|,$$

  where absolute value k because k can be positive or negative (and is not in the complex ansatz and is a real quantity so sign is important.)

  The first branch with plus sign with downward parabola in neighborhood of $k = 0$ is called optical branch. Second with absolute value dependence of $\omega(k)$ near $k = 0$ is called acoustic branch. The optical branch occurs only for multiple atoms per unit cell. The acoustic branch always occurs.

12.2.1   Eigenvectors

- We consider oscillation of lattice near center of first Brillioun zone in both acoustic (i) and optical (ii) branches, and also at the edge of the first Brillioun zone.

- Recall
$$\begin{pmatrix} K+Q-\omega^2 M & -K-Qe^{ika} \\ -K-Qe^{ika} & K+Q-\omega^2 M \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}.$$

First Case 1

- We have $k = 0$ acoustic branch and $\omega^2 = 0$ and get

$$\begin{pmatrix} K+Q & -(K+Q) \\ - & - \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}$$

  The result is $v_0 = u_0$. We conclude $v_n = u_n = u_0$. The solution is translation of the entire crystal. This occurs at $k = 0$ in the acoustic branch.

$k = 0$ **Optical Branch**

- In this case $k = 0$ and $\omega^2 = \frac{2(K+Q)}{M}$.

- We have
$$\begin{pmatrix} -(K+Q) & -(K+Q) \\ - & - \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}$$

  This gives $v_0 = -u_0$ and from there I assume we get the result: $u_n = u_0$ and $v_n = -u_0$.

- See picture of *oscillation-case-1-2*.

3 **Acoustic Case at** $k = \pi/a$

- In this case $k = \pi/a$ and $\omega^2 = \frac{2Q}{M}$.

- Matrix equation reads
$$\begin{pmatrix} K+Q-M\frac{2Q}{M} & -K-Qe^{-i\pi} \\ - & - \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \begin{pmatrix} K-Q & -(K-Q) \\ - & - \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}.$$

  We conclude $v_0 = v_0$. But because on the edge of the first Brillioun zone we have not translation of complete lattice but oscillation solution
$$u_n = u_0 e^{ikna} = (-1)^n u_0$$

  and
$$v_n = v_0 e^{ikna} = (-1)^n v_0 = (-1)^n u_0.$$

  K spring is always at rest in this mode while Q contracts supposedly. See *oscillation-case-3*.

Last Mode

- In this case $k = \pi/a$ in the optical branch. We have $\omega^2 = \frac{2K}{M}$. This is for homework.

13 Thirteenth Exercise Set

13.1 Lattice Oscillations

- Triangular Bravais lattice of identical atoms with mass M.

  Interactions between atoms are modeled by springs with spring constant K.

  Springs are taut. When atoms are at rest, then the springs are already stretched when the atoms are in their equilibrium positions.

  For lattice constant a, taut springs means $a > a_0$ where a_0 is the spring's equilibrium length.

  For simplicity, we consider lattice oscillations for which the atomic displacememts are transverse to the plane of the crystal lattices.

- Consider two neighboring atoms with transverse displacements u_1 and u_2.

  Consider "diagonal" spring connecting the atoms, which results in a force $\boldsymbol{F}$ between the atoms. Decompose $\boldsymbol{F}$ into $F_\perp$ and $F_\parallel$.

  We see $F_\parallel = F \cos \alpha$ and $F_\perp = F \sin \alpha$ where α is in picture.

  Magnitude of force is $F = K \Delta l$ where Δl is change in length,

  $$\Delta l = \sqrt{a^2 + (u_2 - u_1)^2} - a_0$$

  Something about $-a_0$ because taut springs. Taylor expand to get

  $$\Delta l \approx a - a_0 + \frac{(u_2 - u_1)^2}{2a}$$

  Note that correction to length is quadratic in displacement different $u_2 - u_1$.

- Next we note

  $$\cos \alpha = \frac{a}{\sqrt{a^2 + (u_2 - u_1)^2}} \approx 1 + \mathcal{O}\big((u_2 - u_1)^2\big)$$

  And

  $$\sin \alpha = \frac{u_2 - u_1}{\sqrt{a^2 + (u_2 - u_1)^2}} \approx \frac{u_2 - u_1}{a} + \mathcal{O}\big((u_2 - u_1)^3\big)$$

  With these we find

  $$F_\parallel = F \cos \alpha = K(a - a_0) \qquad \text{and} \qquad F_\perp = F \sin \alpha = K(a - a_0)\frac{u_2 - u_1}{a}$$

  Corrections are second order in $u_2 - u_1$ or higher—harmonic theory requires only that force is linear in displacement (e.g. Hooke's law).

- Consider e.g. central atom. There is not force on the central atom in the plane of crystal because forces from neighbors in different directions cancel out.

  There is a $F_\perp$ component. This is

  $$F_\perp = \widetilde{K}(u_2 - u_1), \quad \text{where} \quad \widetilde{K} = K\frac{a - a_0}{a}$$

  Important: Note that if $a = a_0$ there would be no linear relationship between force and displacement because $\widetilde{K} = 0$ and we could then not use linear theory.

Equations of Motion

- Consider perpendicular displacements from sum of all forces (recall forces in plane of paper cancel (in harmonic theory only) and considering only perpendicular force we have)

$$M\ddot{u}_{\boldsymbol{R}} = \sum_{\boldsymbol{R}' \in \{\text{nn}\}} \widetilde{K} \left(u_{\boldsymbol{R}'} - u_{\boldsymbol{R}}\right)$$

From this point situation is similar to previous week's exercise set. Use Bloch-motivated (translation symmetry motivated) ansatz

$$u_{\boldsymbol{R}} = u_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega\tau)}$$

Substitute in to get

$$-M\omega^2 u_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega t)} = \sum_{\boldsymbol{R}' \in \{\text{nn}\}} \widetilde{K} u_0 \left(e^{i(\boldsymbol{k}\cdot\boldsymbol{R}' - \omega t)} - e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega t)}\right)$$

Cancel plane waves and u_0, leaving

$$-M\omega^2 = \sum_{\boldsymbol{R}' \in \{\text{nn}\}} \widetilde{K} \left(e^{i\boldsymbol{k}\cdot(\boldsymbol{R} - \boldsymbol{R}')} - 1\right) =$$

Up to now summed over NN to $\boldsymbol{R}$ now NN to origin.

$$-M\omega^2 = \sum_{\boldsymbol{R}' \in \{\text{nno}\}} \widetilde{K} \left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}'} - 1\right)$$

Note that both $\boldsymbol{R}$ and $-\boldsymbol{R}$ are Bravais lattice vectors. Rename $\boldsymbol{R}' \to \boldsymbol{R}$ to get and multiply by two to avoid double counting

$$-M\omega^2 = \frac{\widetilde{K}}{2} \left[\sum_{\boldsymbol{R}nno} \left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - 1\right) + \sum_{\boldsymbol{R}nno} \left(e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} - 1\right)\right]$$

And then recognize cosing to get

$$\frac{\widetilde{K}}{2} \sum_{\boldsymbol{R}nno} \left(2\cos(\boldsymbol{k}\cdot\boldsymbol{R}) - 2\right) = -2\widetilde{K} \sum_{\boldsymbol{R}nno} \sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}$$

Rearrange to get

$$\omega^2 = \frac{2\widetilde{K}}{M} \sum_{\boldsymbol{R}nno} \sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}$$

Note that this expression would hold for an arbitrary 2D Bravais lattice in which $\boldsymbol{R}$ and $-\boldsymbol{R}$ are both Bravais lattice vectors.

- Now consider triangular lattice structure. We have

$$\boldsymbol{a}_1 = a(1, 0) \qquad \boldsymbol{a}_2 = \frac{a}{2}(1, \sqrt{3}) \qquad \boldsymbol{a}_1 - \boldsymbol{a}_2 = \frac{a}{2}(1, -\sqrt{3})$$

See *pic-13-1-triang*. Note sine squared terms identical for positive or negative vectors I believe (from where we have factor of two before square brackets), then sum over $\boldsymbol{R}nno$ to get

$$\omega^2 = \frac{2\widetilde{K}}{M} \cdot 2 \left[\sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{a}_1}{2} + \sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{a}_2}{2} + \sin^2 \frac{\boldsymbol{k}\cdot(\boldsymbol{a}_1 - \boldsymbol{a}_2)}{2}\right] \tag{13.1}$$

Analyzing Dispersion

- We consider the dispersion near the center of the first Brillioun zone (we assume triangular Brillioun zone is familiar by now). Use ansatz $|\boldsymbol{k}| \ll \pi/a$. (Or equivalently limit of large plane wave wavelength relative to lattice constant)

  Substitute into ω^2 and exand Taylor to get

  $$\omega^2 = \frac{4\widetilde{K}}{M}\left[\left(\frac{\boldsymbol{k}\cdot\boldsymbol{a}_1}{2}\right)^2 + \left(\frac{\boldsymbol{k}\cdot\boldsymbol{a}_2}{2}\right)^2 + \left(\frac{\boldsymbol{k}\cdot(\boldsymbol{a}_1 - a_2)}{2}\right)^2\right]$$

  We then have

  $$\frac{\widetilde{K}}{M}\left[k_x^2 a^2 + \left(\frac{k_x}{2} + \frac{k_y\sqrt{3}}{2}\right)^2 a^2 + \left(\frac{k_x}{2} - \frac{k_y\sqrt{3}}{2}\right) a^2\right]$$

  Mixed terms cancel and leave

  $$\omega^2 = \frac{\widetilde{K}a^2}{M}\left(k_x^2 + \frac{1}{4}k_x^2 + \frac{3}{4}k_y^2 + \frac{k_x^2}{4} + \frac{3k_y^2}{4}\right)$$

  which is

  $$\omega^2 = \frac{3}{2}\frac{\widetilde{K}a^2}{M}(k_x^2 + k_y^2) = \frac{3}{2}\frac{\widetilde{K}}{M}a^2 k^2$$

  This result motivates

  $$\omega = \sqrt{\frac{3}{2}\frac{\widetilde{K}}{M}}ak \equiv ck, \quad \text{where } c = \sqrt{\frac{3}{2}\frac{\widetilde{K}}{M}}a$$

  This is an acoustic dispersion branch (recall one atom per unit cell (as in our case for a Bravais lattice) the dispersion $\omega(k)$ has only an acoustic branch.)

  We stress that in our case $c \neq c(\phi)$, where ϕ is the angle between $\boldsymbol{k}$ and the k_x axis. This not in general the case, but a special property of the triangular lattice. The key point is that ω depends only on the magnitude k and not the components k_x and k_y, i.e. because we had $k_x^2 + k_y^2 = k^2$. An example with a ϕ-dependent dispersion is a 2D rectangular lattice with not equal side lengths.

Contribution of Lattice Oscillations to Specific Heat

- (In passing?) draw ω as a function of k_x and k_y as a 3D graph. Note that near the first Brillioun zone center the dispersion $\omega(\boldsymbol{k})$ is quadratic and conic like—conic because k dependence and rotational symmetry in the $k_x k_y$ plane.

- Goal is to find contribution of transverse lattice oscillations to specific heat (i.e. only contribution of oscillations which are perpendicular to plane of crystal, i.e. the oscillations we have considered in this exercise.)

- Begin with definition of total heat capacity

  $$C = \frac{\mathrm{d}E}{\mathrm{d}t}$$

  We then write heat capaciticy as $C = Nc$, where c is specific heat capacity normalized by number of atoms in lattice.

- We then write energy as

$$E = \sum_{\boldsymbol{k}} \hbar\omega_{\boldsymbol{k}} \left(\frac{1}{e^{\beta\hbar\omega_{\boldsymbol{k}}} - 1} + \frac{1}{2} \right)$$

How many phonons are present in a given ($\boldsymbol{k}$?) oscillation mode is from the Bose-Einstein distribution. The factor one half is from theory and specific to harmonic oscillator energy, but we ignore it cause differentiation of E eliminates constant terms.

- Low temperature limit: We consider only those states which can be described by the linear dispersion relation, which holds near the center of the first Brillioun zone, i.e. low energy.

Without thorough proof, low-frequency are present only in the region of $\boldsymbol{k}$ plane space near the origin of the first Brillioun zone. This holds from Equation 13.1. Because only low-frequency terms occur near origin of first Brillioun zone, we can use linear dispersion for low-temperature limit (because know we don't need to consider $\boldsymbol{k}$ dispersion contributions from anywhere besides the origin of the first Brillioun zone).

Sum over all $\boldsymbol{k}$, even those for which linear dispersion does not apply, because the Bose-Einstein distribution will suppress them anyway.

$$E \approx \sum_{\boldsymbol{k}} \hbar ck \frac{1}{e^{\beta\hbar\omega k} - 1} \approx \frac{S}{(2\pi)^2} \iint \frac{\hbar ck}{e^{\beta\hbar ck} - 1} \, \mathrm{d}^2\boldsymbol{k}$$

Because integrand depends only on magnitude k, switch to polar coordinates to get

$$= \frac{S}{(2\pi)^2} \int_0^\infty \frac{2\pi k \, \mathrm{d}k \hbar ck}{e^{\beta\hbar ck} - 1}$$

Continue and introduce new variable $\beta\hbar ck$ to get

$$\frac{S}{2\pi} \int_0^\infty \frac{(\beta\hbar ck) \, \mathrm{d}(\beta\hbar ck)(\beta\hbar ck)}{e^{\beta\hbar ck} - 1} \frac{1}{\beta^3(\hbar c)^2}$$

We then have

$$E \approx \frac{S}{2\pi} \frac{(k_B T)^3}{(\hbar c)^2} \int_0^\infty \frac{u^2}{e^u - 1} \, \mathrm{d}$$

The integral is $2\zeta(3) \approx 2.4$, but for our purposes is enough to note that the integrand is of order one. We then have

$$E \approx \frac{2.4}{2\pi} S \frac{(k_B T)^3}{(\hbar c)^2}$$

- Finally we have

$$c = \frac{1}{N} \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{2.4}{2\pi} \frac{S}{N} \frac{3 k_B^3 T^2}{(\hbar c)^2}$$

Introduce S/N as the area of a lattice site, which is a rhombus for a triangular (or hexagonal) lattice site and has area $a^2 \frac{\sqrt{3}}{2}$. We then have

$$c = 2.4 \frac{3}{2\pi} \frac{a^2 \sqrt{3}}{2} \left(\frac{k_B T}{\hbar} \right)^2 k_B.$$

Note that c is speed of sound not light! Recall

$$c^2 = \frac{3}{2}\frac{\widetilde{K}}{M}a^2$$

and define $\omega_0^2 = \widetilde{K}/M$ write c as

$$c^2 = \frac{3}{2}\frac{\widetilde{K}}{M}a^2 = \frac{3}{2}\omega_0^2 a^2$$

We then have in terms of ω_0

$$c = 2.4\frac{3}{2\pi}\frac{\sqrt{3}}{2}\frac{2}{3}\left(\frac{k_B T}{\hbar\omega_0}\right)^2 k_B$$

After cancelling leaves

$$c = 2.4\frac{\sqrt{3}}{2\pi}\left(\frac{k_B T}{\hbar\omega_0}\right)^2 k_B$$

Note fraction is ratio of thermal energy $k_B T$ and $\hbar\omega_0$, which is oscillation energy *near edge of first Brillioun zone*. Note this energy is large relative ot $k_B T$. Most important lesson is that $c \propto T^2$.

Note we do not have $c \propto T^3$ as in low-temperature limit in a 3D crystal. When integrating over $\mathrm{d}^2 k$ in expression $E \approx$ we have one fewer power of k, and because of this we have different powers of T in different dimensions.