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.

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1 First Exercise Set

Theoretical Background: Crystal Structure and the Packing Factor

- We model solid-state matter as 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.

  We model 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, i.e.

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

- 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 (whole) atoms fit into a given conventional unit cell.

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

3. Use Equation 1.1 to compute the packing factor.

Think of this problem as an introduction to the learning the crystal structures. The mathematics itself is elementary; we begin the 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 abbreviated SC; its conventional unit cell, shown in Figure 1, consists of 8 atoms placed at the vertices of a perfect cube.

$$\boldsymbol{a}_1 = a\,\hat{\mathbf{x}}$$
$$\boldsymbol{a}_2 = a\,\hat{\mathbf{y}}$$
$$\boldsymbol{a}_3 = a\,\hat{\mathbf{z}}$$
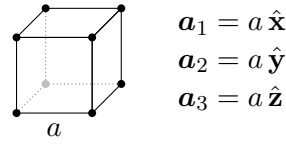
Figure 1: A simple cubic unit cell and its conventional primitive vectors.

- 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 SC 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 abbreviated BCC; its conventional unit cell, shown in Figure 2, consists of 8 atoms placed at the vertices of a perfect cube with one additional atom at the cube's center.

$$\boldsymbol{a}_1 = a\,\hat{\mathbf{x}} \qquad\qquad \boldsymbol{a}_1 = \tfrac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$$
$$\boldsymbol{a}_2 = a\,\hat{\mathbf{y}} \qquad\qquad \boldsymbol{a}_2 = \tfrac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}})$$
$$\boldsymbol{a}_3 = \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}) \quad \boldsymbol{a}_3 = \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$
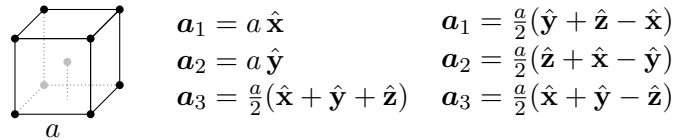
Figure 2: A body-centered cubic unit cell and two common choices for its primitive vectors.

- Like in the simple cubic structure, each outer atom in a BCC cell is equally shared by the eight unit cells surrounding a given vertex. This makes for a net total of $8 \cdot (\frac{1}{8}) = 1$ outer atoms in a given unit cell. Together with the single central atom, which is completely within its cell, there are 2 atoms fully inside a given BCC conventional unit 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 BCC packing factor is

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

1.1.3 Face Centered Cubic

A face-centered cubic structure is abbreviated FCC; its conventional unit cell, shown in Figure 3, consists of 8 atoms placed at the vertices of a perfect cube with an additional six atoms in the center of each of the cell's six faces.

$$\begin{aligned}
\boldsymbol{a}_1 &= \tfrac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}) \\
\boldsymbol{a}_2 &= \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{z}}) \\
\boldsymbol{a}_3 &= \tfrac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})
\end{aligned}$$
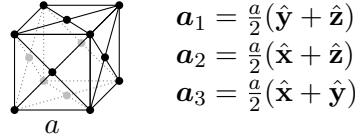
Figure 3: A face-centered cubic unit cell and its conventional primitive vectors.

- Like in the SC and BCC 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 conventional unit 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 FCC 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 Simple Hexagonal

A simple hexagonal structure is abbreviated SH and shown in Figure 4. The structure can be modeled using either a rhombohedral or hexagonal unit cell.
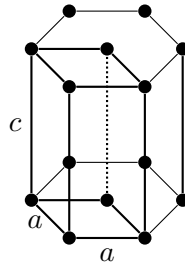
Figure 4: The primitive and conventional unit cell for a simple-hexagonal lattice; the thick lines denote the rhombohedral primitive unit cell.

- We will use the rhombohedral model of the unit cell. 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 $c = a$.

- We now consider 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 atoms 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

- Like the diamond cubic structure, the hexagonal close-packed (HCP) structure is so tightly cluttered with atoms that I have not included a diagram, which would be too crowded to be particularly insightful. Instead, we can visualize the hexagonal close-packed structure by imagining stacking multiple two-dimensional hexagonal layers on top of each other such that the atoms in one layer align with the gaps in the previous layer; every other layer is identical. (See Exercise 2.1 in the next exercise set for a more thorough description of close-packed structures.)

- As for a simple 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

- **Simple hexagonal:** Begin by considering a two-dimensional Bravais hexagonal (triangular) lattice in the xy plane. Then generalize this hexagonal lattice to three dimensions by stacking 2D hexagonal layers directly on top of each other with vertical spacing c. (Precisely, we could specify the concept of layers being "directly on top each other" as the requirement that all layers have identical projections onto the xy plane.) This resulting structure is called a *simple hexagonal* lattice and is the same structure covered in Section 1.1.5 of the previous exercise set.

- **Hexagonal close-packed:** 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 interstitial site—the trigonal interstitial sites are centered at the centroids of the equilateral triangles formed by the hexagonal lattice points.

  Having defined the trigonal interstitial site, 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) above layer A such that the lattice points of layer B align vertically with the trigonal interstitial sites of 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, and is the same structure covered in Section 1.1.6 of the previous exercise set.

- **Cubic close-packed:** Once again, we need some terminology before defining the next lattice structure. Imagine viewing a two-layer HCP lattice (the AB structure) from above. The trigonal interstitial sites in layer B positioned directly above lattice points in layer A are called *tetrahedral interstitial sites*, while the trigonal interstitial sites in layer B positioned directly above trigonal interstitial sites in layer A are called *octahedral interstitial sites*. Note that in the $ABABAB$ structure, the lattice points in the A layers align with the tetrahedral interstitial sites in the B layers.

  Having defined tetrahedral and octahedral interstitial sites, we can now construct a *cubic close-packed* lattice, which we will later show is equivalent to an FCC structure. 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 interstitial sites in A, then stack a third 2D hexagonal lattice (layer C) such that the lattice points in C align with the octahedral interstitial sites in layer B. (Note that placing layer C in the tetrahedral interstitial sites of layer B would result in an $ABABAB$ structure.) When repeated, the resulting $ABCABCABC...$ structure forms a cubic close-packed lattice.

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

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

  from the previous exercise.

- In general, any lattice consisting of vertically superposed 2D hexagonal layers such that lattice points in one layer align with the trigonal interstitial sites (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.

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 interstitial sites in layer A.

Any three neighboring 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

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

The position vector of the layer B atom at the top of the aforementioned regular tetrahedron is then

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

Note the (x, y) position $(a/2, a\sqrt{3}/6)$ is the centroid of a layer A equilateral triangle.

- We already know the primitive vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$; 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 choice, 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

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

if $\boldsymbol{a}_3 = \boldsymbol{r}_{\text{top}}$. 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—this is an atom in an A-type layer, 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 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

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

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.

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

Interpreted 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 equivalent.

- 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.

   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 axes, 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 pseudo-rotation, 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 interpreted as combinations of pseudo-rotations—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 pseudo-rotation, 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 existence 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 $C_4C_3 \neq C_3C_4$. 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 constructing 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 in general preserve the symmetry of the underlying Bravais cubic lattice. For example, the parallelepiped spanned by the BCC lattice's primitive vectors is not invariant under the 48 symmetry operations associated with a BCC cubic lattice, which we discussed in the previous exercise.

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

- The Wigner-Seitz cell associated with a given Bravais lattice structure 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   Wigner-Seitz Cell for a BCC Structure

- We begin by drawing a BCC conventional 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 is a conventional unit cell and not a primitive unit 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.

- 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

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

In vector form, the line's midpoint is

$$\boldsymbol{r}_0 = d \cdot \frac{1}{\sqrt{3}}(1, 1, 1) = \frac{a}{4}(1, 1, 1).$$

For review, the point-normal form of the equation of the plane with normal $\hat{\mathbf{n}}$ passing through the point $\boldsymbol{r}_0$ is $(\boldsymbol{r} - \boldsymbol{r}_0) \cdot \hat{\mathbf{n}} = 0 \implies \boldsymbol{r} \cdot \hat{\mathbf{n}} = \boldsymbol{r}_0 \cdot \hat{\mathbf{n}}$, which in this case comes out to

$$(x, y, z) \cdot \frac{1}{\sqrt{3}}(1, 1, 1) = \frac{a}{4}(1, 1, 1) \cdot \frac{1}{\sqrt{3}}(1, 1, 1).$$

After simplifying and rearranging, the equation of the bisecting plane comes out to

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

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- Next, we consider the line from the origin to the point $\frac{a}{2}(1, -1, 1)$. The line's direction vector is

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

  and the distance from the line's midpoint to the origin is again

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

  After following an identical procedure to that in the previous bullet point, the equation of this perpendicularly-bisecting plane is

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

- 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 place, the equations of the three planes are

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

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

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

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

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

  The coordinate $x = a/2$ is known because the lines lie in the plane $x = a/2$. 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 is enough information to determine the entire Wigner-Seitz cell. Unfortunately, the formulation of the cell from these two edges and single vertex is best understood visually, with the help of three-dimensional

figures, and I see no intuitive way to transfer it into words alone—refer to the figures drawn in the actual exercises.

The resulting Wigner-Seitz turns out to be a structure called a truncated octahedron—its faces are squares and regular hexagons. (Note that an Internet search for something along the lines of "BCC Wigner-Seitz cell truncated octahedron" should quickly lead to a useful three-dimensional figure.) Without proof, appealing only to geometric intuition, this truncated octahedron preserves all of the BCC lattice's symmetries.

3 Third Exercise Set

3.1 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 condition

$$e^{i\boldsymbol{K}\cdot\boldsymbol{R}} = 1$$

  for all lattice site positions $\boldsymbol{R}$ in the Bravais lattice.

- A three-dimensional reciprocal lattice is spanned by the three reciprocal primitive vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ and $\boldsymbol{b}_3$. In other words, all reciprocal lattice positions $\boldsymbol{K}$ can be written as the linear combination

$$\boldsymbol{K} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2 + m_3\boldsymbol{b}_3, \qquad m_i \in \mathbb{N}.$$

- The primitive vectors $\boldsymbol{a}_i$ and reciprocal primitive vectors $\boldsymbol{b}_j$ obey the relationship

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

- Given primitive vectors $\boldsymbol{a}_i$, we find the corresponding reciprocal primitive vectors $\boldsymbol{b}_i$ according to

$$\boldsymbol{b}_1 = 2\pi\frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)} \qquad \boldsymbol{b}_2 = 2\pi\frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)} \qquad \boldsymbol{b}_3 = 2\pi\frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{(\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3)}, \qquad (3.1)$$

  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.

3.2 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.

3.2.1 The SC Reciprocal Lattice

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

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

  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

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

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

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

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

3.2.2 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, 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 the in-class figure), 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 with the combination $n_1 = 0$ and $n_2 = n_3 = 1$ 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

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

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

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

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

Plotting these vectors shows that they form a FCC lattice in reciprocal space. Alternatively, we could just compare the $\boldsymbol{b}_i$ 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 $4\pi/a$.

3.2.3   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

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

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

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

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

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

3.3   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 primitive vectors. The primitive vectors have equal length and an angle of $60°$ between them. 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 $\boldsymbol{b}_j$ 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

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

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

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

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

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

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

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

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

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

- Some notes:

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

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

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

Using the reciprocal primitive vectors $\widetilde{\boldsymbol{b}}_1$ and $\boldsymbol{b}_2$, 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 $\boldsymbol{a}_j$.

3.4 The Geometric Structure Factor for a FCC Lattice

Definition

- The geometric structure factor is a dimensionless quantity encoding how a crystal lattice scatters incident 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 $\boldsymbol{d}_i$.

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, conventional unit cell with lattice vectors $\{\boldsymbol{a}_i\}$ given in Equation 2.2.
     The key is the lack of a basis; the existence 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

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

  3. A simple hexagonal unit cell (a three dimensional rhombus), 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 Section 2.1.3.

  4. A simple 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.

3.4.1 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

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

3.4.2 Simple Cubic with a Basis

- For review, the most common choice of simple cubic primitive vectors is

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

  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 Section 3.2.1, the simple cubic reciprocal primitive vectors corresponding to the above $\{\boldsymbol{a}_i\}$ are

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

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

- For the simple cubic plus 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

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

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

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

GSF

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

$$\begin{aligned} S(\boldsymbol{K}) &= e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_1} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_2} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3} + e^{-i\boldsymbol{K}\cdot\boldsymbol{d}_3} \\ &= 1 + e^{-\frac{2\pi i}{a}(m_1,m_2,m_3)\cdot\frac{a}{2}(0,1,1)} + e^{-\frac{2\pi i}{a}(m_1,m_2,m_3)\cdot\frac{a}{2}(1,0,1)} + e^{-\frac{2\pi i}{a}(m_1,m_2,m_3)\cdot\frac{a}{2}(1,1,0)} \\ &= 1 + e^{-i\pi(m_2+m_3)} + e^{-i\pi(m_1+m_3)} + e^{-i\pi(m_1+m_2)}. \end{aligned} \tag{3.8}$$

  Here are some possible cases for the value of $S(\boldsymbol{K})$, depending on the values of the Miller indices 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 indices 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 indices 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 interpretation: 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 $S(\boldsymbol{K}) = 0$.

3.4.3   Simple Hexagonal Plus a Basis

- First, for review, an example choice of primitive vectors for the simple hexagonal structure 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 simple 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 simple hexagonal Bravais lattice is again a simple hexagonal lattice in reciprocal space. The reciprocal lattice is such that the reciprocal primitive vectors $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ form a 2D hexagonal lattice in reciprocal space (as derived in Exercise 3.3). Meanwhile, the third reciprocal primitive vector is given by,

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

Written out in full, the computation of $\boldsymbol{b}_3$ follows from

$$V_0 = |\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)| = \frac{3a^3}{\sqrt{2}}$$

$$\boldsymbol{b}_3 = 2\pi \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_3}{V_0} = 2\pi \frac{a^2(0,0,\sqrt{3}/2)}{a^3(3/\sqrt{2})} = \frac{2\pi}{a}(0,0,1).$$

The complete set of simple hexagonal reciprocal primitive vectors is thus

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

Note that this choice of reciprocal vectors satisfies $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$. Since $\boldsymbol{b}_1$ and $\boldsymbol{b}_2$ form a two-dimensional triangular lattice while $\boldsymbol{b}_3$ points directly out of the page, the reciprocal primitive vectors $\boldsymbol{b}_j$ form a simple 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
$$\boldsymbol{K} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2 + m_3\boldsymbol{b}_3.$$

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 $\boldsymbol{b}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij}$. We then get

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

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

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

- In any case, $S_{\boldsymbol{K}}$ 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 $S_{\boldsymbol{K}} = 3$ (and 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

$$1 + e^{-i\frac{4\pi}{3}} + e^{-i\frac{8\pi}{3}} = 0.$$

- Interpretation: 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 in this case $1/3 \cdot 3 = 1$ or for SC and basis $1/4 \cdot 4 = 1$.

- Main lesson: 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).

4 Fourth Exercise Set

4.1 An X-Ray Scattering Experiment

A given crystal structue is know to have a simple cubic unit cell with an additional atom somewhere along the main body diagonal. However, the exact position of this atom along the diagonal is unknown.

- *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 the scattering angles $\theta_1 = 83.6°$ and $\theta_2 = 141.1°$, respectively.*

- *In a rotating crystal method experiment with the crystal in single-crystal form, we observe two constructive interference peaks at the scattering angle $\theta_2 = 141.1°$, and these two peaks are found to differ in intensity by a ratio of 1 to 4.*

Use the given 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

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

  and the corresponding basis is

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

  where 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 the 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 indices 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.

Subcases of the BCC case $x = a/2$

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

  1. First, we could simply continue representing 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 3.2.2, is a FCC with lattice constant $4\pi/a$ and reciprocal vectors

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

- 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 Analyzing Scattering Angles from the Powder Method

- We begin with the experimental data from the powder method, which reports two peaks at the 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. (Note, however, it only makes sense to consider $\boldsymbol{K}$ that give nonzero scattering intensity, i.e. those $\boldsymbol{K}$ that lead to a non-zero GSF.)

Simple Cubic Lattice with $x \neq a/2$

- We begin with the possibility that the crystal structure has a simple cubic plus basis representation with $x \neq a/2$. 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

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

The corresponding distance d between lattice planes is

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

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

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

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

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

- 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 with $x = a/2$

- We now consider the possibility that the crystal structure is BCC, corresponding to the diagonal atom occuring at exactly $x = a/2$.

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

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

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 condition, 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

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

- Recall the BCC case divides further into two sub-cases, which for review are

  1. First, we could simply continue representing 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 3.2.2, is a FCC with lattice constant $4\pi/a$ and reciprocal vectors

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

- We first consider the SC plus basis model of the BCC structure, 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 for which the GSF in Equation 1 is non-zero (a zero GSF would mean no scattering). The GSF in Equation 1 is non-zero only when the sum of Miller indices is even, and the smallest possible even number is two, so in the BCC model the first scattering angle θ_1 corresponds to the Miller index combination

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

The Miller indices satisfying 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 consistent, 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 $x = a/2$ sub-case, in which we would represent the unknown crystal directly with a BCC lattice.

4.1.2 Analyzing Peak Intensities from the Rotation Method

- Analyzing the powder method 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 consistent lattice constants.

We thus turn to the second set of experimental data to determine if $x = a/2$. The second experiment, using the single-crystal rotation method, observed two constructive interference peaks at $\theta_2 = 141.1°$, and found that these peaks differed in intensity by a factor of four. Our first step is to compute scattering intensity, which is proportional to the square of the GSF and given by

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

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

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

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

- Assuming a BCC structure with $x = a/2$, valid Miller index combinations for the scattering angle θ_2 are combinations of 0, 0, and ± 2 for θ_2; possible sums of these Miller indices are 2 and -2. In both cases the intensity is the same if $x = a/2$, since

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

produces the same result for $m_1 + m_2 + m_3 = \pm 2$. This theoretically-predicted equal-intensity result for all θ_2 Miller index combinations does not agree with the rotation experiment observation of the two θ_2 scattering peaks differing in intensity by a factor of 4, so we conclude $x \neq a/2$.

- Having determined $x \neq a/2$, we now aim to solve for possible values of x using the experimentally-observed result that the two peak intensities in the crystal rotation experiment varied by a factor of 1 to 4. To make use of this result, we compute the ratio of intensities for two different θ_2 Miller index combinations: one which sums to 2 (e.g. $(1, 1, 0)$) and one which sums to 0 (e.g. $(1, -1, 0)$):

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

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

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 (i.e. has the same value at all points in space), 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 the course *Elektromagnetno polje* that Ohmic energy losses in a conductor are given by the product $\boldsymbol{j} \cdot \boldsymbol{E}$. 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 crystal as a three-dimensional infinite potential well containing 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 beyond 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 wave functions 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 of a Free Electron Gas

Derive the density of states $g(E)$ of a free electron gas 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 direction), 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

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

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

$$g_{2\mathrm{D}}(E) = \frac{1}{S}\frac{\mathrm{d}N(E)}{\mathrm{d}E}. \tag{5.8}$$

- 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 $dE = \hbar^2 k\, dk/m$, the density of states reads

$$g(E) = \frac{k}{\pi} \cdot \frac{m}{\hbar^2 k} = \frac{m}{\pi \hbar^2} \tag{5.9}$$

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

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

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

5.3.3   One Dimension

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

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

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

The spacing in k space between energies E and $E + dE$ is

$$dV^* = 2\, dk;$$

(The factor of two arises because in one dimension any two wave vectors $\pm k$ correspond to the same energy E.) The number of electrons in the energy range E and $E + dE$ is then

$$dN = \frac{dV^*}{V_1^*} = \frac{2\, dk}{2\pi/L} = \frac{L}{\pi}\, dk,$$

and the corresponding density of states is

$$g_{1D}(E) = 2 \cdot \frac{1}{L} \frac{dN(E)}{dE} = \frac{2}{L} \cdot \left(\frac{L}{\pi} \frac{dk}{dE} \right) = \frac{2}{\pi} \frac{dk}{dE},$$

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

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

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

$$g_d(E) \propto E^{\frac{d-2}{2}} H(E), \tag{5.10}$$

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

5.4 Temperature Dependence of the Chemical Potential in a Free Electron Gas

Use the Sommerfeld expansion to derive expressions for the temperature-dependence of a the chemical potential in a one-, two-, and three- dimensional free electorn 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. From 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.

  $$N(T > 0) = V \int_0^{\infty} g(E) f(E) \, dE \equiv V \int_0^{E_{\mathrm{F}}} g(E) \, dE = N\big|_{T=0}. \tag{5.11}$$

  From here, without derivation, we quote the lecture result

  $$\mu(T) \approx E_{\mathrm{F}} - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(E_{\mathrm{F}})}{g(E_{\mathrm{F}})}, \tag{5.12}$$

  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 $k_B T \ll E_{\mathrm{F}}$.

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- 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 5.10.

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

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 5.12, 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 in different dimensions!

6 Sixth Exercise Set

6.1 Two-Dimensional Expansion of Chemical Potential

Without relying on the Sommerfeld expansion (as in the previous exercise), derive an expression for the temperature-dependence of the chemical potential in a two-dimensional free electorn gas.

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

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

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 5.9), 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 5.12 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 5.11, 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 $\mu = \frac{1}{\beta}\ln\left(e^{\beta E_{\mathrm{F}}} - 1\right)$ as follows:

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

Under the assumption $k_B T \ll E_{\mathrm{F}}$ the second term, using $\ln(1 - x) \approx -x$ becomes

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

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

6.2   Theory: 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 wave function ψ_n, where ψ_n denotes the wave function 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 wave function by a distance a, which in our case is the crystal's lattice constant. Interpreted physically, T simply moves a wave function 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 potential. 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 effect on 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 wave function 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 eigenvalue 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 period 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 wave function 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

Using the Kronig-Penney model in the limit of nearly-free electrons to predict the energy band gap of an electron in a one-dimensional crystal.

- 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 wave function 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

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

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 different 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

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

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

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

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

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

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

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

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

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

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

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

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

Use the nearly-free electron model with the Kronig-Penney delta function potential to predict the energy gap in a one-dimensional crystal.

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 occurs at the edge of Brillioun zone $k = \pi/a$, and corresponds to an intersection 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,

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

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the wave functions 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 3.2.3, 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

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

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 equidistant 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 eigenvalue problem

$$
\begin{pmatrix}
E_0 + U_{\boldsymbol{K}_1 - \boldsymbol{K}_1} - E & U_{\boldsymbol{K}_2 - \boldsymbol{K}_1} & U_{\boldsymbol{K}_3 - \boldsymbol{K}_1} & U_{\boldsymbol{K}_4 - \boldsymbol{K}_1} \\
U_{\boldsymbol{K}_1 - \boldsymbol{K}_2} & E_0 + U_{\boldsymbol{K}_2 - \boldsymbol{K}_2} - E & U_{\boldsymbol{K}_3 - \boldsymbol{K}_2} & U_{\boldsymbol{K}_4 - \boldsymbol{K}_2} \\
U_{\boldsymbol{K}_1 - \boldsymbol{K}_3} & U_{\boldsymbol{K}_2 - \boldsymbol{K}_3} & E_0 + U_{\boldsymbol{K}_3 - \boldsymbol{K}_3} - E & U_{\boldsymbol{K}_4 - \boldsymbol{K}_3} \\
U_{\boldsymbol{K}_1 - \boldsymbol{K}_4} & U_{\boldsymbol{K}_2 - \boldsymbol{K}_4} & U_{\boldsymbol{K}_3 - \boldsymbol{K}_4} & E_0 + U_{\boldsymbol{K}_4 - \boldsymbol{K}_4} - E
\end{pmatrix}
\begin{pmatrix}
c_{\boldsymbol{W} - \boldsymbol{K}_1} \\
c_{\boldsymbol{W} - \boldsymbol{K}_2} \\
c_{\boldsymbol{W} - \boldsymbol{K}_3} \\
c_{\boldsymbol{W} - \boldsymbol{K}_4}
\end{pmatrix}
= \boldsymbol{0}.
$$

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 $U_{\boldsymbol{0}} = 0$. 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

$$
\mathbf{R}\boldsymbol{K} \cdot \mathbf{R}(\mathbf{R}^{-1}\boldsymbol{r}) = \boldsymbol{K} \cdot \boldsymbol{R}^{-1}\boldsymbol{r} \implies U_{\mathbf{R}\boldsymbol{K}} = \frac{1}{V_0} \iiint U(\boldsymbol{r}) e^{-i\boldsymbol{K} \cdot \mathbf{R}^{-1}\boldsymbol{r}} \, \mathrm{d}V.
$$

Finally, we introduce the new variable $\mathbf{R}^{-1}\boldsymbol{r} = \boldsymbol{u}$ or $\boldsymbol{r} = \boldsymbol{Ru}$. 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

$$U_{\mathbf{R}\boldsymbol{K}} = \frac{1}{V_0} \iiint U(\boldsymbol{r})e^{-i\boldsymbol{K}\cdot\mathbf{R}^{-1}\boldsymbol{r}}\,\mathrm{d}^3\boldsymbol{r} = \frac{1}{V_0} \iiint U(\mathbf{R}\boldsymbol{u})e^{-i\boldsymbol{K}\cdot\boldsymbol{u}}\,\mathrm{d}^3\boldsymbol{u}$$
$$= \frac{1}{V_0} \iiint U(\boldsymbol{u})e^{-i\boldsymbol{K}\cdot\boldsymbol{u}}\,\mathrm{d}^3\boldsymbol{u} = U_{\boldsymbol{K}},$$

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 $\boldsymbol{k}$ at these points in the first Brillioun zone are points of degeneracy.

- We considered the Brillioun zone vertex point $\boldsymbol{W}$, and found the four values of reciprocal lattice vectors $\boldsymbol{K}$ that were equidistant from $\boldsymbol{W}$. These values of $\boldsymbol{K}$ correspond to degenerate energies (correspond to electron bands intersecting at $\boldsymbol{W}$?).

- 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, then the Fourier components corresponding to those $\boldsymbol{K}$ are real.

- Our next step is to find which Fourier components (or which $\boldsymbol{K}$?) are related by symmetry operations.

Begin New Material

- First, we note that rotation by 90° about the k_z axis maps $U_{\boldsymbol{K}_2-\boldsymbol{K}_1}$ into $U_{\boldsymbol{K}_4-\boldsymbol{K}_3}$, which motivates the more compact definition

$$U_{\boldsymbol{K}_2-\boldsymbol{K}_1} = U_{\boldsymbol{K}_4-\boldsymbol{K}_3} \equiv U_1 \in \mathbb{R}.$$

Second, we note that reflections about the three coordinate planes normal to k_x, k_y and k_z produce symmetry relations between $\boldsymbol{K}_3 - \boldsymbol{K}_1$, $\boldsymbol{K}_4 - \boldsymbol{K}_1$, $\boldsymbol{K}_3 - \boldsymbol{K}_2$ and $\boldsymbol{K}_4 - \boldsymbol{K}_2$, which motivates the definition of U_2 as

$$U_{\boldsymbol{K}_3-\boldsymbol{K}_1} = U_{\boldsymbol{K}_4-\boldsymbol{K}_1} = U_{\boldsymbol{K}_3-\boldsymbol{K}_2} = U_{\boldsymbol{K}_4-\boldsymbol{K}_2} \equiv U_2.$$

In other words, using symmetry considerations, we have reduced the original set of 64 Fourier components to only the two independent components U_1 and U_2. In terms of U_1 and U_2, and setting $U_{\boldsymbol{0}} = 0$, the perturbation matrix equation simplifies to

$$\begin{pmatrix} E_0 - E & U_1 & U_2 & U_2 \\ U_1 & E_0 - E & U_2 & U_2 \\ U_2 & U_2 & E_0 - E & U_1 \\ U_2 & U_2 & U_1 & E_0 - E \end{pmatrix} \begin{pmatrix} c_{\boldsymbol{W}-\boldsymbol{K}_1} \\ c_{\boldsymbol{W}-\boldsymbol{K}_2} \\ c_{\boldsymbol{W}-\boldsymbol{K}_3} \\ c_{\boldsymbol{W}-\boldsymbol{K}_4} \end{pmatrix} = \boldsymbol{0}. \qquad (8.1)$$

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 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.

8.2 Kronig-Penney Model with the Tight Binding Model

Use both the tight-binding model and the Kronig-Penney model to predict the electron energy dispersion relation in a one-dimensional lattice and compare the results.

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 wave functions are far 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 isolated atomic electron states.

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), which will create potential wells generating the localized atomic orbitals as required by the tight-binding model. Letting a denote the lattice constant, our problem's periodic potential 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

  $$E_{\text{at}} = -\frac{m\lambda^2}{2\hbar^2},$$

  while the corresponding wave function is

  $$\psi_{\text{at}}(x) = \sqrt{\kappa_0} e^{-\kappa_0 |x|}, \qquad \kappa_0 = \frac{m\lambda}{\hbar^2},$$

  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 parameter 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 the general analytic Kronig-Penney solution to the current 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 $U(x) = -\lambda\delta(x)$. We first define

$$\widetilde{Q} = \frac{m\widetilde{\lambda}}{\hbar^2} \implies Q = -\widetilde{Q}. \tag{8.2}$$

Then, because $E = E_{\text{at}}$ is a negative energy (since the energy corresponds to a bound state), and so q, which is defined in terms of the square root of E, is imaginary, we define

$$q = i\widetilde{q}.$$

- In terms of the relations $q = i\widetilde{q}$ and $Q = -\widetilde{Q}$, 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 wave functions 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 $\widetilde{q}a \to 0$ and 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

$$\widetilde{q}a = \widetilde{Q}a + \epsilon, \tag{8.3}$$

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 8.3, 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 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

$$E_{\text{at}} = \frac{\hbar^2 \widetilde{Q}^2}{2m} \qquad \text{and} \qquad \gamma \equiv -\frac{\hbar^2}{m} \widetilde{Q}^2 e^{-\widetilde{Q}a},$$

in terms of which the tightly-bound electron energy reads

$$E(k) = E_{\text{at}} - 2\gamma \cos(ka). \tag{8.4}$$

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 $\gamma \propto e^{-\widetilde{Q}a}$; because we assume $\widetilde{Q}a$ is large, the gap γ is small compared to E_{at}.

8.2.3 Using the Tight-Binding Model

Review of TB Model from Lecture

- In three dimensions, the energy of an electron in the tight-binding model is

$$E(\boldsymbol{k}) = E_{\text{at}} - \frac{\beta + \sum_{\boldsymbol{R} \neq \boldsymbol{0}} \gamma(\boldsymbol{R}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}}}{1 + \sum_{\boldsymbol{R} \neq \boldsymbol{0}} \alpha(\boldsymbol{R}) e^{i\boldsymbol{k}\cdot\boldsymbol{R}}}, \tag{8.5}$$

  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

$$\beta = -\iiint_V \psi_{\text{at}}^* \Delta U(\boldsymbol{r}) \psi_{\text{at}}(\boldsymbol{r}) \, \mathrm{d}V, \tag{8.6}$$

  where ψ_{at} is the wave function of an electron on an isolated atom, while the term ΔU is defined as

$$\Delta U(\boldsymbol{r}) = \sum_{\boldsymbol{R} \neq \boldsymbol{0}} U_{\text{at}}(\boldsymbol{r} - \boldsymbol{R}).$$

- The overlap of orbitals on different atoms is encoded by γ and α; these are given by

$$\gamma(\boldsymbol{R}) = -\iiint_V \psi_{\text{at}}^*(\boldsymbol{r}) \Delta U(\boldsymbol{r}) \psi_{\text{at}}(\boldsymbol{r} - \boldsymbol{R}) \, \mathrm{d}V \tag{8.7}$$

$$\alpha(\boldsymbol{R}) = \iiint_V \psi_{\text{at}}^*(\boldsymbol{r}) \psi_{\text{at}}(\boldsymbol{r} - \boldsymbol{R}) \, \mathrm{d}V. \tag{8.8}$$

- *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 tight-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 wave functions, 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 8.4.

9 Ninth Exercise Set

9.1 The FCC Structure in Tight-Binding Model

Use the tight-binding model to analyze the electron dispersion relation, energy band gap, and density of states in an FCC crystal structure.

- Assume overlap integrals are small and neglect the overlap integral α. We consider only the $\gamma(\boldsymbol{R})$ integral, and consider only those $\gamma(\boldsymbol{R})$ for which $\boldsymbol{R}$ is a nearest neighbor to the origin. (Well, a neighbor to the lattice site holding the electron for which we are computing the energy E, but we usually place that site at the origin).

- Consider a FCC crystal and the electron band formed of s orbitals on each atom. Keep in mind that the s orbitals are spherically symmetric, and so the associated overlap integrals only depend on radial distance between atoms.

- The energy of an s orbital electron in the TB approximation is

$$E(\boldsymbol{k}) = \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} \gamma(\boldsymbol{R}) e^{i\boldsymbol{k} \cdot \boldsymbol{R}}, \tag{9.1}$$

  where the sum runs over all vectors in Bravais lattice that are nearest neighbors of origin. Each FCC lattice site has 12 total nearest neighbors; for the origin these are

$$a\left(0, \pm\tfrac{1}{2}, \pm\tfrac{1}{2}\right) \qquad a\left(\pm\tfrac{1}{2}, 0, \pm\tfrac{1}{2}\right) \qquad a\left(\pm\tfrac{1}{2}, \pm\tfrac{1}{2}, 0\right).$$

  Importantly, each nearest neighbor has a pair on the other side of the origin at $\boldsymbol{R} \to -\boldsymbol{R}$. We can then use the identity $e^{i\boldsymbol{k} \cdot \boldsymbol{R}} + e^{-i\boldsymbol{k} \cdot \boldsymbol{R}} = 2\cos \boldsymbol{k} \cdot \boldsymbol{R}$ when computing E from Equation 9.1 and consider only 6 terms instead of 12; this reads

$$E(\boldsymbol{k}) = -2\gamma \left[\cos\frac{k_y + k_z}{2}a + \cos\frac{k_y - k_z}{2}a + \cos\frac{k_x + k_z}{2}a + \cos\frac{k_x - k_z}{2}a \right.$$
$$\left. + \cos\frac{k_x + k_y}{2}a + \cos\frac{k_x - k_y}{2}a \right].$$

  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

$$E(\boldsymbol{k}) = -4\gamma \left[\cos \frac{k_y a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \right]. \qquad (9.2)$$

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. Alternatively, s orbital electrons in a FCC crystal have the above-computed energy band dispersion relation when analyzed with the tight-binding model.

9.1.1 Dispersion Relation Along Symmetry Points

- We now aim to draw the dispersion relation $E(\boldsymbol{k})$ for s orbital electrons in an FCC lattice. This dispersion relation cannot be drawn easily since, the ambient $\boldsymbol{k}$ space is three-dimensional. Since viewing the full dispersion relation is not feasible, crystallographers make a compromise: plotting $E(\boldsymbol{k})$ along curves passing through points of highh symmetry in the first Brillioun zone. These curves can be parameterized by a one-dimensional parameter, and then E along that curve is plotted as a function of the parameter.

- For this problem, first recall that an FCC crystal's reciprocal lattice is a BCC lattice in reciprocal space. As shown in Exercise 2.4, the Wigner-Seitz cell for the BCC structure, and thus the first Brillioun zone for an FCC structure, is a truncated octahedron. We choose a path through this octahedron that:

    - starts in the Brillioun zone's center—the center of a Brillioun zone is conventionally denoted by Γ and has coordinates $\Gamma = (0, 0, 0)$,

    - moves to the center of the right-side square face, which is conventionally called X and has coordinates $X = (\frac{2\pi}{a}, 0, 0)$,

    - moves to the vertex point W, which, as in Exercise 7.4, has coordinates $W = (\frac{2\pi}{a}, 0, \frac{\pi}{a})$,

    - then moves to the center of hexagonal face, which is denoted by L and has coordinates $L = (\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$, and

    - returns to Γ at the center of the first Brillioun zon.

- We introduce the variable q to parameterize the path segment between each of the above neighboring points. We then compute $E(q)$ for each segment along the path using Equation 9.2 and the parameterized expressions for $\boldsymbol{k} = (k_x, k_y, k_z)$ in terms of q. The parameterization of the path is summarized in Table 1.

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	$\left(\frac{2\pi}{a}, 0, 0\right)$	$X \to W$	$\boldsymbol{k} = \left(\frac{2\pi}{a}, 0, q\right)$	$q \in \left[0, \frac{\pi}{a}\right]$
W	$\left(\frac{2\pi}{a}, 0, \frac{\pi}{a}\right)$	$W \to L$	$\boldsymbol{k} = \left(\frac{2\pi}{a} - q, q, 0\right)$	$q \in \left[0, \frac{\pi}{a}\right]$
L	$\left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$	$L \to \Gamma$	$\boldsymbol{k} = \left(\frac{\pi}{a} - q, \frac{\pi}{a} - q, \frac{\pi}{a} - q\right)$	$q \in \left[0, \frac{\pi}{a}\right]$

Table 1: Quantities associated with the parameterization of the path through the FCC lattice's first Brillioun zone used in this exercise.

- For the path segment $\Gamma \to X$ the energy relation $E(q)$ reads

$$E(q) = -4\gamma \left(1 \cdot 1 + \cos\frac{qa}{2} \cdot 1 + \cos\frac{qa}{2} \cdot 1\right) = -4\gamma - 8\gamma \cos\frac{qa}{2}.$$

The energy ranges from -12γ to 4γ along this segment.

- For the segment from X to W, $E(q)$ is

$$E(q) = -4\gamma \left(1 \cdot \cos\frac{qa}{2} + (-1) \cdot \cos\frac{qa}{2} + (-1) \cdot 1\right) = 4\gamma.$$

The energy is evidently constant and equal to 4γ along this segment.

- For the segment from W to L, $E(q)$ is

$$E(q) = -4\gamma \left(\cos\frac{qa}{2} \cdot 1 + (-1) \cdot \cos\frac{qa}{2} \cdot 1 + (-1) \cdot \cos\frac{qa}{2} \cos\frac{qa}{2}\right)$$
$$= 4\gamma \cos^2\frac{qa}{2}.$$

The energy ranges from 4γ to 0 along this segment.

- On the final segment from L to Γ, using $k_x = k_y = k_z = q - \frac{\pi}{a}$, $E(q)$ reads

$$E(q) = -3 \cdot 4\gamma \cos^2\left(\frac{qa}{2} - \frac{\pi}{2}\right) = -12\gamma \sin^2\frac{qa}{2}.$$

Electron 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 graph 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

$$\boldsymbol{k} = \Gamma + \boldsymbol{q} = \boldsymbol{0} + \boldsymbol{q} = \boldsymbol{q}, \qquad |\boldsymbol{q}| \ll \frac{\pi}{a}, \tag{9.3}$$

where $|\boldsymbol{q}| \ll \frac{\pi}{a}$ ensures $\boldsymbol{k}$ remains near the center of the first Brillioun zone. From Equation 9.2, 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 terms in 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 electron 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 9.2, 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

$$E(\boldsymbol{q}) \approx -4\gamma \left(\frac{q_y q_z a^2}{4} + \frac{q_x q_z a^2}{4} + \frac{q_x q_y a^2}{4} \right).$$
$$= -\gamma a^2 (q_y q_z + q_x q_z + q_x q_y). \tag{9.4}$$

- 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

$$E(\boldsymbol{q}) = -4\gamma \left[\left(1 - \frac{1}{2} \left(\frac{q_y a}{2} \right)^2 \right) \left(1 - \frac{1}{2} \left(\frac{q_z a}{2} \right)^2 \right) + \cdots \right.$$
$$- \left(1 - \frac{1}{2} \left(\frac{q_x a}{2} \right)^2 \right) \left(1 - \frac{1}{2} \left(\frac{q_z a}{2} \right)^2 \right) + \cdots$$
$$\left. - \left(1 - \frac{1}{2} \left(\frac{q_x a}{2} \right)^2 \right) \left(1 - \frac{1}{2} \left(\frac{q_y a}{2} \right)^2 \right) + \cdots \right].$$

We then multiply out and neglect fourth-order terms in $q_y q_z$ to get

$$E(\boldsymbol{q}) \approx -4\gamma \left[1 - \frac{a^2}{8} \left(q_y^2 + q_z^2 \right) - 1 + \frac{a^2}{8} \left(q_x^2 + q_z^2 \right) - 1 + \frac{a^2}{8} \left(q_x^2 + q_y^2 \right) \right]$$
$$= -4\gamma \left(-1 + \frac{a^2 q_x^2}{4} \right) = 4\gamma - \gamma a^2 q_x^2.$$

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 the free electron analogy, but adapted to the 4γ energy shift and negative dispersion relation. The result is

$$g(E) \propto \frac{1}{\sqrt{4\gamma - E}}$$

Note however this approximation of $g(E)$ is qualitative only; it's quite rough.

9.2   Tight-Binding Model for a 2D Square Bravais Lattice

Use the tight-binding model to analyze the electron dispersion relation, energy band gap, and density of states in a two-dimensional square lattice. Consider only the electron energy band formed of s orbitals.

- We begin with the tight-binding model approximation for electron energy, i.e.

$$E(\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\text{nn}\}} e^{i\boldsymbol{k} \cdot \boldsymbol{R}},$$

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

$$E(\boldsymbol{k}) = -\gamma \left(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} \right) = -2\gamma(\cos k_x a + \cos k_y a). \qquad (9.5)$$

- 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

$$\left\{ (k_x, k_y) \,\middle|\, k_x \in \left(-\tfrac{\pi}{a}, \tfrac{\pi}{a} \right) \text{ and } k_y \in \left(-\tfrac{\pi}{a}, \tfrac{\pi}{a} \right) \right\}.$$

- 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

- Similarly to the analysis of the FCC Brillioun zone in the previous exercise, we first parameterize the path in $\boldsymbol{k}$ space between the Brillioun zone symmetry points using the parameter q. The parameterization of the path is summarized in Table 2.

point	coordinates		segment	wave vector $\boldsymbol{k}$	parameter range
Γ	$(0,0)$		$\Gamma \to X$	$\boldsymbol{k} = (q, 0)$	$q \in \left[0, \tfrac{\pi}{a}\right]$
X	$\left(\tfrac{\pi}{a}, 0\right)$		$X \to M$	$\boldsymbol{k} = \left(\tfrac{\pi}{a}, q\right)$	$q \in \left[0, \tfrac{\pi}{a}\right]$
M	$\left(\tfrac{\pi}{a}, \tfrac{\pi}{a}\right)$		$M \to \Gamma$	$\boldsymbol{k} = \left(\tfrac{\pi}{a} - q, \tfrac{\pi}{a} - q\right)$	$q \in \left[0, \tfrac{\pi}{a}\right]$

Table 2: Quantities associated with the parameterization of the path through first Brillioun zone of the 2D square lattice used in this exercise.

- We begin with general square lattice dispersion relation from Equation 9.5, which for review reads

$$E(\boldsymbol{k}) = -2\gamma(\cos k_x a + \cos k_y a).$$

For the first path segment from Γ to X we substitute in $\boldsymbol{k} = (q, 0)$ to get

$$E(q) = -2\gamma(\cos qa + 1).$$

The electron 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   Density of States and 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

$$E(\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} e^{i\boldsymbol{k} \cdot \boldsymbol{R}},$$

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

$$E(\mathbf{S}\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} e^{i\mathbf{S}\boldsymbol{k} \cdot \boldsymbol{R}} = -\gamma \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} e^{i\mathbf{S}\boldsymbol{k} \cdot (\mathbf{S}\mathbf{S}^{-1})\boldsymbol{R}},$$

where in the last equality we have simply introduced $\boldsymbol{R} = \mathbf{I}\boldsymbol{R} = (\mathbf{S}\mathbf{S}^{-1})\boldsymbol{R}$—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

$$E(\mathbf{S}\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} e^{i\boldsymbol{k} \cdot (\mathbf{S}^{-1}\boldsymbol{R})}.$$

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

$$E(\mathbf{S}\boldsymbol{k}) = -\gamma \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} e^{i\boldsymbol{k} \cdot (\mathbf{S}^{-1}\boldsymbol{R})} = -\gamma \sum_{\boldsymbol{R} \in \{\mathrm{nn}\}} e^{i\boldsymbol{k} \cdot \boldsymbol{R}} = E(\boldsymbol{k})$$

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 reciprocal 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 9.5, 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.

- 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 Equation 9.3 from Section 9.1.2, 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. 9.5) 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 from -4γ to $+4\gamma$ found at the end of Section 9.2.1.

- Next, (rather in passing) we sketched curves of constant energy—these are circles of radius q—centered around Γ in $\boldsymbol{k}$ space. We then 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

$$E(\boldsymbol{q}) \approx -2\gamma\left[-1 + \frac{q_x^2 a^2}{2} + 1 - \frac{q_y^2 a^2}{2}\right] = \gamma a^2(-q_x^2 + q_y^2). \tag{9.6}$$

As for the FCC L point in Equation 9.4 of Section 9.1.3, 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 dispersion relation.

We ran out of time at this point; the analysis of the 2D square lattice's point X continues in the next exercise.

10   Tenth Exercise Set

10.1   Tight-Binding Model for a Square Bravais Lattice (continued)

Continuing from the previous exercise set, we now aim to compute the electron density of states at the saddle point X in the 2D square lattices first Brillioun zone.

- Because the point X is a saddle point, we cannot use free electron results to approximate the electron density of states at X (free electron approximations apply only to parabolic dispersion relations). Instead, we turn to formal definition of the density of states in two dimensions (see Equation 5.8 from Section 5.3.2), i.e.

$$g(E) = \frac{1}{S}\frac{\mathrm{d}N}{\mathrm{d}E} = \frac{1}{L^2}\frac{\mathrm{d}N}{\mathrm{d}E},$$

  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 the number of states $\mathrm{d}N$ between E and $E + \mathrm{d}E$.

  To make this easier, we define the function $N(E)$ giving number of energies between $E = 0$ and E. We can find density of the states by differentiating $N(E)$ with respect to energy, i.e.

$$g(E) = \frac{1}{S}\frac{\mathrm{d}}{\mathrm{d}E}\big[N(E)\big].$$

  Note the subtle difference (which will have equivalent results)—instead of dividing two differentials $\mathrm{d}N$ and $\mathrm{d}E$, we differentiate the function $N(E)$ with respect to E.

- We first define a coordinate system with the 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 Equation 9.6 that near X, the electron 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, because $g(E)$ is an even function, it suffices to consider only $g(E)$'s behavior for $E > 0$, since $g(E) = g(-E)$. 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 the integration limits are tricky because the expression for q_y relies on a Taylor approximation of $E(\boldsymbol{q})$, which is valid only for a limited range of $\boldsymbol{q}$. We use q_c for the time being but, without proof, it turns out the value of the this integeration limit won't matter for our problem In any case, the function $N(E)$ comes out to

$$N(E) = \frac{4L^2}{\pi^2}\int_0^{q_c}\left(\sqrt{q_x^2 + \frac{E}{\gamma a^2}} - q_x\right)\mathrm{d}q_x.$$

- Having constructed an expression for $N(E)$, we substitute $N(E)$ into the equation

$$g(E) = \frac{1}{S} \frac{\mathrm{d}}{\mathrm{d}E} \big[N(E) \big]$$

(and change the order of integration and differentiation?) to get

$$g(E) = \frac{1}{L^2} \frac{4L^2}{\pi^2} \int_0^{q_\mathrm{c}} \frac{\frac{1}{\gamma a^2}}{2\sqrt{q_x^2 + \frac{E}{\gamma a^2}}} \, \mathrm{d}q_x = \frac{2}{\pi^2 \gamma a^2} \left[\sinh^{-1} \frac{q_x}{\sqrt{E/(\gamma a^2)}} \right]_0^{q_\mathrm{c}},$$

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

$$g(E) = \frac{2}{\pi^2 \gamma a^2} \sinh^{-1} \frac{q_\mathrm{c}}{\sqrt{E/(\gamma a^2)}}$$

- For small energies $E \ll \gamma$, argument of $\sinh^{-1}$ function will grow large. Recall the 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

$$g(E) \approx \frac{2}{\pi^2 \gamma a^2} \ln \frac{2q_\mathrm{c}}{\sqrt{E/(\gamma a^2)}}.$$

Next, we split up the logarithm using the identity $\ln(A/B) = \ln A - \ln B$ into an energy-dependent term and a constant term (note the power $1/2$ cancelling with the factor 2). The result is

$$g(E) = \frac{1}{\pi^2 \gamma a^2}(- \ln E) + \frac{2}{\pi^2 \gamma a^2} \ln\left(2q_\mathrm{c} \sqrt{\gamma a^2} \right).$$

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, for our purposes, is that the density of states scales 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

Use a generalization of the single-orbital tight-binding model to analyze the electron energy dispersion in graphene (which is a structure described by a Bravais lattice with a diatomic basis).

- So far when using the tight-binding model we have always considered only crystal structures well-described by one atomic orbital per primitive cell. This prevents us from analyzing energy bands that arise from orbitals that are not of type s (for example in situations where the p and d bands are important or for basis structures with multiple atomic orbitals per primitive cell.)

- For review, graphene has a honeycomb lattice, which is not a Bravais lattice. We will model graphene using a triangular Bravais lattice together with a basis. The triangular lattice's primitive vectors $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ (see Equation 3.5 for review) are equally long and have angle $60°$ degrees between them. We model the atoms in graphene with the 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 atoms have three nearest neighbors.

- For better understanding, we consider orbital structure of carbon: $1s^2 2s^2 2p^2$. Now the 1s orbitals are "frozen" deep below the Fermi energy (or so localized around the atomic nucleus that their is no appreciable overlap with neighbors). Thus the 1s do not contribute to energy bands. 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 thus consider only the contribution of $2p_z$ orbitals to energy band formation.

- Summary: Model graphene with a triangular Bravais lattice and a basis with two atoms, A and B, per unit cell of graphene. Each atom has three nearest neighbors. We consider only one p_z orbital per atom, or equivalently $2p_z$ orbitals per unit cell. We can't use the usual lecture formula electron energy in the tight-binding model, because that formula applies only in situations with one orbital per unit cell. To analyze graphene using two orbitals per unit cell, we must derive an appropriate tight-binding electron energy formula "from scratch".

Derivation of Electron Energy in Graphene

- We first form the basis of the Hilbert space of electron orbitals in which we will work. This basis consists of orbitals specified by a vector in the Bravais lattice $\boldsymbol{R}$ and an index α specifying an orbital. Orbital states are labelled by $|\boldsymbol{R}_\alpha\rangle$. In our case $\alpha \in \{A, B\}$ where $\alpha = A$ corresponds to the orbital p_z around the A atom.

- In the 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).

- We then aim to solve the stationary Schrödinger equation

$$H |\psi\rangle = E |\psi\rangle,$$

where we write $|\psi\rangle$ using the ansatz

$$|\psi\rangle = \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} |\boldsymbol{R}'_{\alpha'}\rangle.$$

Substituting this ansatz into the Schrödinger equation produces

$$H \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} |\boldsymbol{R}'_{\alpha'}\rangle = \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} H |\boldsymbol{R}'_{\alpha'}\rangle = E \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} |\boldsymbol{R}'_{\alpha'}\rangle.$$

We then project the state $\langle \boldsymbol{R}_\alpha |$ onto this equation, producing

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | H | \boldsymbol{R}'_{\alpha'} \rangle = E \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle . \tag{10.1}$$

Note that the basis of $|\boldsymbol{R}_\alpha\rangle$ states is not orthonormal, so that $\langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle \neq \delta_{\alpha\alpha'}$.

- 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

$$H^{\text{atom}}_{\boldsymbol{R}_\alpha} |\boldsymbol{R}_\alpha\rangle = E_\alpha |\boldsymbol{R}_\alpha\rangle .$$

We then substitute this ansatz for H into Equation 10.1 to get

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left(E^{\text{atom}}_\alpha \langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle + \langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle \right) = E \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle .$$

Next, we combine the like $\langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle$ terms, which produces

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle = \left(E - E^{\text{atom}}_\alpha \right) \sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle .$$

We then decompose the sum on the RHS and apply $\langle \boldsymbol{R}_\alpha | \boldsymbol{R}_\alpha \rangle = 1$ to get

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle = \left(E - E^{\text{atom}}_\alpha \right) \left(c_{\boldsymbol{R}_\alpha} + \sum_{\boldsymbol{R}'_{\alpha'} \neq \boldsymbol{R}_\alpha} c_{\boldsymbol{R}'_{\alpha'}} \langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle \right) . \tag{10.2}$$

Note the LHS matrix element $\langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle$ plays the same role as the β and γ overlap integrals in the single-orbital tight-binding model, while the RHS plays the same role as the α overlap integrals.

- Next, we introduce the shorthand notation

$$A_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} \equiv \langle \boldsymbol{R}_\alpha | \Delta U_{\boldsymbol{R}_\alpha} | \boldsymbol{R}'_{\alpha'} \rangle \qquad \text{and} \qquad B_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} \equiv \langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle ,$$

in terms of which Equation 10.2 becomes

$$\sum_{\boldsymbol{R}'_{\alpha'}} A_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} = \left(E - E^{\text{atom}}_\alpha \right) \sum_{\boldsymbol{R}'_{\alpha'}} B_{\boldsymbol{R}_\alpha, \boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} .$$

In equivalent matrix form, the above equation reads

$$\mathbf{A} \boldsymbol{c} = \left(E - E^{\text{atom}}_\alpha \right) \mathbf{B} \boldsymbol{c},$$

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 $\langle \boldsymbol{R}_\alpha | \boldsymbol{R}'_{\alpha'} \rangle \neq \delta_{\alpha\alpha'}$) make it a generalized eigenvalue problem.

- We solve Equation 10.2 with the ansatz

$$\mathbf{B} = \mathbf{I} + \delta\mathbf{B}$$

which we substitute into Equation 10.2, then invert, to get

$$\mathbf{B}^{-1}\mathbf{A}\boldsymbol{c} = \left(E - E_\alpha^{\text{atom}}\right)\boldsymbol{c}$$

where $\mathbf{B}^{-1} = \mathbf{I} + \delta\widetilde{\mathbf{B}}$. We then neglect $\widetilde{\mathbf{B}}$ term, because $\delta\widetilde{\mathbf{B}}$ produces only small energy corrections (similar to neglecting the α and β overlap integrals in the single-orbital tight-binding model). We then end up with regular eigenvalue problem

$$\mathbf{A}\boldsymbol{c} = \left(E - E_\alpha^{\text{atom}}\right)\boldsymbol{c}.$$

Written out in bra-ket from, this reads

$$\sum_{\boldsymbol{R}'_{\alpha'}} c_{\boldsymbol{R}'_{\alpha'}} \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'} \right\rangle = \left(E - E_\alpha^{\text{atom}}\right) c_{\boldsymbol{R}_\alpha}.$$

Finally, we decompose the sum on the RHS into diagonal and off-diagonal terms, which gives the final expression

$$\left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}_\alpha \right\rangle c_{\boldsymbol{R}_\alpha} + \sum_{\boldsymbol{R}'_{\alpha'} \neq \boldsymbol{R}_\alpha} \left\langle \boldsymbol{R}_\alpha \middle| \Delta U_{\boldsymbol{R}_\alpha} \middle| \boldsymbol{R}'_{\alpha'} \right\rangle c_{\boldsymbol{R}'_{\alpha'}} = \left(E - E_\alpha^{\text{atom}}\right) c_{\boldsymbol{R}_\alpha}. \quad (10.3)$$

10.2.1   Special Case: One Orbital Per Unit Cell

- As an exercise, we first analyze the simple case of one electron orbital per unit cell, which is essentially the single-orbital 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 $e^{-i\mathbf{k}\cdot\mathbf{R}}$ to and cancel c_0 to get

$$-\sum_{\mathbf{R}'\neq\mathbf{R}}\gamma(\mathbf{R}'-\mathbf{R})e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}=E-\left(E^{\mathrm{atom}}-\beta\right),$$

which we then solve for E to get the dispersion relation

$$E(\mathbf{k})=E^{\mathrm{atom}}-\beta-\sum_{\mathbf{R}'\neq\mathbf{R}}\gamma(\mathbf{R}'-\mathbf{R})e^{i\mathbf{k}\cdot(\mathbf{R}'-\mathbf{R})}\quad=E^{\mathrm{atom}}-\beta-\sum_{\mathbf{R}\neq\mathbf{0}}\gamma(\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}.$$

The takeaway here is that we have reproduced the tight-binding model result for the dispersion relation $E(\mathbf{k})$ in terms of the overlap integrals β and γ (and assuming $\alpha=0$; compare to e.g. Equation 8.5 if $\alpha=0$).

10.2.2   Graphene—Two Orbitals Per Lattice Site

- The above single-orbital analysis was mostly a pedagogical exercise—we now perform and analysis with two orbitals per unit cell, which is a more realistic model for graphene. Recall from this exercise's introduction that we will consider only the contribution of $2p_z$ orbitals to electron energy bands, and that these orbitals are perpendicular to the plane of graphene.

- We begin with the relationship from Equation 10.3, which for review reads

$$\langle\mathbf{R}_\alpha|\Delta U_{\mathbf{R}_\alpha}|\mathbf{R}_\alpha\rangle c_{\mathbf{R}_\alpha}+\sum_{\mathbf{R}'_{\alpha'}\neq\mathbf{R}_\alpha}\langle\mathbf{R}_\alpha|\Delta U_{\mathbf{R}_\alpha}|\mathbf{R}'_{\alpha'}\rangle c_{\mathbf{R}'_{\alpha'}}=\left(E-E_\alpha^{\mathrm{atom}}\right)c_{\mathbf{R}_\alpha},$$

and define

$$\langle\mathbf{R}_\alpha|\Delta U_{\mathbf{R}_\alpha}|\mathbf{R}_\alpha\rangle\equiv-\beta_\alpha\qquad\text{and}\qquad\langle\mathbf{R}_\alpha|\Delta U_{\mathbf{R}_\alpha}|\mathbf{R}'_{\alpha'}\rangle\equiv-\gamma_\alpha(\mathbf{R}'-\mathbf{R}).$$

- Next, we note the equalities

$$E_A^{\mathrm{atom}}=E_B^{\mathrm{atom}}\equiv E^{\mathrm{atom}}\qquad\text{and}\qquad\beta_A=\beta_B\equiv\beta.$$

We then have for $\mathbf{R}_{\mathrm{B}}$

$$-\gamma c_{\mathbf{R}_A}-\gamma c_{\mathbf{R}+\mathbf{a}_{1_A}}-\gamma c_{\mathbf{R}+\mathbf{a}_{2_A}}=E-E^{\mathrm{atom}}=\left[E-(E^{\mathrm{atom}}-\beta)\right]c_{\mathbf{R}_B}$$

And for $\mathbf{R}_A$ we have

$$-\gamma c_{\mathbf{R}_B}-\gamma c_{\mathbf{R}-\mathbf{a}_{1_B}}-\gamma c_{\mathbf{R}-\mathbf{a}_{2_B}}=E-E^{\mathrm{atom}}=\left[E-(E^{\mathrm{atom}}-\beta)\right]c_{\mathbf{R}_A}$$

- We solve these equations with the Bloch ansatz

$$c_{\mathbf{R}_A}=c_Ae^{i\mathbf{k}\cdot\mathbf{R}}\qquad\text{and}\qquad c_{\mathbf{R}_B}=c_Be^{i\mathbf{k}\cdot\mathbf{R}}$$

which we substitute into the above equations to get

$$-\gamma c_Ae^{i\mathbf{k}\cdot\mathbf{R}}-\gamma c_Ae^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{a}_1)}-\gamma c_Ae^{i\mathbf{k}\cdot(\mathbf{R}+\mathbf{a}_2)}=\left[E-\left(E^{\mathrm{atom}}-\beta\right)\right]c_B$$

$$-\gamma c_Be^{i\mathbf{k}\cdot\mathbf{R}}-\gamma c_Be^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{a}_1)}-\gamma c_Be^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{a}_2)}=\left[E-\left(E^{\mathrm{atom}}-\beta\right)\right]c_A.$$

We end up with a set of only two equations because the Bloch ansatz terms $e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$ 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.

We ran out of time at this point and continue analyzing graphene in the next exercise set.

11 Eleventh Exercise Set

11.1 Graphene in the 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

$$E(\boldsymbol{k}) = \pm\gamma \left| 1 - e^{i\boldsymbol{\kappa}\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right|.$$

- Next, we will analyze the dispersion relation at points of high symmetry in graphene's first Brillioun zone. For review, we model graphene using a triangular Bravais lattice (see Exercise 3.3) with primitive vectors

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

together with the basis

$$\boldsymbol{d}_A = \boldsymbol{0} \qquad \text{and} \qquad \boldsymbol{d}_B = \frac{\boldsymbol{a}_1 + \boldsymbol{a}_2}{3}.$$

From Exercise 3.3, the triangular lattice's reciprocal lattice is again a triangular lattice with reciprocal vectors

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

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 procedure, 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

$$E(\boldsymbol{k}) = \pm\gamma \left| 1 - e^{i\boldsymbol{\kappa}\cdot\boldsymbol{a}_1} + e^{i\boldsymbol{k}\cdot\boldsymbol{a}_2} \right|$$

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

$$E(\boldsymbol{q}) = \pm\gamma\left|e^{-i\frac{2\pi}{3}}i\boldsymbol{q}\cdot\boldsymbol{a}_1 + e^{i\frac{2\pi}{3}}i\boldsymbol{q}\cdot\boldsymbol{a}_2\right|$$

- We then apply 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 simplify 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 $E(\boldsymbol{q})$ using a three-dimensional plot with energy on the z axis and the 2D Brillioun zone coordinates in the xy plane—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

Using the semi-classical equations of motion for charged particles in a periodic potential, derive an expression for the cylcotron effective mass of an electron near the minimum of an energy band in a crystal exposed to a homogneneous external magnetic field $\boldsymbol{B} = (0,0,B)$.

- We consider electrons near the minimum of an energy band with a quadratic dispersion relation of the form

$$E(\boldsymbol{k}) = \frac{\hbar^2}{2}\boldsymbol{k} \cdot \left(\mathsf{m}^*\right)^{-1}\boldsymbol{k} + E_0,$$

where 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

$$\hbar\dot{\boldsymbol{k}} = q\boldsymbol{v} \times \boldsymbol{B}, \tag{11.1}$$

where we have replaced classical acceleration with $\hbar\dot{\boldsymbol{k}}$. Our second expression relates electron velocity $\boldsymbol{v}$ and energy E, and reads

$$\boldsymbol{v} = \frac{1}{\hbar}\frac{\partial E}{\partial \boldsymbol{k}}. \tag{11.2}$$

- Using the summation with α as a dummy index, we begin our analysis by substituting E into Equation 11.2 to get

$$\begin{aligned}
v_\alpha &= \frac{1}{\hbar}\frac{\partial E}{\partial k_\alpha} = \frac{1}{\hbar}\frac{\hbar^2}{2}\frac{\partial}{\partial k_\alpha}\left(k_i\left(\mathsf{m}^*\right)^{-1}_{ij}k_j\right) = \frac{\hbar}{2}\left[\delta_{i\alpha}\left(\mathsf{m}^*\right)^{-1}_{ij}k_j + k_i\left(\mathsf{m}^*\right)^{-1}_{ij}\delta_{j\alpha}\right] \\
&= \frac{\hbar}{2}\left[(\mathsf{m}^*)^{-1}_{\alpha j}k_j + k_i(\mathsf{m}^*)^{-1}_{i\alpha}\right] \\
&= \frac{\hbar}{2}\left[(\mathsf{m}^*)^{-1}_{\alpha j}k_j + k_i(\mathsf{m}^*)^{-1}_{\alpha i}\right],
\end{aligned}$$

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

$$\boldsymbol{v} = \hbar\left(\mathsf{m}^*\right)^{-1}\boldsymbol{k} \implies \mathsf{m}^*\boldsymbol{v} = \hbar\boldsymbol{k} \implies \hbar\dot{\boldsymbol{k}} = \mathsf{m}^*\dot{\boldsymbol{v}},$$

which we substitute into Equation 11.1 to get

$$\mathsf{m}^* \dot{\boldsymbol{v}} = q\boldsymbol{v} \times \boldsymbol{B}. \tag{11.3}$$

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 components v_α. We will solve the equations with the ansatz,

$$\boldsymbol{v} = \boldsymbol{v}_0 e^{-i\omega t} \implies \dot{\boldsymbol{v}} = -i\omega \boldsymbol{v} = -i\omega \boldsymbol{v}_0 e^{-i\omega t},$$

which we substitute into Equation 11.3 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, using $\boldsymbol{B} = (0, 0, B)$, 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 homogeneous equation has a nontrivial solution.

- We compute 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

$$\omega = \frac{|q|B\sqrt{m_{zz}}}{\sqrt{\det \mathsf{m}^*}} = |q|B\sqrt{\frac{m_{zz}}{\det \mathsf{m}^*}} \equiv \frac{|q|B}{m_{\mathrm{c}}^*},$$

where we have defined the cyclotron effective mass m_{c}^*.

$$m_{\mathrm{c}}^* = \sqrt{\frac{\det \mathsf{m}^*}{m_{zz}^*}} = \sqrt{\frac{\det \mathsf{m}^*}{\hat{\mathbf{e}}_{\boldsymbol{B}} \cdot \mathsf{m}^* \cdot \hat{\mathbf{e}}_{\boldsymbol{B}}}},$$

where we have introduced the coordinate-free vector expression $\boldsymbol{B} = \hat{\mathbf{e}}_{\boldsymbol{B}} B$. Note resemblance of $\omega = |q|B/m_{\mathrm{c}}^*$ to classical electron cyclotron frequency result

$$\omega_{\mathrm{c}} = \frac{|q|B}{m}$$

- A anisotropic dispersion relation (i.e. one requiring an effective mass tensor instead of a scalar effect mass) leads to common physical quantities being expressed in as effective-mass quantities in terms of the determinant of m^*. For example, an isotropic electron density of states reads

$$g(E) = \frac{\sqrt{2m}}{\pi^2 \hbar^3} \sqrt{E},$$

  but generalized to an anisotropic sceneraio near the bottom of a dispersion band this reads

$$g(E) = \frac{\sqrt{2m^*}}{\pi^2 \hbar^3} \sqrt{E - E_0}, \quad \text{where } \mathsf{m}^* \equiv \sqrt[3]{\det \mathsf{m}^*}.$$

  In other words, the classical, scalar mass is replaced by different functions of the effective mass tensor.

11.3   Chemical Potential in a Doped Semiconductor

Derive the temperature dependence of

(i) *the chemical potential and*

(ii) *the number density of conduction band electrons*

in a doped semiconductor.

- As a brief review from lecture, we generally consider two energy bands in semiconductors physics: 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* $E_\mathrm{g} = E_\mathrm{c} - E_\mathrm{v}$, which is just the energy difference between the top of the valence band and bottom of the conduction band.

- The density of electron states near the bottom of the conduction band is

$$g_\mathrm{c} = \frac{\sqrt{2m_\mathrm{c}^*}}{\pi^2 \hbar^3} \sqrt{E - E_\mathrm{c}}, \quad \text{where } m_\mathrm{c}^* \equiv \sqrt[3]{\det \mathsf{m}_\mathrm{c}^*},$$

  while the density of hole states near the top of the valence band is

$$g_\mathrm{v} = \frac{\sqrt{2m_\mathrm{v}^*}}{\pi^2 \hbar^3} \sqrt{E_\mathrm{v} - E}, \quad \text{where } m_\mathrm{v}^* \equiv \sqrt[3]{\det \mathsf{m}_\mathrm{v}^*}.$$

  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. In this exercise 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 $n_c = p_v = p_d = 0$. 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 $n_c = n_c(T)$, $p_v = p_v(T)$, $p_d = p_d(T)$, 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 $n_c(T)$ and $p_v(T)$.

- 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, which will in turn be used to find the semiconductor's Fermi function, from which we can find n_c and p_v and other temperature-dependent quantities. Our plan is thus to first find $\mu(T)$, then $n_c(T)$ and $p_v(T)$.

More Review from Lecture

- Concentration of electrons in conduction band is found from integrating over the conduction band

$$n_c = \int_{E_c}^{\infty} g_c(E) f(E) \, \mathrm{d}E. \tag{11.4}$$

  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-approximated by

$$n_c = N_c e^{-\beta(E_c - \mu)}, \quad \text{where } N_c = \frac{1}{4} \left(\frac{2m_c^* k_B T}{\pi \hbar^2} \right)^{3/2}. \tag{11.5}$$

  Note that n_c is the product of N_c (a weakly temperature-dependent quantity) and $e^{-\beta}$ (a very strongly temperature-dependent quantity.)

- Similarly, the exact expression for the number of holes in the valence band is

$$p_v = \int_{-\infty}^{E_v} g_v(E) \big[1 - f(E) \big] \, \mathrm{d}E, \tag{11.6}$$

  which is well approximated for a non-degenerate semiconductor by

$$p_v = P_v e^{-\beta(\mu - E_v)}, \quad \text{where } P_v = \frac{1}{4} \left(\frac{2m_v^* k_B T}{\pi \hbar^2} \right)^{3/2}. \tag{11.7}$$

  Important: as covered in lecture, deriving the expression for n_c in Equation 11.5 from exact integral expression in Equation 11.4 (and similarly deriving the expression for p_v in Equation 11.7 from exact integral expression in Equation 11.6) involves the approximation that $E_c - \mu$ and $\mu - E_v$, which is called the non-degenerate semiconductor approximation. In other words, the approximate expressions for n_c and p_v

implicitly assume the shifts of chemical potential from the edges of the band gap are much larger than the thermal energy $k_B T$.

In practice, the non-degenerate semiconductor 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, again quoting from lecture, we write the concentration of holes on donor levels as

$$p_d = \frac{N_d}{1 + 2e^{-\beta(E_d - \mu)}}.$$

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.

We ran out of time at this point; we continue the discussion of the fundamentals of semiconductor physics in the next exercises set.

12 Twelfth Exercise Set

12.1 Chemical Potential in a Doped Semiconductor (continued)

- We first review some of the fundamental relationships in semiconductor physics. First, conservation of charge requires

$$n_{\rm c} = p_{\rm v} + p_{\rm d}.$$

The density of conduction band electrons in a non-degenerate semiconductor is

$$n_{\rm c} = N_{\rm c} e^{-\beta(E_{\rm c}-\mu)},$$

where

$$N_{\rm c} = \frac{1}{4}\left(\frac{2m_{\rm c}^* k_B T}{\pi\hbar^2}\right)^{3/2}.$$

Simlarly, the density of valence band holes in a non-degenerate semiconductor is

$$p_{\rm v} = P_{\rm v} e^{-\beta(\mu-E_{\rm v})},$$

where

$$P_{\rm v} = \frac{1}{4}\left(\frac{2m_{\rm v}^* k_B T}{\pi\hbar^2}\right)^{3/2}.$$

The quantities $N_{\rm c}$ and $P_{\rm v}$ can often be approximated as temperature-independent constants. Finally, the concentration of holes in donor levels is given by

$$p_{\rm d} = \frac{N_{\rm d}}{1 + 2e^{-\beta(E_{\rm d}-\mu)}},$$

where $N_{\rm d}$ is the volume density of donor levels in the semiconductor.

12.1.1 Finding Chemical Potential

- We now return to the problem from the previous exercise set of finding the chemical potential $\mu(T)$ in a doped semiconductor, which we will find using the convservation of charge relation

$$n_{\rm c} = p_{\rm v} + p_{\rm d}.$$

In general (if were to substitute in the expressions for $n_{\rm c}$, $p_{\rm v}$, and $p_{\rm d}$) this procedure leads to a polynomial of third degree in μ. We will simplify the situation with an approximation: we will assume a low-enough temperature such that the excitation of electrons from the valence to conduction band is negligible, and so $p_{\rm v} \ll n_{\rm c}, p_{\rm d}$ and the conservation of charge relation $n_{\rm c} = p_{\rm v} + p_{\rm d}$ simplifies to $n_{\rm c} \approx p_{\rm d}$. (We will retrospectively check the validity of this approximation at the end of the exercise.)

- Substituting the expresions for $n_{\rm c}$ and $p_{\rm d}$ into $n_{\rm c} \approx p_{\rm d}$ produces the equality

$$N_{\rm c} e^{-\beta(E_{\rm c}-\mu)} = \frac{N_{\rm d}}{1 + 2e^{-\beta(E_{\rm d}-\mu)}}.$$

We then multiply through by the denominator and rearrange to get

$$N_{\rm c} e^{-\beta E_{\rm c}} e^{\beta\mu} + 2N_{\rm c} e^{-\beta(E_{\rm c}+E_{\rm d})} e^{2\beta\mu} - N_{\rm d} = 0.$$

We then interpret this equality as a quadratic polynomial in $e^{\beta\mu}$ and rearrange to get

$$e^{2\beta\mu} + \frac{1}{2}e^{\beta E_\mathrm{d}}e^{\beta\mu} - \frac{N_\mathrm{d}}{2N_\mathrm{c}}e^{\beta(E_\mathrm{c}+E_\mathrm{d})} = 0.$$

Using the quadratic formula, the solution is

$$
\begin{aligned}
e^{\beta\mu} &= -\frac{1}{4}e^{\beta E_\mathrm{d}} \pm \sqrt{\left(\frac{1}{4}e^{\beta E_\mathrm{d}}\right)^2 + \frac{N_\mathrm{d}}{2N_\mathrm{c}}e^{\beta(E_\mathrm{c}+E_\mathrm{d})}} \\
&= \frac{1}{4}e^{\beta E_\mathrm{d}}\left[-1 \pm \sqrt{1 + \frac{8N_\mathrm{d}}{N_\mathrm{c}}e^{\beta(E_\mathrm{d}-E_\mathrm{d})}}\right].
\end{aligned}
\tag{12.1}
$$

We then take a logarithm to find μ; only the positive solution is physical.

12.1.2   Limit Cases of Chemical Potential

Low-Temperature Limit

- We first consider the limit case

$$\frac{8N_\mathrm{d}}{N_\mathrm{c}}e^{\beta(E_\mathrm{d}-E_\mathrm{d})} \gg 1$$

Because $N_\mathrm{c} \propto T^{3/2}$ and $\beta \propto T^{-1}$, this limit case corresponds physically a low temperature regime. (Note that $E_\mathrm{c} - E_\mathrm{d} > 0$, so the exponent is positive.) In any case, in this low-temperature limit the expression for $e^{\beta\mu}$ in Equation 12.1 simplifies to

$$e^{\beta\mu} \approx \frac{1}{4}e^{\beta E_\mathrm{d}}\sqrt{\frac{8N_\mathrm{d}}{N_\mathrm{c}}}e^{\beta\frac{1}{2}(E_\mathrm{c}-E_\mathrm{d})} = \sqrt{\frac{N_\mathrm{d}}{2N_\mathrm{c}}}e^{\beta\frac{E_\mathrm{c}+E_\mathrm{d}}{2}}.$$

We then take the equation's logarithm and divide through by β to solve for μ, giving

$$\mu = \frac{1}{\beta}\left(\ln\sqrt{\frac{N_\mathrm{d}}{2N_\mathrm{c}}} + \beta\frac{E_\mathrm{c}+E_\mathrm{d}}{2}\right) = \frac{E_\mathrm{c}+E_\mathrm{d}}{2} + k_BT\ln\sqrt{\frac{N_\mathrm{d}}{2N_\mathrm{c}}}.$$

As the temperature approaches zero, the chemical potential simplifies further to

$$\mu \to \frac{E_\mathrm{c}+E_\mathrm{d}}{2},$$

which lies in between the conduction and donor energy bands.

High-Temperature Limit

- We now consider the limit case

$$\frac{8N_\mathrm{d}}{N_\mathrm{c}}e^{\beta(E_\mathrm{d}-E_\mathrm{d})} \ll 1,$$

which corresponds physically to the high-temperature limit of chemical potential. We first recall the more general expression

$$e^{\beta\mu} = \frac{1}{4}e^{\beta E_\mathrm{d}}\left[-1 \pm \sqrt{1 + \frac{8N_\mathrm{d}}{N_\mathrm{c}}e^{\beta(E_\mathrm{d}-E_\mathrm{d})}}\right],$$

Which we then Taylor expand in the high-temperature limit to get

$$e^{\beta\mu} = \frac{1}{4}e^{\beta E_{\mathrm{d}}} \cdot \left(\frac{1}{2} \frac{8 N_{\mathrm{d}}}{N_{\mathrm{c}}} e^{\beta(E_{\mathrm{c}} - E_{\mathrm{d}})} \right) = \frac{N_{\mathrm{d}}}{N_{\mathrm{c}}} e^{\beta E_{\mathrm{c}}}.$$

We then solve the resulting equality for μ, which compes out to

$$\mu = E_{\mathrm{c}} + k_B T \ln \frac{N_{\mathrm{d}}}{N_{\mathrm{c}}}.$$

If we recall $N_{\mathrm{c}} \propto T^{3/2}$ and apply the logarithm property $\ln T^{-3/2} = -(3/2)\ln T$ (and ignore constant terms in the logarithm), we see the high-temperature chemical potential scales as

$$\mu \approx E_{\mathrm{c}} - \frac{3}{2} k_B T \ln T.$$

In other words, 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.

Remarks

- To use the non-degenerate semiconductor approximation and the resulting expressions for n_{c} and N_C, the chemical potential cannot be too close to edge of band gap.

- Another problem: although the high-temperature analysis predicted that $\mu(T)$ increases with temperature, on physical grounds $\mu(T)$ cannot fall infinitely with temperature. Once μ approaches the top of the valence band, significant numbers of electrons will be thermally excited from the valence band to conduction band, p_{v} will grow comparable to n_{c} and p_{d}, and the approximation $p_{\mathrm{v}} \ll n_{\mathrm{c}}, p_{\mathrm{v}} \implies n_{\mathrm{c}} \approx p_{\mathrm{d}}$ used in the above analysis is no longer valid.

  At high enough temperatures for valence electrons to be easily excited into the conduction band, valence band holes overwhelm dopant electrons, leading again to a simpler case $n_{\mathrm{c}} \approx p_{\mathrm{v}}$.

12.1.3 Electron Concentration in Conduction Band

- Finally, we aim to derive expressions for conduction band electron concentration as a function of temperature in the high- and low-temperature limits analyzed above.

  We begin by writing conduction band electron concentration in the form

  $$n_{\mathrm{c}} = N_{\mathrm{c}} e^{-\beta(E_{\mathrm{c}} - \mu)} = N_{\mathrm{c}} e^{-\beta E_{\mathrm{c}}} e^{\beta\mu}.$$

  To find the low-temperature limit of n_{c}, we substitute the low-temperature limit for $e^{\beta\mu}$, which for review reads

  $$e^{\beta\mu} = \sqrt{\frac{N_{\mathrm{d}}}{2 N_{\mathrm{c}}}} e^{\beta \frac{E_{\mathrm{c}} + E_{\mathrm{d}}}{2}},$$

  into the expression for n_{c} (and recall $N_{\mathrm{c}} \propto T^{3/2}$) to get

  $$n_{\mathrm{c}}(T) = N_{\mathrm{c}} e^{-\beta E_{\mathrm{c}}} \sqrt{\frac{N_{\mathrm{d}}}{2 N_{\mathrm{c}}}} e^{\beta \frac{E_{\mathrm{c}} + E_{\mathrm{d}}}{2}} = \sqrt{\frac{N_{\mathrm{d}} N_{\mathrm{c}}}{2}} e^{-\beta \frac{E_{\mathrm{c}} - E_{\mathrm{d}}}{2}} \propto T^{3/4} e^{-\frac{E_{\mathrm{c}} - E_{\mathrm{d}}}{2 k_B T}}.$$

  The electron concentration is $n_{\mathrm{c}} = 0$ at $T = 0$, then increases with T.

- To find the high limit of n_c, we substitute the high limit for $e^{\beta\mu}$, which for review reads

$$e^{\beta\mu} = \frac{N_d}{N_c}e^{\beta E_c},$$

into the expression for n_c to get

$$n_c = N_c e^{-\beta(E_c - \mu)} = N_c e^{-\beta E_c} \cdot \frac{N_d}{N_c}e^{\beta E_c} = N_d.$$

In the high-temperature limit (of the regime $n_c \approx p_d$), electron concentration $n_c(T)$ is thus constant. Physical interpretation: the high-temperature limit of the regime $n_c \approx p_d$ is large enough that all donor electrons are excited into the conduction band, but the regime $n_c \approx p_d$ in general is low enough that no valence band electrons are excited into the conduction band. In other words, the availablity of donor-level electrons is saturated, but valence band electrons are still thermally inert, so n_c is constant.

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 frequency-wave vector dispersion relation $\omega(k)$ describing the lattice oscillations.
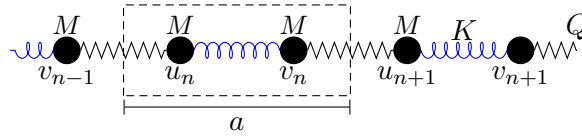

Figure 5: A model of the one-dimensional lattice used in Exercise 12.2. All atoms have mass M; blue, coiled springs have spring constant K while black, zigzag springs have spring constant Q. The unit cell spans two atoms and holds one of each type of spring.

- Figure 5 shows the model of the lattice used in this exercise; the dotted box denotes a unit cell. Let u_n denote the displacement from equilibrium of the n-th atom with a Q spring on the left and a K spring on the right; let v_n denote the displacement from equilibrium of the n-th atom with a K spring on the left and a Q spring on the right, and let the positive x axis point in the direction of increasing n. In this notation, Newton's law for the atom with displacement u_n reads

$$M\ddot{u}_n = K(v_n - u_n) - Q(u_n - v_{n-1}). \tag{12.2}$$

Note that if $v_n > u_n$, the term $K(v_n - u_n)$ contributes a force to the right on the chosen u_n 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 u_n atom via the Q spring. Analogously, Newton's law for the atom with displacement v_n reads

$$M\ddot{v}_n = Q(u_{n+1} - v_n) - K(v_n - u_n). \tag{12.3}$$

- Currently, Equations 12.2 and 12.3 are a coupled system of $2N$ equations where N is the number of lattice sites in the lattice. Such a large system is not practically solvable, but it is straightforward to decouple the equations by leveraging 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 12.2 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

$$-\omega^2 M u_0 = K(v_0 - u_0) - Q(u_0 - v_0 e^{-ika}).$$

- Analogously, we substitute the ansatzes into Equation 12.3 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

$$-\omega^2 M v_0 = Q(u_0 e^{ika} - v_0) - K(v_0 - v_0). \tag{12.4}$$

In matrix form, Equations 12.2 and 12.2 can be written as the 2×2 matrix equation

$$\begin{pmatrix} K + Q - \omega^2 M & -K - Q e^{-ika} \\ -K - Q e^{ika} & K + Q - \omega^2 M \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}$$

for the oscillation amplitudes u_0 and v_0. We require the matrix's determinant equal zero for a non-trivial solution, which produces

$$0 \equiv (K + Q - \omega^2 M)^2 - \left| K + Q e^{ika} \right|^2.$$

We then rearrange and isolate the oscillation frequency ω^2 to get

$$\omega^2 M = K + Q \pm \left| K + Q e^{ika} \right|.$$

We solve for ω (skipping a few steps of basic algebra) to get

$$\omega^2 = \frac{K+Q}{M} \pm \frac{1}{M} \sqrt{K^2 + Q^2 + \underbrace{2KQ \cos ka}_{2KQ + 2KQ(-1+\cos ka)}},$$

then use the identity $-1 + \cos ka = -2 \sin^2 \frac{ka}{2}$ to get the complete square

$$\omega^2 = \frac{K+Q}{M} \pm \frac{1}{M} \sqrt{(K+Q)^2 - 4KQ \sin^2 \frac{ka}{2}}.$$

Finally, we factor out $(K+Q)/M$ to get the final result

$$\omega^2 = \frac{K+Q}{M} \left[1 \pm \sqrt{1 - \frac{4KQ}{(K+Q)^2} \sin^2 \frac{ka}{2}} \right].$$

12.2.1   Dispersion Relation Eigenfrequencies

- We first graphed the dispersion relation $\omega(k)$; as for electron states, to avoid counting the same state multiple times, we restrict ourselves to the first Brillioun zone, which spans $|k| < \pi/a$.

- We first consider $\omega(k)$ at the center of first Brillioun zone, i.e at $k = 0$. We begin with the equation

$$\omega^2 M = K + Q \pm \left| K + Q e^{ika} \right|,$$

which we evaluate at $k = 0$ to get two possible solutions for ω^2:

$$\omega^2 = \frac{K + Q}{M} \pm \frac{|K + Q|}{M} \implies \omega^2 \in \left\{ \frac{2(K + Q)}{M}, 0 \right\}.$$

- We now consider $\omega(k)$ at $k = \frac{\pi}{a}$ (i.e. at the edge of the first Brillioun zone). We again begin with the equation

$$\omega^2 M = K + Q \pm \left| K + Q e^{ika} \right|,$$

and substitute in $k = \pi/a$ (recall $e^{i\pi} = -1$) to get

$$\omega^2 = \frac{K + Q}{M} \pm \frac{|K - Q|}{M}.$$

The possible solutions for ω^2 in this case are

$$\omega^2 = \frac{K + Q}{M} \pm \frac{|K - Q|}{M} \implies \omega^2 \in \left\{ \frac{2K}{M}, \frac{2Q}{M} \right\}.$$

Dispersion Near Center of First Brillioun Zone

- We now consider $\omega(k)$ in a neighborhood of first Brillioun zone's center where $|k| \ll \pi/a$. We begin with the general result

$$\omega^2 = \frac{K + Q}{M} \left[1 \pm \sqrt{1 - \frac{4KQ}{(K + Q)^2} \sin^2 \frac{ka}{2}} \right]$$

and expand the sine in the limit $|k| \ll \pi/a$ to get

$$\omega^2 \approx \frac{K + Q}{M} \left[1 \pm \sqrt{1 - \frac{4KQ}{(K + Q)^2} \frac{(ka)^2}{4}} \right].$$

We then expand the square root to get

$$\omega^2 \approx \frac{K + Q}{M} \left[1 \pm \left(1 - \frac{KQ}{2(K + Q)^2} (ka)^2 \right) \right].$$

We consider the positive branch, which reads

$$\omega^2 = \frac{2(K + Q)}{M} - \mathcal{O}\big((ka)^2\big).$$

Meanwhile, the negative branch reads

$$\omega^2 = \frac{K+Q}{M}\frac{KQ}{2(K+Q)^2}(ka)^2 = \frac{KQ}{2(K+Q)M}(ka)^2$$

and leads to the oscillation frequency

$$\omega = \sqrt{\frac{KQa^2}{2(K+Q)}M}|k| \equiv c|k|,$$

where we have surrounded k with absolute value signs because k can be either positive or negative.

The positive branch, in which $\omega(k)$ is a downward-pointing parabola in neighborhood of $k = 0$, is called the dispersion relation's optical branch. The negative branch, with absolute value dependence of $\omega(k)$ near $k = 0$, is called the dispersion's acoustic branch. The optical branch only occurs in lattices with multiple atoms per unit cell, while the acoustic branch occurs for all lattices.

12.2.2   Dispersion Relation Eigenmodes

- We aim to find the oscillation amplitudes u_0 and v_0 (and deduce the associated oscillation modes) near the center of first Brillioun zone in both the acoustic and optical branches near $k = 0$, and also at the edge of the first Brillioun zone.

  Our starting point will be the 2×2 matrix equation from Equation 12.2, which for review reads
  $$\begin{pmatrix} K + Q - \omega^2 M & -K - Qe^{ika} \\ -K - Qe^{ika} & K + Q - \omega^2 M \end{pmatrix}\begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}.$$

Acoustic Branch at $k = 0$

- We begin with the $\omega^2 = 0$ solution in the acoustic branch at $k = 0$, the center of the first Brillioun zone. This case results in

  $$\begin{pmatrix} K + Q & -(K + Q) \\ - & - \end{pmatrix}\begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0},$$

  which leads to $v_0 = u_0$. We conclude $v_n = u_n = u_0$. The solution corresponds to translation of the entire crystal (a translation solution in this case should make sense—$\omega^2 = 0$ means no oscillation).

Optical Branch at $k = 0$

- We now consider the $\omega^2 = \frac{2(K+Q)}{M}$ solution in the optical branch at $k = 0$, which results in
  $$\begin{pmatrix} -(K + Q) & -(K + Q) \\ - & - \end{pmatrix}\begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}$$

  This gives $v_0 = -u_0$, which corresponds physically to the two atoms in each unit cell oscillating half a period out of phase.

Acoustic Branch at $k = \pi/a$

- Finally, we consider the $\omega^2 = \frac{2Q}{M}$ solution in the acoustic branch at the Brillioun zone edge $k = \pi/a$, which results in

$$\begin{pmatrix} K + Q - M\frac{2Q}{M} & -K - Qe^{-i\pi} \\ - & - \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \begin{pmatrix} K - Q & -(K - Q) \\ - & - \end{pmatrix} \begin{pmatrix} u_0 \\ v_0 \end{pmatrix} = \mathbf{0}.$$

We conclude $v_0 = u_0$ in a given unit cell, meaning that both atoms in a given unit cell oscillate in phase. Because this solution occurs on the edge of the first Brillioun zone where $k = \pi/a$, u_n and v_n come out to

$$u_n = u_0 e^{ikna} = (-1)^n u_0$$
$$v_n = v_0 e^{ikna} = (-1)^n v_0 = (-1)^n u_0.$$

The general lattice motion involves both atoms in a given unit cell oscillating in phase, but the direction of oscillation alternating in phase by π between alternating unit cells.

13 Thirteenth Exercise Set

13.1 Lattice Oscillations in a Triangular Lattice with Taut Springs

Consider a two-dimensional Bravais lattice with atoms of mass M, in which the interaction between atoms is modelled by a spring of spring constant K. Assume the springs are taut when the atoms are at rest, i.e. that the lattice constant a is larger than the springs' equilibrium length. Find the frequency-wave vector dispersion relation $\omega(\boldsymbol{k})$ for lattice oscillation in which the atomic displacements are transverse to the plane of the crystal lattice.
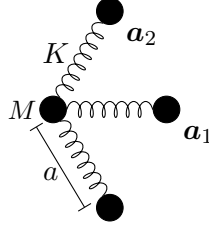

Figure 6: A model of the two-dimensional triangular lattice used in Exercise 13.1. All atoms have mass M and all springs have spring constant K; some springs are omitted to avoid cluttering the picture.
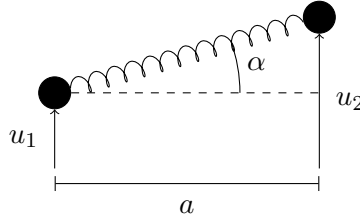

Figure 7: Visualization of transverse oscillations in a 2D lattice; the displacements u_1 and u_2 are perpendicular to the plane of the lattice.

- Consider two neighboring atoms with transverse displacements u_1 and u_2 as shown in Figure 7, and let $\boldsymbol{F}$ denote the force between the two atoms. We first decompose $\boldsymbol{F}$ into $F_\parallel = F \cos\alpha$ and $F_\perp = F \sin\alpha$, where α is shown in Figure 7.

  The force's magnitude is $F = K\Delta l$ where Δl is change in spring length, given by

  $$\Delta l = \sqrt{a^2 + (u_2 - u_1)^2} - a_0,$$

  where we have subtracted off the spring equilibrium distance a_0 to account for the fact that the springs are taut. We then expand the Taylor expand the expression for Δl in the limit $|u_2 - u_1| \ll a$ to get

  $$\Delta l \approx a - a_0 + \frac{(u_2 - u_1)^2}{2a}.$$

  Note that the length change is quadratic in the displacement difference $u_2 - u_1$. We then make the additional approximations

  $$\cos\alpha = \frac{a}{\sqrt{a^2 + (u_2 - u_1)^2}} \approx 1 + \mathcal{O}\big((u_2 - u_1)^2\big)$$

  $$\sin\alpha = \frac{u_2 - u_1}{\sqrt{a^2 + (u_2 - u_1)^2}} \approx \frac{u_2 - u_1}{a} + \mathcal{O}\big((u_2 - u_1)^3\big),$$

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in terms of which the force components become

$$F_\| = F \cos \alpha = K(a - a_0) \qquad \text{and} \qquad F_\perp = F \sin \alpha = K(a - a_0)\frac{u_2 - u_1}{a}.$$

Note that the forces are linear in the displacement $u_2 - u_1$, in agreement with harmonic theory (e.g. Hooke's law).

- For any given atom in the triangular lattice, there is on average no net force on the atom in the plane of the lattice, because the forces from neighboring atoms acting in different directions cancel out—each atom thus experiences only a force component $F_\perp$ perpendicular to the plane of the lattice. This component is

$$F_\perp = \widetilde{K}(u_2 - u_1), \quad \text{where } \widetilde{K} = K\frac{a - a_0}{a}$$

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 harmonic theory.

13.1.1   Computing Dispersion Relation

- Considering only the forces perpendicular to the plane of the lattice resulting from interactions with nearest neighbords, the equation of motion for a general atom in the triangular lattice is

$$M\ddot{u}_{\boldsymbol{R}} = \sum_{\boldsymbol{R}' \in \{\text{nn}\}} \widetilde{K}\left(u_{\boldsymbol{R}'} - u_{\boldsymbol{R}}\right). \tag{13.1}$$

From this point forward the analysis is similar to previous exercise set. Motivated by the lattice's invariance under translations by multiples of $\boldsymbol{R}$, we use the ansatz

$$u_{\boldsymbol{R}} = u_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega\tau)},$$

which we substitute into Equation 13.1 to get

$$-M\omega^2 u_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega t)} = \sum_{\boldsymbol{R}' \in \{\text{nn}\}} \widetilde{K}u_0\left(e^{i(\boldsymbol{k}\cdot\boldsymbol{R}' - \omega t)} - e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega t)}\right).$$

We then cancel plane wave terms and the constant amplitude u_0, leaving

$$-M\omega^2 = \sum_{\boldsymbol{R}' \in \{\text{nn}\}} \widetilde{K}\left(e^{i\boldsymbol{k}\cdot(\boldsymbol{R} - \boldsymbol{R}')} - 1\right).$$

We then modify the summation indices slightly—instead of summing over all nearest neighbors to the position $\boldsymbol{R}$ and having $(\boldsymbol{R} - \boldsymbol{R}')$ in the exponent, which make the shift $\boldsymbol{R} \to \boldsymbol{0}$ and sum over all nearest neighbors to the origin, giving

$$-M\omega^2 = \sum_{\boldsymbol{R}' \in \{\text{nno}\}} \widetilde{K}\left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}'} - 1\right).$$

We then rename $\boldsymbol{R}' \to \boldsymbol{R}$, use the fact that both $\boldsymbol{R}$ and $\boldsymbol{R}'$ are Bravais lattice vectors to break up the sum into two exponential terms (in anticipation of switching from

complex exponentials to cosines), and divide by two to account for the two sum terms to get

$$-M\omega^2 = \frac{\widetilde{K}}{2}\left[\sum_{\boldsymbol{R}\in\{\mathrm{nno}\}}\left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}}-1\right) + \sum_{\boldsymbol{R}\in\{\mathrm{nno}\}}\left(e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}-1\right)\right]$$

$$= \frac{\widetilde{K}}{2}\sum_{\boldsymbol{R}\in\{\mathrm{nno}\}}\left(2\cos(\boldsymbol{k}\cdot\boldsymbol{R})-2\right)$$

$$= -2\widetilde{K}\sum_{\boldsymbol{R}\in\{\mathrm{nno}\}}\sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}.$$

We then solve for ω^2, which comes out to

$$\omega^2 = \frac{2\widetilde{K}}{M}\sum_{\boldsymbol{R}\in\{\mathrm{nno}\}}\sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}. \tag{13.2}$$

Note that this expression would hold for an arbitrary 2D Bravais lattice in which both $\boldsymbol{R}$ and $-\boldsymbol{R}$ are Bravais lattice vectors.

- We now evaluate the expression in Equation 13.2 for the specific case of a triangular lattice, in which (see Figure 6 at the start of the exercise) the primitive vectors are

$$\boldsymbol{a}_1 = a(1,0) \qquad \boldsymbol{a}_2 = \frac{a}{2}(1,\sqrt{3}) \qquad \boldsymbol{a}_1 - \boldsymbol{a}_2 = \frac{a}{2}(1,-\sqrt{3}). \tag{13.3}$$
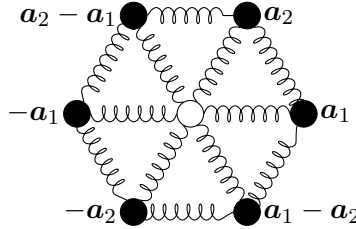

Figure 8: The nearest neighbors to the origin (center, in white) of the 2D triangular lattice used in Exercise 13.1.

Using Figure 8 and the primitive vectors in Equation 13.3 for reference, we then evaluate Equation 13.2 for all of the origin's nearest neighbors to get

$$\omega^2 = \frac{2\widetilde{K}}{M}\cdot 2\left[\sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{a}_1}{2} + \sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{a}_2}{2} + \sin^2\frac{\boldsymbol{k}\cdot(\boldsymbol{a}_1-\boldsymbol{a}_2)}{2}\right]. \tag{13.4}$$

(Note that the squared sine terms are identical for positive and negative vectors, hence the factor of two and only three terms (instead of six) in Equation 13.4.)

13.1.2   Analyzing Dispersion Near Brillioun Zone Center

- We will analyze the dispersion relation near the center of the lattice's first Brillioun zone (recall a triangular lattice's first Brillioun zone is again a triangular lattice in

reciprocal space), where an appropriate wave vector ansatz is $|\boldsymbol{k}| \ll \pi/a$. (Physically, $|\boldsymbol{k}| \ll \pi/a$ corresponds to large wavelength relative to the lattice constant a.)

We substitute $|\boldsymbol{k}| \ll \pi/a$ into Equation 13.4 and Taylor expand the sine terms to get

$$\omega^2 = \frac{4\widetilde{K}}{M}\left[\left(\frac{\boldsymbol{k}\cdot\boldsymbol{a}_1}{2}\right)^2 + \left(\frac{\boldsymbol{k}\cdot\boldsymbol{a}_2}{2}\right)^2 + \left(\frac{\boldsymbol{k}\cdot(\boldsymbol{a}_1-\boldsymbol{a}_2)}{2}\right)^2\right].$$

Next, we substitute in the primitive vectors from Equation 13.3 and evaluate the dot products to get

$$\frac{\widetilde{K}}{M}\left[k_x^2 a^2 + \left(\frac{k_x}{2}+\frac{k_y\sqrt{3}}{2}\right)^2 a^2 + \left(\frac{k_x}{2}-\frac{k_y\sqrt{3}}{2}\right) a^2\right]$$

We then multiply out and cancel mixed terms, leaving

$$\omega^2 = \frac{\widetilde{K}a^2}{M}\left(k_x^2 + \frac{1}{4}k_x^2 + \frac{3}{4}k_y^2 + \frac{k_x^2}{4} + \frac{3k_y^2}{4}\right)$$

$$= \frac{3}{2}\frac{\widetilde{K}a^2}{M}(k_x^2 + k_y^2)$$

$$= \frac{3}{2}\frac{\widetilde{K}}{M}a^2 k^2.$$

Finally, we solve for ω, which comes out to

$$\omega = \sqrt{\frac{3}{2}\frac{\widetilde{K}}{M}}\,ak \equiv ck, \quad \text{where } c = \sqrt{\frac{3}{2}\frac{\widetilde{K}}{M}}\,a. \tag{13.5}$$

This solution corresponds to an acoustic (and not an optical) branch—an acoustic-only solution is to be expected, since a triangular structure may be fully described by Bravais lattice with one atom per unit cell, i.e. without a basis.

We stress that $c \neq c(\phi)$ in Equation 13.5, 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 $k_x^2 + k_y^2 = k^2$. Without proof, an example with a ϕ-dependent dispersion is a 2D rectangular lattice with non-equal side lengths.

14 Fourteenth Exercise Set

14.1 Specific Heat of Lattice Oscillations in a Triangular Lattice

Compute the contribution of transverse lattice oscillations to the specific heat of the two-dimensional triangular lattice analyzed in the previous exercise set in both the low-temperature and high-temperature limits. Consider only oscillatoins perpendicular to the plane of the crystal lattice.

14.1.1 Low-Temperature Specific Heat

- We begin with definition of heat capacity

$$C = \frac{\mathrm{d}E}{\mathrm{d}t}.$$

Quoting from lecture, the internal energy of a harmonic lattice takes the general form

$$E = \sum_{s,\boldsymbol{k}} \hbar\omega_s(\boldsymbol{k}) \left(\frac{1}{e^{\beta\hbar\omega_s(\boldsymbol{k})} - 1} + \frac{1}{2} \right),$$

where the index s runs over all of the dispersion relation's branches (e.g. acoustic and optical branches). Here we will consider only a simplified one-branch expression (without s) of the form

$$E = \sum_{\boldsymbol{k}} \hbar\omega(\boldsymbol{k}) \left(\frac{1}{e^{\beta\hbar\omega(\boldsymbol{k})} - 1} + \frac{1}{2} \right). \tag{14.1}$$

Because we are eventually interested in heat capacity, which is the derivative of E with respect to temperature, we will drop the constant, temperature-independent $1/2$ term (which will disappear later anyway after differentiating E with respect to T) to reduce clutter, and define

$$\widetilde{E} = \sum_{\boldsymbol{k}} \frac{\hbar\omega(\boldsymbol{k})}{e^{\beta\hbar\omega(\boldsymbol{k})} - 1}; \qquad C = \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{\mathrm{d}\widetilde{E}}{\mathrm{d}T}. \tag{14.2}$$

- At low temperature ($k_B T \ll \hbar\omega(\boldsymbol{k})$) only low-frequency phonon modes are excited. As a result the contribution to the lattice internal energy of both (i) acoustic modes far from $\boldsymbol{k} = \boldsymbol{0}$ and (ii) optical modes in general is negligible. More so, at low temperature we may approximate the acoustic branch near $\boldsymbol{k} = \boldsymbol{0}$ with a linear dispersion of the form

$$\omega(\boldsymbol{k}) = ck,$$

where c is the (assumed-to-be-constant) speed at which phonons propagate through the lattice (i.e. that speed of sound in the lattice). We then substitute $\omega(\boldsymbol{k}) = ck$ into Equation 14.2 to get

$$\widetilde{E} \approx \sum_{\boldsymbol{k}} \frac{\hbar ck}{e^{\beta\hbar ck} - 1}.$$

(Note that we may sum over all $\boldsymbol{k}$, even those for which the approximation of a linear dispersion does not apply, because the Bose-Einstein distribution will suppress large $|\boldsymbol{k}|$ modes at low temperatures anyway.)

We then approximate the sum with an integral over $\boldsymbol{k}$ to get

$$\widetilde{E} = \sum_{\boldsymbol{k}} \frac{\hbar c k}{e^{\beta \hbar c k} - 1} \approx \frac{S}{(2\pi)^2} \iint \frac{\hbar c k}{e^{\beta \hbar c k} - 1} \, \mathrm{d}^2 \boldsymbol{k},$$

where S is the area of the entire 2D lattice. Because the integrand depends only on magnitude k, we may switch to integration in polar coordinates to get

$$\widetilde{E} = \frac{S}{(2\pi)^2} \int_0^\infty \frac{\hbar c k}{e^{\beta \hbar c k} - 1} (2\pi k) \, \mathrm{d}k. \tag{14.3}$$

To evaluate the integral, we introduce the new variable $x \equiv \beta \hbar c k$, which leads to

$$\widetilde{E} = \frac{S}{2\pi} \frac{1}{\beta^3 (\hbar c)^2} \int_0^\infty \frac{x^2}{e^x - 1} \, \mathrm{d}x.$$

The integral comes out to $2 \cdot \zeta(3) \approx 2.4$, where $\zeta(x)$ is the Riemman-Zeta function, but for our purposes is enough to note that the integrand is of the order one. Approximating the integral with the numerical value 2.4, we have

$$\widetilde{E} \approx 2.4 \cdot \frac{S}{2\pi} \frac{1}{\beta^3 (\hbar c)^2} = 2.4 \cdot \frac{S}{2\pi} \frac{(k_B T)^3}{(\hbar c)^2}.$$

- The corresponding number-normalized lattice specific heat c_N is

$$c_N = \frac{1}{N} \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{1}{N} \frac{\mathrm{d}\widetilde{E}}{\mathrm{d}T} = 3 \cdot \frac{2.4}{2\pi} \frac{S}{N} \frac{k_B^3 T^2}{(\hbar c)^2}$$

We then recognize that S/N corresponds physically to the area of a lattice site, which for the triangular lattice in this problem is a rhombus with area $a^2 \frac{\sqrt{3}}{2}$. Using $S/N = a^2 \frac{\sqrt{3}}{2}$ gives

$$c_N = 3 \cdot \frac{2.4}{2\pi} \frac{a^2 \sqrt{3}}{2} \left(\frac{k_B T}{\hbar c} \right)^2 k_B.$$

From Equation 13.5 recall that the speed of sound in the triangular lattice near the Brillioun zone is

$$c^2 = \frac{3}{2} \frac{\widetilde{K}}{M} a^2 \equiv \frac{3}{2} \omega_0^2 a^2,$$

where we have defined $\omega_0^2 = \widetilde{K}/M$ write c. In terms of ω_0, the heat capacity c_N is

$$c_N = 3 \frac{2.4}{2\pi} \frac{\sqrt{3}}{2} \frac{2}{3} \left(\frac{k_B T}{\hbar \omega_0} \right)^2 k_B$$

$$= 2.4 \frac{\sqrt{3}}{2\pi} \left(\frac{k_B T}{\hbar \omega_0} \right)^2 k_B.$$

The important lesson here is the low-temperature result $c_N \propto T^2$ and not $c_N \propto T^3$ as in low-temperature limit in a 3D harmonic crystal. (The behavior $c_N \propto T^2$ results from integrating over the 2D differential $\mathrm{d}^2 k$ in Equation 14.3 and not the 3D differential $\mathrm{d}^3 k$, which leads to power of T one lower than in three dimensions.)

14.1.2 High-Temperature Specific Heat

- We begin with the lattice energy $\widetilde{E}$ from Equation 14.2, which for review reads

$$\widetilde{E} = \sum_{\boldsymbol{k}} \frac{\hbar\omega(\boldsymbol{k})}{e^{\beta\hbar\omega(\boldsymbol{k})} - 1}.$$

The high-temperature limit corresponds to the regime $\beta\hbar\omega(\boldsymbol{k}) \ll 1$, in which case

$$e^{\beta\hbar\omega(\boldsymbol{k})} \approx 1 + \beta\hbar\omega(\boldsymbol{k})$$

and the lattice energy $\widetilde{E}$ simplifies to

$$E = \sum_{\boldsymbol{k}} \frac{\hbar\omega(\boldsymbol{k})}{e^{\beta\hbar\omega(\boldsymbol{k})} - 1} \approx \sum_{\boldsymbol{k}} \frac{\hbar\omega(\boldsymbol{k})}{1 + \beta\hbar\omega(\boldsymbol{k}) - 1} = \sum_{\boldsymbol{k}} \frac{1}{\beta} = Nk_BT,$$

where N is the number of lattice sites in the crystal. (Recall from lecture that a lattice accommodates exactly as many wave vectors as it contains lattice sites.)

The lattice's lattice site number-normalized specific heat capacity is then

$$c_N = \frac{1}{N}\frac{\mathrm{d}E}{\mathrm{d}T} = k_B;$$

the result $c_n = k_B$ is a manifestation of the equipartition principle. That the equipartition principle appears in the high-temperature (and not the low-temperature) limit should make sense—the equipartition principle is a classical principle, and quantum effects are negligible at hight temperatures, when the lattice's quantized energy states grow so close together that they are effectively continuous.

14.2 Lattice Oscillations in the Lagrangian Formalism

Consider a generic (one-, two-, or three-dimensional) crystal structure fully described by a Bravais lattice with one atom of mass M per unit cell, in which the interaction between neighboring atoms is modelled by a relaxed spring of spring constant K. Find the frequency-wave vector dispersion relation $\omega(\boldsymbol{k})$ for lattice oscillation in the crystal.

- *Note*: although we will eventually apply the results of this exercise to a 2D triangular lattice (In Exercise 15.1 of the next exercise set), the Lagrangian formalism developed in this exercise is quite general, and could apply to any lattice with one atom per unit cell. (In other words, the previous exercises' restrictions to interactions modelled by taut springs and oscillations perpendicular to the plane of a 2D lattice are no longer required.)

- Our first step in this exercise involves constructing the lattice's Lagrangian function

$$L = T - V,$$

where T and V are the lattice's kinetic and potential energy, respectively. We will then find the lattice's equation of motion from the Lagrange-Euler equations

$$\frac{\partial L}{\partial \boldsymbol{u_R}} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{\boldsymbol{u}}_{\boldsymbol{R}}} = \boldsymbol{0},$$

where $\boldsymbol{u_R}$ denotes the (vector) displacement from equilibrium of the atom at position $\boldsymbol{R}$ in the Bravais lattice describing the crystal. The expression for the lattice's kinetic energy T is relatively straightforward and given by

$$T = \sum_{\boldsymbol{R}} \frac{M}{2}(\dot{\boldsymbol{u}}_{\boldsymbol{R}})^2;$$

this is just the sum of the individual atoms' kinetic energies. Computing a useful expression for the lattice's potential energy is more complicated. We begin with the general expression

$$V = \frac{1}{2} \sum_{\boldsymbol{R};\boldsymbol{R}' \in \{\text{nn}(\boldsymbol{R})\}} \frac{1}{2} K \Delta \ell^2$$

where the sum over $\boldsymbol{R}$ runs over all lattice sites in the crystal lattice and the sum over $\boldsymbol{R}'$ runs over all nearest neighbors of each $\boldsymbol{R}$ and $\Delta \ell$ is the distance a spring is stretched from its equilibrium position. The construction of the sum in the expression for V counts each atom in the lattice twice, hence the use of the factor of $1/2$ so as to only count the contribution of an atom once to the value of V.

Constructing a useful expression for V mostly comes down to computing a simple form of the spring displacement $\Delta \ell$. The general form of $\Delta \ell$ is

$$\Delta \ell = \left| \boldsymbol{R}' + \boldsymbol{u}_{\boldsymbol{R}'} - (\boldsymbol{R} + \boldsymbol{u}_{\boldsymbol{R}}) \right| - \left| \boldsymbol{R}' - \boldsymbol{R} \right|;$$

the quantity $\left| \boldsymbol{R}' + \boldsymbol{u}_{\boldsymbol{R}'} - (\boldsymbol{R} + \boldsymbol{u}_{\boldsymbol{R}}) \right|$ is the total length of a stretched spring and $\left| \boldsymbol{R}' - \boldsymbol{R} \right|$ is the length of a relaxed spring; the difference of these quantities gives the distance the spring is stretched from equilibrium. Continuing, we express $\Delta \ell$ as

$$\Delta \ell = \sqrt{(\boldsymbol{R}' - \boldsymbol{R} + \boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}})^2} - \left| \boldsymbol{R}' - \boldsymbol{R} \right|$$
$$\approx \sqrt{(\boldsymbol{R}' - \boldsymbol{R})^2 + 2(\boldsymbol{R}' - \boldsymbol{R}) \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}})} - \left| \boldsymbol{R}' - \boldsymbol{R} \right|,$$

where approximation the last line ignores the quadratic $\mathcal{O}(|\boldsymbol{u}|^2)$ terms, which is valid under the assumption that the displacements $|\boldsymbol{u}|$ are small relative to the spacing between atoms. We then factor out the quantity $|\boldsymbol{R}' - \boldsymbol{R}|$ to get

$$\Delta \ell = \left| \boldsymbol{R}' - \boldsymbol{R} \right| \left[\sqrt{1 + 2\frac{(\boldsymbol{R}' - \boldsymbol{R}) \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}})}{|\boldsymbol{R}' - \boldsymbol{R}|^2}} - 1 \right].$$

We then Taylor expand the square root in the limit $2\frac{(\boldsymbol{R}' - \boldsymbol{R}) \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}})}{|\boldsymbol{R}' - \boldsymbol{R}|^2} \ll 1$ to get

$$\Delta \ell \approx \left| \boldsymbol{R}' - \boldsymbol{R} \right| \left[1 + \frac{\boldsymbol{R}' - \boldsymbol{R}}{|\boldsymbol{R}' - \boldsymbol{R}|^2} \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}}) - 1 \right]$$
$$= \frac{\boldsymbol{R}' - \boldsymbol{R}}{|\boldsymbol{R}' - \boldsymbol{R}|} \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}})$$
$$\equiv \hat{\mathbf{e}}_{\boldsymbol{R}' - \boldsymbol{R}} \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}}), \tag{14.4}$$

where in the last line we have defined $\hat{\mathbf{e}}_{\boldsymbol{R}' - \boldsymbol{R}}$ as the dimensionless unit vector in the direction pointing from $\boldsymbol{R}$ to $\boldsymbol{R}'$.

We then substitute the expression for $\Delta \ell$ in Equation 14.4 into the lattice potential energy to get

$$V = \frac{1}{2} \sum_{\boldsymbol{R};\boldsymbol{R}' \in \{\text{nn}(\boldsymbol{R})\}} \frac{1}{2} K \left[\hat{\mathbf{e}}_{\boldsymbol{R}' - \boldsymbol{R}} \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}}) \right]^2.$$

The lattice's Lagrangian function is then

$$L = T - V = \sum_{\boldsymbol{R}} \frac{M}{2} |\dot{\boldsymbol{u}}_{\boldsymbol{R}}|^2 - \frac{K}{4} \sum_{\boldsymbol{R};\boldsymbol{R}'\in\{\mathrm{nn}(\boldsymbol{R})\}} \left[\, \hat{\mathbf{e}}_{\boldsymbol{R}'-\boldsymbol{R}} \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}}) \right]^2. \qquad (14.5)$$

Equations of Motion

- For review, the Lagrange-Euler equations are

$$\frac{\partial L}{\partial \boldsymbol{u}_{\boldsymbol{R}}} - \frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial L}{\partial \dot{\boldsymbol{u}}_{\boldsymbol{R}}} = \boldsymbol{0};$$

for the position-independent kinetic energy and velocity-independent potential energy in Equation 14.5, the Lagrange-Euler equations simplify to

$$-\frac{\partial V}{\partial \boldsymbol{u}_{\boldsymbol{R}}} = \frac{\mathrm{d}}{\mathrm{d}t} \frac{\partial T}{\partial \dot{\boldsymbol{u}}_{\boldsymbol{R}}}.$$

We then substitute in the lattice potential energy V and kinetic energy T and differentiate to get the equation of motion for an atom at position $\boldsymbol{R}_0$:

$$M\ddot{\boldsymbol{u}}_{\boldsymbol{R}_0} = -\frac{K}{2} \sum_{\boldsymbol{R};\boldsymbol{R}'\in\{\mathrm{nn}(\boldsymbol{R})\}} \left[\, \hat{\mathbf{e}}_{\boldsymbol{R}'-\boldsymbol{R}} \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}}) \right](\delta_{\boldsymbol{R}'\boldsymbol{R}_0} - \delta_{\boldsymbol{R}\boldsymbol{R}_0})\, \hat{\mathbf{e}}_{\boldsymbol{R}'-\boldsymbol{R}}$$

Each of the individual Kronecker delta terms, i.e. $\delta_{\boldsymbol{R}'\boldsymbol{R}_0}$ and $\delta_{\boldsymbol{R}\boldsymbol{R}_0}$, will transform the double sum over $\boldsymbol{R}$ and $\boldsymbol{R}'$ into a single sum; the result is

$$M\ddot{\boldsymbol{u}}_{\boldsymbol{R}_0} = -\frac{K}{2} \left[\sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{R}_0)\}} (\hat{\mathbf{e}}_{\boldsymbol{R}_0-\boldsymbol{R}}) \cdot (\boldsymbol{u}_{\boldsymbol{R}_0} - \boldsymbol{u}_{\boldsymbol{R}})\, \hat{\mathbf{e}}_{\boldsymbol{R}_0-\boldsymbol{R}} \right.$$
$$\left. - \sum_{\boldsymbol{R}'\in\{\mathrm{nn}(\boldsymbol{R}_0)\}} (\hat{\mathbf{e}}_{\boldsymbol{R}'-\boldsymbol{R}_0}) \cdot (\boldsymbol{u}_{\boldsymbol{R}'} - \boldsymbol{u}_{\boldsymbol{R}_0})\, \hat{\mathbf{e}}_{\boldsymbol{R}'-\boldsymbol{R}_0} \right]$$

Because both $\boldsymbol{R}$ and $\boldsymbol{R}'$ are dummy indices, we can just as well rename $\boldsymbol{R}' \to \boldsymbol{R}$ in the second sum to get

$$M\ddot{\boldsymbol{u}}_{\boldsymbol{R}_0} = -\frac{K}{2} \left[\sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{R}_0)\}} (\hat{\mathbf{e}}_{\boldsymbol{R}_0-\boldsymbol{R}}) \cdot (\boldsymbol{u}_{\boldsymbol{R}_0} - \boldsymbol{u}_{\boldsymbol{R}})\, \hat{\mathbf{e}}_{\boldsymbol{R}_0-\boldsymbol{R}} \right.$$
$$\left. - \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{R}_0)\}} (\hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0}) \cdot (\boldsymbol{u}_{\boldsymbol{R}} - \boldsymbol{u}_{\boldsymbol{R}_0})\, \hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0} \right].$$

We then use the identity $\hat{\mathbf{e}}_{\boldsymbol{R}_0-\boldsymbol{R}} = -\,\hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0}$ to combine the two sums into one, giving

$$M\ddot{\boldsymbol{u}}_{\boldsymbol{R}_0} = +K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{R}_0)\}} (\hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0}) \cdot (\boldsymbol{u}_{\boldsymbol{R}} - \boldsymbol{u}_{\boldsymbol{R}_0})\, \hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0}. \qquad (14.6)$$

- Next, we introduce the ansatz

$$\boldsymbol{u}_{\boldsymbol{R}} = \boldsymbol{u}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{R}-\omega t)}$$

to model atomic displacements $\boldsymbol{u_R}$, which we substitute into Equation 14.6 and cancel like terms to get

$$-M\omega^2\boldsymbol{u}_0 = K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{R}_0)\}} \hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0} \cdot \boldsymbol{u}_0 \left(e^{i\boldsymbol{k}\cdot(\boldsymbol{R}-\boldsymbol{R}_0)} - 1\right) \hat{\mathbf{e}}_{\boldsymbol{R}-\boldsymbol{R}_0} \tag{14.7}$$

The above equation of motion describes motion of an arbitrary atom $\boldsymbol{R}_0$. To simplify notation, we will consider the motion of the atom at the origin (i.e. the atom with $\boldsymbol{R}_0 = \boldsymbol{0}$), for which Equation 14.7 reads

$$-M\omega^2\boldsymbol{u}_0 = K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{0})\}} (\hat{\mathbf{e}}_{\boldsymbol{R}} \cdot \boldsymbol{u}_0)\, \hat{\mathbf{e}}_{\boldsymbol{R}} \left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - 1\right). \tag{14.8}$$

We will now leverage a useful property of any Bravais lattice: if $\boldsymbol{R}$ the nearest neighbor to an atom at the origin, then $-\boldsymbol{R}$ will also be a nearest neighbor to the origin. As a result, the $e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - 1$ term in the sum over the origin's nearest neighbor's in Equation 14.8 may be written

$$e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - 1 = \frac{1}{2}\left[(e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - 1) + (e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} - 1)\right] = -2\sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2},$$

which we substitute into Equation 14.8 and cancel negative signs to get

$$M\omega^2\boldsymbol{u}_0 = 2K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{0})\}} (\hat{\mathbf{e}}_{\boldsymbol{R}} \cdot \boldsymbol{u}_0)\, \hat{\mathbf{e}}_{\boldsymbol{R}} \sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}.$$

- Finallly, for future use, we quote the vector identity

$$\left[(\boldsymbol{a}\cdot\boldsymbol{b})\boldsymbol{a}\right]_i = \sum_j a_j b_j a_i = \sum_j a_i a_j b_j = \sum_j (\boldsymbol{a}\otimes\boldsymbol{a})_{ij} b_j = (\boldsymbol{a}\otimes\boldsymbol{a}\boldsymbol{b})_i,$$

where $\otimes$ denotes the outer product. We then apply this identity to Equation 14.2 to get

$$M\omega^2\boldsymbol{u}_0 = \left[2K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{0})\}} \sin^2\frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}(\hat{\mathbf{e}}_{\boldsymbol{R}}\otimes\hat{\mathbf{e}}_{\boldsymbol{R}})\right]\boldsymbol{u}_0.$$

The resulting equations is in fact an eigenvalue problem—the quantity $(\hat{\mathbf{e}}_{\boldsymbol{R}}\otimes\hat{\mathbf{e}}_{\boldsymbol{R}})$ is a matrix (2×2 in two dimensions and (3×3) in three dimensions) that acts on the vector $\boldsymbol{u}_0$. The eigenvalues of the matrix $(\hat{\mathbf{e}}_{\boldsymbol{R}}\otimes\hat{\mathbf{e}}_{\boldsymbol{R}})$ will produce the oscillation eigenfrequencies at a given wave vector $\boldsymbol{k}$.

15 Fifteenth Exercise Set

15.1 Lattice Oscillations in a Triangular Lattice

Use the Lagrangian formalism developed in the previous exercise to find the eigenfrequencies and eigenmodes associated with lattice oscillations in the plane of a two-dimensional triangular lattice (see Figure 9).
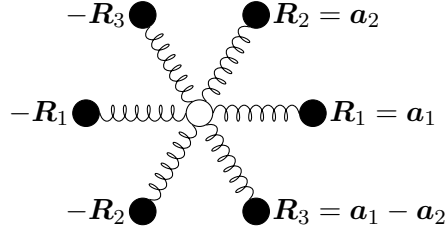

Figure 9: The nearest neighbors to the origin (center, in white) of the 2D triangular lattice used in Exercise 15.1.

- For review we had used the ansatz $\boldsymbol{u_R} = \boldsymbol{u}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{R} - \omega t)}$ and left off with

$$M\omega^2 \boldsymbol{u}_0 = \left[2K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{0})\}} \sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}(\hat{\mathbf{e}}_{\boldsymbol{R}} \otimes \hat{\mathbf{e}}_{\boldsymbol{R}}) \right] \boldsymbol{u}_0.$$

  We first rearrange this equation to make the underlying eigenvalue problem more clear. The result is a homogeneous system of the form

$$\left[2K \sum_{\boldsymbol{R}\in\{\mathrm{nn}(\boldsymbol{0})\}} \sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}(\hat{\mathbf{e}}_{\boldsymbol{R}} \otimes \hat{\mathbf{e}}_{\boldsymbol{R}}) - M\omega^2 \mathbf{I} \right] \boldsymbol{u}_0 = \boldsymbol{0}, \qquad (15.1)$$

  where $\mathbf{I}$ is the identity matrix.

- For later use, we first make the auxiliary calculations shown in Table 15.1.

	$\boldsymbol{R}$	$\hat{\mathbf{e}}_{\boldsymbol{R}}$	$\hat{\mathbf{e}}_{\boldsymbol{R}} \otimes \hat{\mathbf{e}}_{\boldsymbol{R}}$	$\sin^2 \frac{\boldsymbol{k}\cdot\boldsymbol{R}}{2}$
$\pm\boldsymbol{R}_1$	$a(1,0)$	$(1,0)$	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$	$\sin^2 \frac{k_x a}{2}$
$\pm\boldsymbol{R}_2$	$a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$	$\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$	$\begin{pmatrix} 1/4 & \sqrt{3}/4 \\ \sqrt{3}/4 & 3/4 \end{pmatrix}$	$\sin^2 \frac{(k_x + \sqrt{3}k_y)a}{4}$
$\pm\boldsymbol{R}_3$	$a\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)$	$\left(\frac{1}{2}, -\frac{\sqrt{3}}{2}\right)$	$\begin{pmatrix} 1/4 & -\sqrt{3}/4 \\ -\sqrt{3}/4 & 3/4 \end{pmatrix}$	$\sin^2 \frac{(k_x - \sqrt{3}k_y)a}{4}$

- To find the lattice's eigenfrequencies, and to ensure that the eigenvalue problem in Equation 15.1 has a non-trivial solution, we require the determinant of the matrix in square brackets equal zero, i.e.

$$\det \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = 0,$$

where the matrix elements are

$$M_{11} = 4K \left[\sin^2 \frac{k_x a}{2} + \sin^2 \frac{(k_x + \sqrt{3}k_y)a}{4} + \sin^2 \frac{(k_x - \sqrt{3}k_y)a}{4} \right] - M\omega^2$$

$$M_{12} = 4K \frac{\sqrt{3}}{4} \left[\sin^2 \frac{(k_x + \sqrt{3}k_y)a}{4} - \sin^2 \frac{(k_x - \sqrt{3}k_y)a}{4} \right]$$

$$M_{21} = M_{12} = 4K \frac{\sqrt{3}}{4} \left[\sin^2 \frac{(k_x + \sqrt{3}k_y)a}{4} - \sin^2 \frac{(k_x - \sqrt{3}k_y)a}{4} \right]$$

$$M_{22} = 4K \frac{3}{4} \left[\sin^2 \frac{(k_x + \sqrt{3}k_y)a}{4} + \sin^2 \frac{(k_x - \sqrt{3}k_y)a}{4} \right] - M\omega^2.$$

Eigenfrequencies in the Limit of $|\boldsymbol{k}| \ll \pi/a$

- We will consider only the long-wavelength limit $|\boldsymbol{k}| \ll \pi/a$ in which phonon wavelength is much larger than lattice constant (i.e. we consider only $\boldsymbol{k}$ near the center of the lattice's first Brillioun zone). We first expand the matrix elements in the long-wavelength limit to get

$$M_{11} = Ka^2 \left(k_x^2 + \frac{1}{8}k_x^2 + \frac{3}{8}k_y^2 \right) - M\omega^2$$

$$M_{12} = Ka^2 \sqrt{3}2k_x \sqrt{3}k_y \cdot 2 \cdot \frac{1}{16}$$

$$M_{21} = M_{12}$$

$$M_{22} = 3Ka^2 \left(\frac{1}{8}k_x^2 + \frac{3}{8}k_y^2 \right) - M\omega^2,$$

which we then simplify to get

$$M_{11} = \frac{3}{8}Ka^2 \left(3k_x^2 + k_y^2 \right) - M\omega^2$$

$$M_{12} = \frac{3}{4}Ka^2 k_x k_y$$

$$M_{21} = M_{12}$$

$$M_{22} = \frac{3}{8}Ka^2 \left(k_x^2 + 3k_y^2 \right) - M\omega^2.$$

We then note the identities

$$3k_x^2 + k_y^2 = 2k^2 + k_x^2 - k_y^2$$
$$k_x^2 + 3k_y^2 = 2k^2 - (k_x^2 - k_y^2)$$

which we use to rearrange the diagonal matrix elements in the form

$$M_{11} = \left(\frac{3}{4}Ka^2 k^2 - M\omega^2 \right) + \frac{3}{8}Ka^2(k_x^2 - k_y^2)$$

$$M_{12} = \frac{3}{4}Ka^2 k_x k_y$$

$$M_{21} = M_{12}$$

$$M_{22} = \left(\frac{3}{4}Ka^2 k^2 - M\omega^2 \right) - \frac{3}{8}Ka^2(k_x^2 - k_y^2).$$

Having simplified the matrix elements somewhat, we now compute the determinant

$$\det \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = M_{11}M_{22} - M_{12}M_{21}$$

$$= \left(\frac{3}{4}Ka^2k^2 - M\omega^2\right)^2 - \left[\frac{3}{8}Ka^2(k_x^2 - k_y^2)\right]^2 - \left(\frac{3}{4}Ka^2k_xk_y\right)^2$$

$$= \left(\frac{3}{4}Ka^2k^2 - M\omega^2\right)^2 - \left(\frac{3}{8}Ka^2\right)^2 \left(k_x^4 - 2k_x^2k_y^2 + k_y^4 + 4k_x^2k_y^2\right)$$

$$= \left(\frac{3}{4}Ka^2k^2 - M\omega^2\right)^2 - \left(\frac{3}{8}Ka^2\right)^2 \left(k_x^2 + k_y^2\right)^2$$

$$= \left(\frac{3}{4}Ka^2k^2 - M\omega^2\right)^2 - \left(\frac{3}{8}Ka^2\right)^2 k^4.$$

We then rearrange to get

$$\left(\frac{3}{4}Ka^2k^2 - M\omega^2\right)^2 = \left(\frac{3}{8}Ka^2\right)^2 k^4,$$

then take the square root of both sides of equation and solve for $M\omega^2$ to get

$$M\omega^2 = \frac{3}{4}Ka^2k^2 \pm \frac{3}{8}Ka^2k^2.$$

The solutions for ω^2 are then

$$\omega^2 \in \left\{\frac{9}{8}\frac{K}{M}a^2k^2, \frac{3}{8}\frac{K}{M}a^2k^2\right\}.$$

We can then introduce the phonon speeds c_1 and c_2 via $\omega \in \{c_1k, c_2k\}$, where

$$c_1 = \sqrt{\frac{9}{8}\frac{K}{M}}a \qquad \text{and} \qquad c_2 = \sqrt{\frac{3}{8}\frac{K}{M}}a.$$

Both solutions correspond to acoustic branches. Note: as expected from the theory developed in lecture, the solution has (i) two acoustic branches because oscillations in a two-dimensional plane have two degrees of freedom; and (ii) no optical branches, because the triangular crystal structure is fully described by a Bravais lattice with one atom per unit cell.

Eigenmodes in the Limit of $|\boldsymbol{k}| \ll \pi/a$

- We now aim to find the oscillation amplitudes associated with the eigenfrequencies ω_1 and ω_2 computed above. We begin with the matrix equation

$$\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} u_{0_x} \\ u_{0_y} \end{pmatrix} = \boldsymbol{0},$$

where we will use the matrix element expressions

$$M_{11} = \frac{3}{8}Ka^2\left(3k_x^2 + k_y^2\right) - M\omega^2$$

$$M_{12} = \frac{3}{4}Ka^2k_xk_y$$

$$M_{21} = M_{12}$$

$$M_{22} = \frac{3}{8}Ka^2\left(k_x^2 + 3k_y^2\right) - M\omega^2.$$

$$\begin{pmatrix} \frac{3}{8}Ka^2\left(3k_x^2 + k_y^2\right) - M\omega^2 & \frac{3}{4}Ka^2k_xk_y \\ \frac{3}{4}Ka^2k_xk_y & \frac{3}{8}Ka^2\left(k_x^2 + 3k_y^2\right) - M\omega^2 \end{pmatrix} \begin{pmatrix} u_{0_x} \\ u_{0_y} \end{pmatrix} = \boldsymbol{0}. \qquad (15.2)$$

- We first consider the higher frequency $\omega_1^2 = \frac{9}{8}\frac{K}{M}a^2k^2$, which we substitute into Equation 15.2 to get

$$\begin{pmatrix} -\frac{3}{4}Ka^2k_y^2 & \frac{3}{4}Ka^2k_xk_y \\ - & - \end{pmatrix} \begin{pmatrix} u_{0_x} \\ u_{0_y} \end{pmatrix} = \mathbf{0}.$$

Note that to find eigenmodes, we only need to consider one row of the matrix. We then factor and divide out $\frac{3}{4}Ka^2k_y$ from the upper row to get

$$\begin{pmatrix} -k_y & k_x \\ - & - \end{pmatrix} \begin{pmatrix} u_{0_x} \\ u_{0_y} \end{pmatrix} = \mathbf{0} \implies k_y u_{0_x} = k_x u_{0_y}.$$

The result $k_y u_{0_x} = k_x u_{0_y}$ implies the relationship $\boldsymbol{u}_0 \parallel \boldsymbol{k}$, i.e. that the wave vector $\boldsymbol{k}$ and the amplitude vector $\boldsymbol{u}_0$ are parallel.

The eigenmode with $\boldsymbol{u}_0 \parallel \boldsymbol{k}$ corresponds to longitudinal waves.

- For the sake of completeness, we can make a rather long-handed confirmation that $k_y u_{0_x} = k_x u_{0_y} \implies \boldsymbol{u}_0 \parallel \boldsymbol{k}$ as follows: two vectors are parallel if they satisfy the Cauchy-Schwartz equality $|\boldsymbol{k} \cdot \boldsymbol{u}| = |\boldsymbol{k}||\boldsymbol{u}|$. We will show that $\boldsymbol{u}_0$ and $\boldsymbol{k}$ satisfying the Cauchy-Schwartz equality is equivalent to $k_y u_{0_x} = k_x u_{0_y}$. We begin with the Cauchy-Schwartz equality

$$|\boldsymbol{k} \cdot \boldsymbol{u}| = \left| k_x u_{0_x} + k_y u_{0_y} \right| = \sqrt{k_x^2 + k_y^2}\sqrt{u_{0_x}^2 + u_{0_y}^2}.$$

We then square both sides to get

$$(k_x u_{0_x})^2 + 2\left| k_x u_{0_x} k_y u_{0_y} \right| + (k_y u_{0_y})^2 = (k_x^2 + k_y^2)(u_{0_x}^2 + u_{0_y}^2)$$
$$= (k_x u_{0_x})^2 + k_y^2 u_{0_x}^2 + k_x^2 u_{0_y}^2 + (k_y u_{0_y})^2,$$

then cancel like terms to get

$$2\left| k_x u_{0_x} k_y u_{0_y} \right| = k_y^2 u_{0_x}^2 + k_x^2 u_{0_y}^2.$$

We then rearrange and factor to get

$$\left| k_x u_{0_y} - k_y u_{0_x} \right|^2 = 0 \implies k_x u_{0_y} = k_y u_{0_x}.$$

In other words, the relationship $k_x u_{0_y} = k_y u_{0_x}$. is equivalent to $\boldsymbol{u}_0$ and $\boldsymbol{k}$ satisfying the Cauchy-Schwartz equality, which is equivalent to $\boldsymbol{u}_0 \parallel \boldsymbol{k}$.

- We now consider the smaller eigenfrequency $\omega_2^2 = \frac{3}{8}\frac{K}{M}a^2k^2$, which we substitute into Equation 15.2 to get

$$\begin{pmatrix} \frac{3}{4}Ka^2k_x^2 & \frac{3}{4}Ka^2k_xk_y \\ - & - \end{pmatrix} \begin{pmatrix} u_{0_x} \\ u_{0_y} \end{pmatrix} = \mathbf{0}.$$

(Again we consider only the upper row for the purposes of computing eigenmodes.) We then factor out and cancel $\frac{3}{4}Ka^2k_x$ from the upper row to get

$$\begin{pmatrix} k_x & k_y \\ - & - \end{pmatrix} \begin{pmatrix} u_{0_x} \\ u_{0_y} \end{pmatrix} = \mathbf{0} \implies k_x u_{0_x} + k_y u_{0_y} = 0.$$

The result $k_x u_{0_x} + k_y u_{0_y} = 0$ implies $\boldsymbol{u}_0 \cdot \boldsymbol{k} = 0$, meaning that the wave vector $\boldsymbol{k}$ and the amplitude vector $\boldsymbol{u}_0$ are perpendicular.

The eigenmode with $\boldsymbol{u}_0 \perp \boldsymbol{k}$ corresponds to transverse waves.