

Summary of SK2758 Solid State Physics

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March 26, 2020

Abstract

This is a summary of SK2758 Solid State Physics. It contains the most essential formulae and discussions of the theory, I think.

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1 Crystals

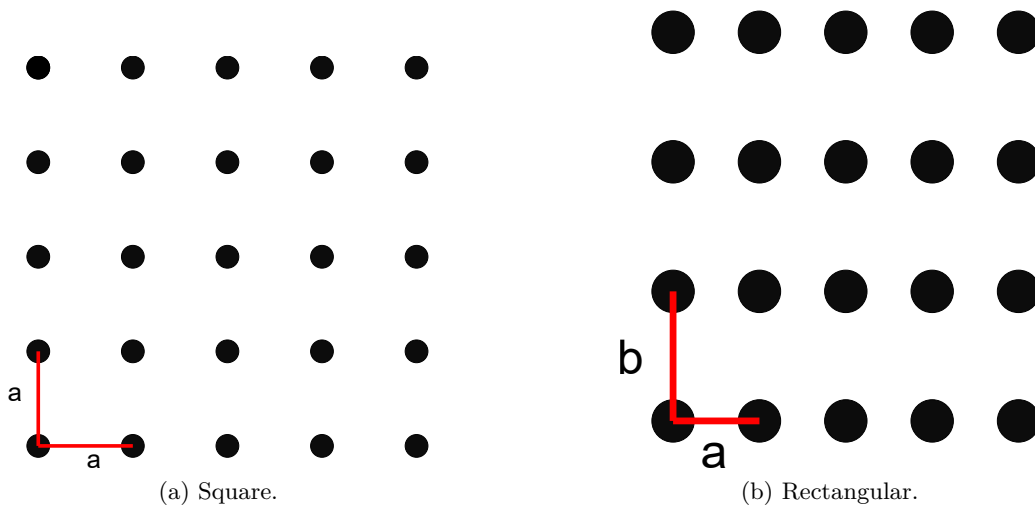
Crystals Solid state physics, as we will study it, is concerned with crystals. A crystal is an arrangement of atoms which is repeated periodically. When developing the physics of crystals, we will assume their repetition to be infinite.

Basis The arrangement of atoms which is repeated in a crystal is termed the basis.

Lattices The set of points to which the basis is attached is termed the lattice.

Bravais Lattices A Bravais lattice is a lattice such that the arrangement of lattice points looks exactly equal from any lattice point. This turns out to be equivalent to the lattice being infinite and symmetric under certain discrete translations. We will treat crystal lattices as Bravais lattices.

The two-dimensional Bravais lattices are the rectangular,



Lattice Vectors The set $\{\mathbf{a}_i\}$ of lattice vectors of a Bravais lattice is the smallest possible set of vectors such that translating the lattice by $u_i\mathbf{a}_i$, where the u_i are integers, leaves the lattice unchanged. There is an infinite number of ways to define the lattice vectors of a given lattice.

Primitive Lattice Vectors A set of lattice vectors is primitive if any two equivalent points are connected by integer combinations of the lattice vectors.

Crystal Axes The crystal axes are a set of directions that span space. These may be chosen according to, for instance, the primitive lattice vectors or other directions connected to the symmetry of the lattice.

Crystal Cell The crystal cell is the repeat unit of the crystal. It may be constructed in an infinite number of ways.

Lattice Constants Lattice constants are a set of parameters defining the dimensions of the cell.

Primitive Cell The primitive cell is a minimum-volume cell. It contains only one lattice point, and is thus termed a unit cell. Its infinite translation throughout space yields the lattice.

Primitive Basis The primitive basis is the basis associated with the primitive cell.

Wigner-Seitz Cell The Wigner-Seitz Cell is the cell constructed by for any lattice point dividing space into two at the middle of and normal to the line between the point in question and all other points, and choosing the smallest possible region of space containing the point from this.

Lattice Point Group The lattice point group is the group of operations which, applied about a lattice point (i.e. keeping this point fixed), leaves the lattice unchanged. Examples of possible fundamental operations include:

- rotations.
- reflections.

Lattice Space Group The space group of the Bravais lattices is the group of symmetries of all Bravais lattices of a given dimensionality. It contains both point groups and translations.

n -Fold Rotations An n -fold rotation is a rotation operation such that it reduces to the identity operation when applied n times. Lattices cannot be symmetric under 5-fold rotation.

Crystal Planes In a cell it is useful to define crystallographic planes. These are indicated by a set of indices (hkl), the computation of which we will return to. A bar above any element indicates that element to be negative.

A set of parallel planes such that all lattice points are contained in the set may be denoted $\{hkl\}$.

Crystallographic Directions Likewise we define crystallographic directions by the notation $[uvw]$. The indices are the set of the smallest integers such that they form a vector parallel to the one in question.

Random Stacking Randomly stacked crystals are formed by densely packed layers of atoms being stacked without long-range order in the stacking direction.

Polytypism Polytypism is a milder variation of random stacking, where the order of the stacked layers is extremely long-range.

X-Ray Diffraction X-ray diffraction is the process of shining X-rays onto a material in order to characterize it. Before atomic physics, it was discovered that solids scattered X-rays intensely in specific directions, as opposed to light, which was reflected by the solid. In the context of solid-state physics, we can interpret this as crystal planes acting as diffraction grids that scatter the X-rays. This interpretation makes sense because the wavelength of X-rays is comparable to interatomic distances in a solid, consistent with the regime in which classical wave physics predicts that diffraction phenomena are significant, and the scattered light being localized is consistent with diffraction of other waves.

Bragg's Law Bragg's law was a first attempt at explaining X-ray diffraction patterns. To derive it, consider a solid composed of aligned and stacked atomic planes separated by a distance d on which electromagnetic radiation of wavelength λ is incident at angle θ to the planes, and suppose each plane reflects the radiation specularly (following the law of reflection) and elastically (preserving the wavelength). Comparing radiation reflected from two adjacent layers, the light in the lower layer travels a distance $2d \sin \theta$ longer. In order for the radiation from these layers to interfere constructively, we must have

$$2d \sin \theta = n\lambda, \quad n = 1, 2, \dots$$

This is Bragg's law. It is a very rough description of X-ray diffraction, but predicts the phenomenology correctly. It also predicts that diffraction occurs for $\lambda < 2d$, which is why light, for instance, is not diffracted by solids.

Fourier Analysis and Reciprocal Space The translational symmetry of the lattice implies that the tools of Fourier analysis are applicable when studying solid-state physics. Any observable A defined on the crystal lattice may be written as

$$A = \sum_{\mathbf{G}} A_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}.$$

The coefficients in the series expansion are given by

$$A_{\mathbf{G}} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d^d \mathbf{r} A(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}.$$

In order for A to be an observable, we must have $A_{-\mathbf{G}} = A_{\mathbf{G}}^*$. The fact that A is an observable on the crystal lattice implies that it must have the same symmetries - in particular translational symmetry. This implies

$$A(\mathbf{r} + u_i \mathbf{a}_i) = A(\mathbf{r}) \implies u_i \mathbf{G} \cdot \mathbf{a}_i = 2\pi n$$

where n is an integer. The vectors \mathbf{G} must have reciprocal length as their dimension, and are thus vectors in what is termed reciprocal space.

The Reciprocal Lattice The simplest choice of vectors satisfying

$$u_i \mathbf{G} \cdot \mathbf{a}_i = 2\pi n$$

is integer combinations of a set of vectors $\{\mathbf{b}_i\}$ such that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$. The set of vectors $\{\mathbf{b}_i\}$ thus defines a Bravais lattice in reciprocal space, termed the reciprocal lattice. In three dimensions, the explicit formula for the reciprocal lattice vectors is

$$\mathbf{b}_1 = \frac{2\pi}{V_{\text{cell}}} \mathbf{a}_2 \times \mathbf{a}_3, \quad V_{\text{cell}} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

with cyclic permutation of the indices yielding the other two.

Crystal Planes and the Reciprocal Lattice Assume that there is a lattice point in the origin and that the closest crystal plane with orientation specified by the normal vector \mathbf{n} is a distance d from the origin. Any plane parallel to the plane in question is described by

$$\mathbf{r} \cdot \mathbf{n} = md, \quad m = 0, \pm 1, \dots$$

Consider now a translation by \mathbf{T} such that the lattice is left invariant. Assuming the translation to be between lattice points, the translation must satisfy the equation of some crystal plane, implying

$$\mathbf{T} \cdot \mathbf{n} = md.$$

In particular, if the translation is to a point in a plane adjacent to the origin, we have

$$\mathbf{T} \cdot \frac{2\pi}{d} \mathbf{n} = 2\pi.$$

Comparing this to the definition of the reciprocal lattice implies that the plane is normal to a reciprocal lattice vector

$$\mathbf{G} = \frac{2\pi}{d} \mathbf{n}.$$

This is the shortest reciprocal lattice vector describing the plane. The expression above implies

$$d = \frac{2\pi}{|\mathbf{G}|}.$$

Miller Indices Returning to the indexing system for crystal planes, we may decompose the normal vector as

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

These indices are exactly the indices used to describe a crystal plane, and are termed Miller indices. As \mathbf{G} is the shortest vector describing the plane, the indices cannot contain any common factors.

The Miller indices may also be computed from the real lattice according to the following rules:

1. For each axis, defined by the lattice vectors, identify the intercepts of the plane with the axis as units of the lattice parameters.
2. Compute the reciprocals of each intercept.
3. Reduce to three integers with the same ratio.

Interplanar Distances Consider the set of $\{hkl\}$ planes. We are interested in computing the distance between two adjacent such planes. To do this, we will first need a unit normal to any such plane. According to the construction of the Miller indices, the vectors

$$\mathbf{v}_1 = \frac{1}{h}\mathbf{a}_1 - \frac{1}{k}\mathbf{a}_2, \quad \mathbf{v}_2 = \frac{1}{h}\mathbf{a}_1 - \frac{1}{l}\mathbf{a}_3$$

span the plane, apart from some constant spatial shift. Hence we are interested in a vector that is simultaneously normal to both of these. One possible choice is

$$\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

From this, obtaining a unit normal is trivial. Next we need a vector from one plane to the other. One possible choice is

$$\mathbf{T} = \frac{1}{h}\mathbf{a}_1,$$

as one cell has space for h planes of this type when counted along the \mathbf{a}_1 direction. From this, the distance is given by

$$d = \frac{1}{|\mathbf{G}_{hkl}|} \mathbf{G}_{hkl} \cdot \mathbf{T} = \frac{2\pi}{|\mathbf{G}_{hkl}|},$$

which is true for any Bravais lattice.

Diffraction by Solids Using the language of Fourier analysis and reciprocal space, we will try to derive a more sophisticated diffraction condition.

To do this, consider a crystal exposed to far-field radiation described by a wave vector \mathbf{k} which is scattered elastically by the crystal in an arbitrary direction and observed in the far-field region in some direction, in which the wave vector is \mathbf{k}' . Considering the interference between two points displaced by \mathbf{r} , the phase difference between the radiation from the two points is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$. Supposing that the amplitude of the scattered wave is proportional to the electron density (or, really, any property defined on the lattice), the total scattered amplitude is proportional to the (confusingly termed) scattering amplitude

$$F = \int d^d\mathbf{r} n(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}}.$$

Adding the series expansion of the electron density yields

$$F = \int d^d\mathbf{r} \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} e^{-i\Delta\mathbf{k} \cdot \mathbf{r}} = \int d^d\mathbf{r} \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i(\mathbf{G}-\Delta\mathbf{k}) \cdot \mathbf{r}} = \sum_{\mathbf{G}} \int d^d\mathbf{r} n_{\mathbf{G}} e^{i(\mathbf{G}-\Delta\mathbf{k}) \cdot \mathbf{r}}.$$

For the case $\Delta\mathbf{k} = \mathbf{G}$ for any one particular reciprocal lattice vector, the exponential in this term vanishes, leaving a term $V n_{\mathbf{G}}$. It can be shown that all other terms in the scattering amplitude vanish, yielding $F = V n_{\mathbf{G}}$ for this case and $F = 0$ otherwise. The most fundamental diffraction condition is thus

$$\Delta\mathbf{k} = \mathbf{G}.$$

While we have in principle obtained a diffraction condition now, we can simplify it by using the fact that the scattering is elastic. We obtain

$$2\mathbf{k} \cdot \mathbf{G} + G^2 = 0.$$

It may be rewritten by swapping \mathbf{G} for $-\mathbf{G}$, which is also a reciprocal lattice vector, to yield

$$2\mathbf{k} \cdot \mathbf{G} = G^2.$$

Note that this implies that information about the reciprocal lattice, and therefore the lattice itself, may be obtained from diffraction experiments.

Laue's Equations The fundamental diffraction criterion implies

$$\Delta \mathbf{k} \cdot \mathbf{a}_i = 2\pi v_i$$

for some integer v_i , simultaneously for all lattice vectors. This implies that reflections are only found at the intersection of three cones in reciprocal space. This is very strict, and such reflections must be found by sweeping in crystal orientation and/or wavelength or by chance.

The Ewald Sphere The Ewald sphere is a tool for visualizing the necessary conditions for diffractions. To construct it, draw the incident wave vector starting in a point such that it terminates in a reciprocal lattice point. From the starting point, draw a sphere of radius k . All reciprocal lattice points corresponding to a diffraction peak are found on this sphere.

Brillouin Zones To introduce the concept of Brillouin zones, rewrite the diffraction condition as

$$\mathbf{k} \cdot \frac{1}{2} \mathbf{G} = \left(\frac{1}{2} G \right)^2.$$

For a fixed \mathbf{G} , this equation defines the set of wave vectors terminating on the bisector of \mathbf{G} . This is similar to the construction of the Wigner-Seitz cell in real space, but now extended to construct zones using all points in the reciprocal lattice. Constructing these bisectors divides the reciprocal space into Brillouin zones (a single Brillouin zone is the combinations of all zones a fixed number of zones from the central zone). The central zone, which is the Wigner-Seitz cell in reciprocal space, is the first Brillouin zone.

Volume of the Brillouin Zone We would like to compute the volume of the Brillouin zone in terms of the volume of the unit cell. To do this, we note that the unit cell volume is given by

$$V_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3).$$

Using this, the volume of the Brillouin zone is given by

$$V_r = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3).$$

The vector in the parenthesis is given by

$$\begin{aligned} \mathbf{b}_2 \times \mathbf{b}_3 &= \frac{(2\pi)^2}{V_c^2} (\mathbf{a}_3 \times \mathbf{a}_1) \times (\mathbf{a}_1 \times \mathbf{a}_2) \\ &= \frac{(2\pi)^2}{V_c^2} ((\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)) \mathbf{a}_1 - (\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_1)) \mathbf{a}_2) \\ &= \frac{(2\pi)^2}{V_c} \mathbf{a}_1, \end{aligned}$$

and thus the volume of the Brillouin zone is given by

$$V_r = \frac{(2\pi)^3}{V_c}.$$

The Structure Factor and Atomic Form Factor The diffraction condition is stated in terms of reciprocal lattice vectors obtained from the primitive lattice vectors. However, especially in experimental contexts, the primitive unit cell is not the geometry of choice for studying materials. Instead, one can use inherent ambiguities in choices of repeat units of the crystal to study geometries with, for instance, more or simpler symmetries. When considering such geometries, the diffraction conditions is only necessary, not sufficient. We will now study diffraction for such cases.

Consider a crystal built up of some kind of cell, not necessarily a primitive one. When the diffraction condition is satisfied, i.e. $\Delta \mathbf{k} = \mathbf{G}$ for some reciprocal lattice vector corresponding to the chosen cell, the scattering amplitude for a crystal of N cells becomes

$$F = \int d^d \mathbf{r} n(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} = N \int_{\text{cell}} d^d \mathbf{r} n(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} = N S_{\mathbf{G}},$$

where we have introduced the structure factor $S_{\mathbf{G}}$, which describes the effect of the electron distribution in the cell on the scattering amplitude for a given diffraction peak.

Writing the electron density as a superposition of contributions from each atom in the basis (this decomposition is not unique, but somehow this is not a problem), we obtain

$$S_{\mathbf{G}} = \int_{\text{cell}} d^d \mathbf{r} \sum n_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G} \cdot \mathbf{r}}$$

where the \mathbf{r}_j are the positions of the atoms in the basis. We rewrite this as

$$S_{\mathbf{G}} = \sum \int_{\text{cell}} d^d \mathbf{r} n_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G} \cdot \mathbf{r}} = \sum e^{-i\mathbf{G} \cdot \mathbf{r}_j} \int_{\text{cell}} d^d \mathbf{r} n_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}.$$

Defining the atomic form factor

$$f_{j,\mathbf{G}} = \int_{\text{cell}} d^d \mathbf{r} n_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}$$

we have

$$S_{\mathbf{G}} = \sum f_{j,\mathbf{G}} e^{-i\mathbf{G} \cdot \mathbf{r}_j}.$$

The requirement for diffraction is thus that $\Delta \mathbf{k} = \mathbf{G}$ and the structure factor being non-zero.

When observing electron distributions in solids, these appear close to those of free atoms. This does not mean that electrons are not distributed in a solid versus for free atoms, but that these corrections do not have a major effect on the atomic form factors. Thus it may be relevant to write these as

$$f_{j,\mathbf{G}} = \int d^d \mathbf{r} n_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}$$

where the electron distribution is that of a free atom and the integration is performed over all of space.

The astute reader might have noticed that when considering the primitive unit cell of a crystal with one atom in the basis, the structure factor is trivial. One could thus ask whether this was really necessary. The answer to the latter question is left to experimentalists, but I can confirm that this derivation neither adds nor subtracts to our knowledge. If you have chosen the primitive cell, the structure factor is trivial and diffraction occurs for every observation such that the diffraction criterion is satisfied. For other choices of cells, certain reciprocal lattice vectors will produce a structure factor equal to zero. This is because these do not correspond to reciprocal lattice vectors of the primitive cell. Someone should prove this more rigorously. Can we be sure that other choices of cells cover all possible reciprocal lattice vectors of the primitive cell? Yes, as non-primitive cells must have longer lattice vectors, corresponding to shorter reciprocal lattice vectors, implying that the reciprocal lattice vectors of the primitive cell should be possible to express as combinations of the reciprocal lattice vectors of the non-primitive cell.

Cohesive Energy The cohesive energy of a crystal is the energy required to separate the crystal into neutral free atoms at rest at infinite separation.

Types of Crystal Binding The different types of crystal binding and their origins are

- van der Waals binding, which occurs due to fluctuating electric dipoles in atoms and molecules.
- ionic binding, which occurs due to Coulomb forces between ions.
- covalent binding, which occurs due to the filling of electron states localized between atoms.
- metal binding, where valence electrons form a gas throughout the crystal and balance repulsion between the metal atoms in the lattice.

van der Waals Energy The van der Waals interaction between two atoms in a crystal or molecule is modelled as a potential of the form

$$V = 4\varepsilon \left(\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right)$$

with a positive term from Pauli repulsion and a negative term from attraction between fluctuating dipoles.

For a crystal of N atoms the cohesive energy due to van der Waals interaction becomes

$$U = 2N\varepsilon \left(\sum_{i \neq j} \left(\frac{\sigma}{R_{ij}} \right)^{12} - \left(\frac{\sigma}{R_{ij}} \right)^6 \right).$$

Reexpressing this in terms of nearest-neighbour distances R in the lattice, we can write $R_{ij} = p_{ij}R$ to obtain

$$U = 2N\varepsilon \left(\left(\frac{\sigma}{R} \right)^{12} \sum_{i \neq j} \frac{1}{p_{ij}^{12}} - \left(\frac{\sigma}{R} \right)^6 \sum_{i \neq j} \frac{1}{p_{ij}^6} \right).$$