I. SYLLABUS AND INTRODUCTION

The course is taught on basis of lecture notes which are supplemented by the textbook Ashcroft and Mermin. Some practical information:

- Professor: Michel van Veenendaal
- Office: Faraday West 223
- Tel: 815-753-0667 (NIU), 630-252-4533 (Argonne)
- e-mail: veenendaal@niu.edu
- web page: www.niu.edu/ veenendaal
- Office hours: I am at NIU Tu/Th. Feel free to walk into my office at any time. You can always make an appointment if you are worried that I might not be there. Official office hours will be established if you feel that the "open door" policy does not work.
- Prerequisites: there are no official prerequisites for the course. However, a knowledge of quantum mechanics at the 560/561 level is recommended. In addition, it makes a lot of sense to have taken Solid-State Physics I (566). Mathematical concepts that will be used are calculus, vector algebra, Fourier transforms, differential equations, linear algebra (in particular matrices and eigenvalues problems).
- Homework: several homework sets will be given. They will be posted on the web site.
- Midterm: one midterm will be given.
- Attendence: There is no required attendence.
- Additional further reading
  F. Wooten, *Optical Properties of Solids* (Academic Press, New York, 1972).

CONTENTS

- *Background*: A sort background and history of solid-state physics is given.
- *Electronic structure*: The lecture notes reverse the order of some of the topics the way they are usually presented. Ashcroft and Mermin (AM) start out with the free electron model and show that it fails and give then a very extended description of crystal structures. The course starts out with electronic structure focusing on simple systems, such as one-dimensional chains. Although not very realistic, the concepts are much more easily introduced in one dimension, since it avoids many complications due to the crystal structure. The tight-binding and the nearly-free electron model will be introduced and compared. After obtaining a good feeling for the important aspects of a solid, some concepts from 566 will be briefly recapitulated (Bloch theorem, crystal structure).
- *Electronic structure of selected materials* Several materials will be discussed in detail, such as alkali metals, trivalent metals, transition metals, semiconductors, rare earths.
- *Optical properties of materials*. The optical properties of materials is discussed using the ideas of polarization and oscillators. The optical spectra for simple metals, such as aluminum, noble metals (Cu, Ag, Au), and insulators are described.

II. BACKGROUND

From Hoddeson, Braun, Teichamnn, Weart, Out of the crystal maze, (Oxford University Press, 1992).

Obviously, people have been interested in the proporties of solids since the old ages. The ancient Greeks (and essentially all other cultures) classified the essential elements as earth, wind, air, and fire or in modern terms: solids, liquids, gases, and combustion (or chemical reactions in general). Whole periods have been classified by the ability to master certain solids: the stone age, the bronze age, the iron age. And even our information age is based for a very large part on our ability to manipulate silicon. Many attempts have been made to understand solids: from Greek philosophers via medieval alchemists to cartesian natural philosophers. Some macroscopic properties could be framed into classical mechanics. Optical conductivity in solids was worked out in the theories of Thomas Young and Jean Fresnel in the late eighteenth and early nineteenth century. Elastical phenomena in solids had a long history. Macroscopic theories for electrical conductivity were developed by, e.g. Georg Ohm and Ludwig Kirchhoff. Another good example of a mechanical model for a solid are the theories of heat conductivity developed in the early nineteenth century by Joseph Fourier. Franz Ernst Neumann developed a mechanical theory for the interaction between elasticity and optics, allowing him to understand anisotropy in materials such as the birefringence that occurs when an isotropic medium is subjected to pressure or uneven heating.

Another important ingredient to understanding solids is symmetry. Already in 1690, it was suggested by Huygens that the regular form of solids in intricately related to their physics. The first scientific theory of crystal symmetry was set up by René-Just Haüy in 1801-2, based on atomistic principles. This was extended upon by mineralogist Christian Samuel Weiss, who, however, completely rejected the atomistic approach. He introduced the concepts of crystallographic axis. The crowning achievement is the classification by Auguste Bravais that the are only 14 ways to order a set of points so that the neighborhood of any individual lattice point looks the same. In 1901, Woldemar Voight published his book on crystallography classifying the 230 different space groups (and was shocked by the large number).

Another important nineteenth century development is the reemergence of the atomistic theories. The success of continuum theories (classical mechanics, electricity and magnetism, thermodynamics) had pushed atomistic thought to the background, in particular in physics (remember the trials and tribulation Ludwig Boltzmann went through in the acceptance of his statistical approach to thermodynamics which was often considered a nice thought experiment, but hopelessly complicated). However, chemical reactions clearly indicated the discrete nature of matter.

A microscopic theory proved elusive until the advent of quantum mechanics in the early twentieth century. Quantum mechanics is crucial in understanding condensed matter. For example, gases can be reasonably well described in a classical framework due to their low density. This means that we do not require quantum (Fermi-Dirac) statistics and we do not have to deal with atomic levels.

Theories started accelerating after the discovery of the electron by J. J. Thompson and Hendrik Lorentz (and mind you, Lorentz and Zeeman determined the e/m ratio before Thompson). The classical theory of solids essentially treats a solid as a gas of electrons in the same fashion as Boltzmann's theory of gases. This model was developed by Paul Drude (who, inexplicably, committed suicide at each 42, only a few days after his inauguration as professor at the University of Berlin). The theory was elaborated by Hendrik Lorentz. Although a useful attempt, the use of Maxwell-Boltzmann statistics as opposed to Fermi-Dirac statistics leads to gross errors with the thermal conductivity κ and the conducivity σ off by several orders of magnitude. The theory gets a lucky break with the Wiedemann-Franz law that the ratio κ/σ is proportional to the temperature T. (It is not quite clear to me why AM wants to start out with an essentially incorrect theory, apart from historic reasons... Then again, we also do not teach the Ptolemean system anymore). However, it was very important in that it was one of the first microscopic theories of a solid.

Early attempts to apply quantum mechanics to solids focused on specific heat as measured by Nernst. Specific heat was studied theoretically by Einstein and Debye. The difference in their approaches lies in their assumption on the momentum dependence of the oscillators. Einstein assumed one particular oscillator frequency representing optical modes. Debye assume sound waves where the energy is proportional to the momentum. Phonon dispersion curves were calculated in 1912 by Max Born and Theodore von Kármán. However, again, this can again be done from Newton's equations.

However, further progess had to weight the development of quantum statistics which were not developed untill 1926. In the meantime, the number of experimental techniques to study condensed matter was increasing. In 1908, Kamerlingh-Onnes and his low-temperature laboratory managed to produce liquid Helium. This led to the discovery of superconductivity in mercury (and in some ways the onset of "big" physics).

After discussions with Peter Paul Ewald in 1912, who was working on his dissertation with Sommerfeld on optical birefringence, Max von Laue successfully measured the diffraction of X-rays from a solid. The experiments were interpreted by William Henry Bragg and his son William Lawrence opening up the way for x-ray crystal analysis.

In 1926-7, Enrico Fermi and Paul Dirac established independently a statistical theory that included Wolfgang

Pauli's principle that quantum states can be occupied by only one electron. This property is inherently related to the antisymmetry of the wavefunctions for fermions. In 1927, Arnold Sommerfeld attempted a first theory of solids using Fermi-Dirac statistics. It had some remarkable improvements over the Drude-Lorentz model. The specific heat was significantly lower due to the fact that not all electrons participate in the conductive properties, but only the ones with the highest energies (i.e. the ones close to the Fermi level). However, the model still completely ignores the effect of the nuclei leading to significant discrepancies with various experiments including resistivity. Werner Heisenberg also had an interest in metals and proposed the problem to his doctoral student Felix Bloch. The first question that he wanted Bloch to address was how to deal with the ion in metals? Bloch assumed that the potential of the nuclei was more important that the kinetic energy. A tight-binding model as opposed to Sommerfeld's free-electron model and ended up with the theorem that the wavefunction can be written as $\psi = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r})$, plane wave modulated by a function that has the periodicity of the lattice. Another important development Rudolf Peierls and Léon Brillouin was the effect of the periodic potential in the opening of gaps at particular values of the momentum k, now known as Brillouin zones.

III. THE ELECTRONIC STRUCTURE

IV. TIGHT-BINDING METHOD

AM Chapter 10

A solid has many properties, such as crystal structure, optical properties (i.e. whether a crystal is transparent or opaque), magnetic properties (magnetic or antiferromagnetic), conductive properties (metallic, insulating), etc. Apart from the first, these properties are related to what is known as the electronic structure of a solid. The electronic structure essentially refers to the behavior of the electrons in the solid. Whereas the nuclei of the atoms that form the solid are fixed, the electronic properties vary wildly for different systems. Unfortunately, the electronic structure is complicated and needs to be often approximated using schemes that sometimes work and at other times fail completely. The behavior of the electrons is, as we know from quantum mechanics, described by a Hamiltonian H. In general, this Hamiltonian contains the kinetic energy of the electron, the potential energy of the nuclei, and the Coulomb interactions between the electrons. Especially, the last one is very hard to deal with. Compare this with a running competition. For the 100 m, the runners have their own lane and the interaction between the runners is minimal. One might consider each runner running for him/herself (obviously, this is not quite correct). However, for larger distances, the runners leave their lanes and start running in a group. We can no longer consider the runners as running independently, since they have to avoid each other, they might bump into each other, etc. This is a much more complicated problem. The same is true for solids. In some solids, we can treat the electrons as being more or less independent. In some solids, we have to consider the interactions between the electrons explicitly. For the moment, we will neglect the interactions between the electrons, even though for some systems, they can turn the conductive properties from metallic to insulating. Systems with strong electron-electron interactions are an important (and still largely unsolved) topic in current condensed-matter physics research. The enormous advantage is that we do not have a problem with N particles (where N is of the order of 10^{23}), but N times a one-particle problem. Of course, this is what you were used to so far. You probably remember the free-electron model (to which we will return later on). First, the bands were obtained (pretty easy since $E_{\mathbf{k}} = \hbar^2 k^2/2m$), and in the end you just filled these eigenstates up to the Fermi level. So far, you might not have realized that this was actually an approximation. This is the type of system we will be considering at the moment. So we are left with a Hamiltonian containing the kinetic energy of the electron, the potential to the nuclei, and some average potential due to the other electrons in the solid.

In 666 (formerly known as 566), the nearly free-electron model was treated. This is essentially an extension on the quantum-mechanical model of particles in a box with the periodic potential of the nuclei added later. We will come back to that in a while, but we start with a model that puts in the atoms explicitly (known as the tight-binding model). This allows us to start thinking about the crystal immediately, instead of putting it in as some afterthought. Crystal can be very complicated, so let us start with something simple: a chain of atoms. Although some materials can indeed be described as a one-dimensional chain, we are more interested in the concepts, which are very similar in any dimension. Unfortunately, even a chain is rather complicated to start out with, so let us begin with just two atoms and later add more atoms to it to form the chain. Let us also consider the simplest system: a system of Hydrogen-like atoms (again not very practical, since Hydrogen forms H_2 molecules at room temperature, but still a model often used in theoretical physics). For each site, we only consider one orbital (in our Hydrogen example, this would be the $1s$ orbital). So in total, we have two orbitals $\varphi_1(\mathbf{r})$ and $\varphi_2(\mathbf{r})$, since we have two sites. However, this creates the impression that we have two different orbitals, whereas we only have one type of orbital but located at two different sites. We can therefore also write $\varphi(\mathbf{r}-\mathbf{R}_1)$ and $\varphi(\mathbf{r}-\mathbf{R}_2)$, where $\varphi(\mathbf{r})$ is the atomic orbital at the

origin. With two orbitals in our basis set, we have a total of four matrix elements

$$\varepsilon = \int d\mathbf{r}\varphi^*(\mathbf{r}-\mathbf{R}_1)H\varphi(\mathbf{r}-\mathbf{R}_1) = \int d\mathbf{r}\varphi^*(\mathbf{r}-\mathbf{R}_2)H\varphi(\mathbf{r}-\mathbf{R}_2) \tag{1}$$

and

$$t = \int d\mathbf{r}\varphi^*(\mathbf{r}-\mathbf{R}_1)H\varphi(\mathbf{r}-\mathbf{R}_2) = \left(\int d\mathbf{r}\varphi^*(\mathbf{r}-\mathbf{R}_1)H\varphi(\mathbf{r}-\mathbf{R}_2)\right)^*, \tag{2}$$

where we use vector notation to allow easy generalization to arbitrary dimension even though we are considering only problems in one dimension for the moment. In the end, we only have two parameters ε and t. Note that for ε the two matrix elements are equivalent, since the on-site energy does not depend on the position in space (or, for an Hydrogen atom, $\varepsilon = -13.6$ eV, no matter where you put it in space. The origin ($\mathbf{R}$=0) is only chosen for convenience). For t, the matrix elements are just each others conjugate. t is known as the tranfer matrix element or hopping integral. Let us take t to be a real number (which it is for Hydrogen atoms, since everything is real). We can also write this in a bra-ket notation

$$\varepsilon = \langle\mathbf{R}_1|H|\mathbf{R}_1\rangle = \langle\mathbf{R}_2|H|\mathbf{R}_2\rangle \tag{3}$$
$$t = -\langle\mathbf{R}_1|H|\mathbf{R}_2\rangle = -\langle\mathbf{R}_2|H|\mathbf{R}_1\rangle, \tag{4}$$

where $\mathbf{R}_i\rangle$ denotes the atomic wavefunction at site $\mathbf{R}_i$. For s-like orbitals, the matrix element would be negative, so t would be a positive number. This allows us to write the Hamiltonian for the two orbitals in the basis set as a matrix

$$H = \begin{pmatrix} \varepsilon & -t \\ -t & \varepsilon \end{pmatrix}. \tag{5}$$

Any vector can now be written as a linear combination of $|\mathbf{R}_1\rangle$ and $|\mathbf{R}_2\rangle$, i.e. $|\psi\rangle = a_1|\mathbf{R}_1\rangle + a_2|\mathbf{R}_2\rangle$. We would like to solve the Schrödinger equation

$$H|\psi\rangle = E|\psi\rangle. \tag{6}$$

We can split this out into different components as

$$\langle\mathbf{R}_i|H|\psi\rangle = E\langle\mathbf{R}_i|\psi\rangle, \tag{7}$$

with $i = 1, 2$. There is a complication in that the overlap matrix elements $S = \langle\mathbf{R}_1|\mathbf{R}_2\rangle = \int d\mathbf{r}\varphi^*(\mathbf{r}-\mathbf{R}_1)\varphi(\mathbf{r}-\mathbf{R}_2) \neq 0$. Taking this into account, we obtain

$$\begin{pmatrix} \varepsilon & -t \\ -t & \varepsilon \end{pmatrix}|\psi\rangle = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix}|\psi\rangle \tag{8}$$

Note that $\langle\mathbf{R}_1|\mathbf{R}_1\rangle = \langle\mathbf{R}_2|\mathbf{R}_2\rangle = 1$. The eigenvalues can be found by solving the determinant

$$\begin{vmatrix} \varepsilon - E & -t - ES \\ -t - ES & \varepsilon - E \end{vmatrix} = 0. \tag{9}$$

This gives the equation

$$(\varepsilon - E)^2 - (-t - ES)^2 = 0 \quad \Rightarrow \quad \varepsilon - E = \pm(-t - ES) \quad \Rightarrow \quad E_{B/AB} = \frac{\varepsilon \pm t}{1 \mp S}. \tag{10}$$

The calculation becomes simpler if we forget about the overlap between the orbitals, which we will do in the remainder, and take $S = 0$. This gives $E_{B/AB} = \varepsilon \mp t$. The eigenstates are also easily obtained and are

$$|\psi_{B/AB}\rangle = \frac{1}{\sqrt{2}}(|\mathbf{R}_1\rangle \pm |\mathbf{R}_2\rangle). \tag{11}$$

Note that for $\langle\mathbf{R}_1|H|\mathbf{R}_2\rangle < 0$ the bonding (B) combination is the lowest (the antibonding (AB) is the lowest for $\langle\mathbf{R}_1|H|\mathbf{R}_2\rangle > 0$). An electron spends an equal amount of time on atom 1 as it does on atom 2, as it should, because there is atom 1 is equivalent to atom 2. In the bonding orbital, the wavefunction is a lot smoother (note that the anti bonding orbital has a node between the two atoms). This reduces the kinetic which is proportional to the

FIG. 1: The eigenvalues of a linear chain of $2, 5, 9, 15, 100$ atoms with a hopping matrix element t between neighboring atoms.

gradient of the wavefunction through to the $\nabla^2\psi$ term in the Hamiltonian. These are the typical bonding-antibonding combinations of a H_2 molecule. Each atom contributes one electron. The two electrons will go into the bonding orbital, giving

$$|\psi_{B\uparrow}\psi_{B\downarrow}\rangle = \frac{1}{2}(|\mathbf{R}_1 \uparrow \mathbf{R}_1 \downarrow\rangle + |\mathbf{R}_1 \uparrow \mathbf{R}_2 \downarrow\rangle + |\mathbf{R}_2 \uparrow \mathbf{R}_1 \downarrow\rangle + |\mathbf{R}_2 \uparrow \mathbf{R}_2 \downarrow\rangle), \tag{12}$$

where we can put two electrons in the bonding orbital due to the spin degree of freedom. Note that the probability of finding the two electrons on the same atom equal that of finding one electron on each atom. This would be surprising if electrons really interacted strongly with each other. However, we neglected that.

Obviously, this is not much of a solid. However, it is straightforward to extend this procedure to chains of arbitrary length N. Let us take the atoms on a chain to be numbered $1, 2, 3, \cdots, N$. General wavefunctions for N sites can then be written as

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} a_{\mathbf{R}}\phi(\mathbf{r} - \mathbf{R}) \quad \text{or} \quad |\psi\rangle = \sum_{\mathbf{R}} a_{\mathbf{R}}|\mathbf{R}\rangle. \tag{13}$$

Again, we want to solve the Schrödinger equation $H|\psi\rangle = E|\psi\rangle$. For the $\mathbf{R}'$'th component, we obtain

$$\langle\mathbf{R}'|H|\psi\rangle = E\langle\mathbf{R}'|\psi\rangle \quad \Rightarrow \quad \sum_i \langle\mathbf{R}'|H|\mathbf{R}\rangle a_{\mathbf{R}} = E\sum_{\mathbf{R}}\langle\mathbf{R}'|\mathbf{R}\rangle a_{\mathbf{R}} = Ea_{\mathbf{R}'}, \tag{14}$$

where we have assumed $\langle\mathbf{R}'|\mathbf{R}\rangle = \delta_{\mathbf{R},\mathbf{R}'}$. We can write this in matrix form as

$$\begin{pmatrix} H_{11} & \cdots & H_{1N} \\ . & & . \\ H_{N1} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ . \\ . \\ a_N \end{pmatrix} = E \begin{pmatrix} a_1 \\ . \\ . \\ a_N \end{pmatrix}, \tag{15}$$

where $H_{ij} = \langle\mathbf{R}_i|H|\mathbf{R}_j\rangle$. As before, we have $H_{nn} = \varepsilon$. If atoms are on neighboring sites, we have $H_{n,n+1} = -t$. In principle, $H_{n,n+2}$. $H_{n,n+3}$, etc. are nonzero (known as next-nearest neighbor and next-next nearest neighbor hopping matrix elements), but we will take them zero for simplicity. This gives a matrix

$$H = \begin{pmatrix} \varepsilon & t & 0 & 0 & \cdots & & & & & \\ t & \varepsilon & t & 0 & 0 & \cdots & & & & \\ 0 & t & \varepsilon & t & 0 & 0 & \cdots & & & \\ 0 & 0 & t & \varepsilon & t & 0 & 0 & \cdots & & \\ \cdots & 0 & 0 & t & \varepsilon & t & 0 & 0 & \cdots & \\ & \cdots & 0 & 0 & t & \varepsilon & t & 0 & 0 & \cdots \\ & & & & . & . & . & . & & \end{pmatrix} \tag{16}$$

Although, not easily solvable by hand, the energies can be found using some computer program that solves eigenvalue problems. For different lengths N, the eigenvalues are given in Fig. 1. We have taken the constant shift $\varepsilon = 0$. The eigenvalues E_n with $n = 1, \cdots, N$ are ordered and plotted as a function of $(n-1)/(N-1)$, i.e. from 0 to 1. As we have seen before, for $N = 2$, the eigenvalues are $\pm t$. However, if we increase the the length of the chain, we see that the eigenvalues approach a continuous curve. The extrema of the curve are $\pm 2t$. The question is what is this curve and can we obtain this curve in different fashion apart from solving the matrix by brute force?

First, we have to realize that we want to study bulk systems or systems that are essentially infinity. The study of surfaces is a whole field in itself but not our focus at the moment. For small chains the number of atoms close to the edge of the chain is relatively large. So we can study a large system, but we can also introduce a mathematical trick. Note, that none of the atoms in the chain is equivalent, since they all have a different distance to the end of the chain. However, if we connect the two ends of the chain to each other, all the atoms become equivalent. This is known as periodic boundary conditions. Although, this is essentially a mathematical trick, in some systems this is

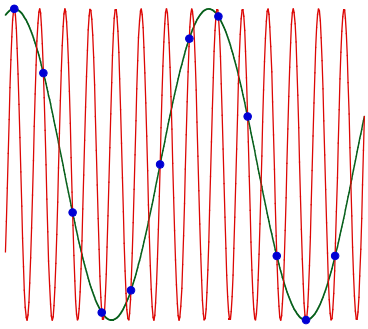


FIG. 2: The lines give the values of e^{ikx} and $e^{(k+K)x}$ as a function of x. We have taken $k = 0.3\pi$ and $K = 2\pi$. The dots indicate the values at the atomic positions. Note that the Fourier transform only includes these values.

physically realized. The best known example would be a benzene ring consisting of six carbon atoms. However, in two and three dimensions, this is more difficult to realize. In two dimensions, the system would be a torus (which could be achieved, maybe, with a carbon nanotube), but in three dimension, it is impossible to realize. Let us go back to the diatomic molecule. Applying periodic boundary condition implies that 1 is connected to 2, but 2 is again connected to 1. This leads to a doubling of the transfer matrix element, giving a Hamiltonian:

$$H = \begin{pmatrix} \varepsilon & -2t \\ -2t & \varepsilon \end{pmatrix}. \tag{17}$$

The eigenvalues are $E_{1,2} = \mp 2t$. Note that this is equal to the extrema in the continuous curve we obtained for large N. This is a significant difference from the $\pm t$, we obtained earlier. We could expect that, because all atoms in the "chain" are at the end of the chain. For larger

$$H = \begin{pmatrix} \varepsilon & t & 0 & 0 & \cdots & & & & 0 & t \\ t & \varepsilon & t & 0 & 0 & \cdots & & & 0 & 0 \\ 0 & t & \varepsilon & t & 0 & 0 & \cdots & & & \\ 0 & 0 & t & \varepsilon & t & 0 & 0 & \cdots & & \\ \cdots & 0 & 0 & t & \varepsilon & t & 0 & 0 & \cdots & \\ & \cdots & 0 & 0 & t & \varepsilon & t & 0 & 0 & \cdots \\ & & & & . & . & . & . & & \\ 0 & 0 & & & . & . & 0 & t & \varepsilon & t \\ t & 0 & & & . & . & . & 0 & t & \varepsilon \end{pmatrix} \tag{18}$$

Obviously, when N is very large (and number of atoms are generally very large numbers), this one extra matrix element will not affect the majority of the eigenvalues, so the eigenvalues with and without periodic boundary conditions should virtually identical. If you solve this matrix you find out that the eigenvalues always lie on the curve that is obtained when $N \to \infty$.

So what is missing here? The essential ingredient is translational symmetry. Although we are all attached to real space, it is the periodicity that is really important. When there are milemarkers along the road, you do not say there is a mile marker at 1 mile, and one a 2 miles, and one at 3 miles. You say there is a mile marker every 1 mile. In a more mathematical term, we should be considering Fourier transforms. The quantity that is related to space by Fourier transform is momentum (the other important dimension is time, which is related to frequency by Fourier transform, which, in quantum mechanics is directly related to energy). In free space, space is continuous, and therefore the momentum is continuous as well. Conservation of momentum in classical mechanics is inherently related to the translational symmetry of space. When we go to a solid, the translational symmetry of space is no longer continuous, but related to the interatomic distances and therefore discrete. We applied periodic boundary conditions so we need to satisfy:

$$e^{ik(x+L)} = e^{ikx} \tag{19}$$

where the length of the chain is $L = Na$, with a the distance between the atoms. This means is we displace ourselves by L (the lenght of the chain), we end up at the same position due to the periodic boundary conditions. This implies that

$$kL = \pm 2n\pi \Rightarrow k = \pm \frac{2n\pi}{L}, \tag{20}$$

where n is an integer. This would lead to an infinite amount of wavenumbers k. This is not entirely correct. Before doing a Fourier transform, we had N orbitals, one for each site. After the Fourier transform, we should still end up with the same number of states. Therefore, since we have positive and negative numbers, the maximum n is $N/2$. The allowed k values are therefore

$$k = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \pm\frac{\pi}{a}. \tag{21}$$

So we only have k values in the region $[-\frac{\pi}{a}, \frac{\pi}{a}]$. You might wonder what happened to all the other k values. From a point a view of periodicity, they are exactly equivalent. Figure 2 shows a comparison between e^{ikx} and $e^{i(k+2\pi/a)x}$ (where for the example k is taken 0.3π). Although the function are of course different, the have the same values at the sites of the atoms (indicated by the blue dots). However, you might remember from Fourier analysis that you often need all k values to build special functions (e.g. a square or a delta function) and there might be structure in the wavefunction that Fourier components with a larger k value. However, the k is only related the periodic part of the wavefunction. These smaller structures are related to the atomic part of the wavefunction

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \varphi(\mathbf{r} - \mathbf{R}). \tag{22}$$

Note that the Fourier transform only includes the values of the exponentials at the atomic positions. Therefore, any $k + 2\pi n$, with n and integer, is equivalent to k. Essentially, this is a unitary transformation of N wavefunction in real space to a $\mathbf{k}$ dependent basis. We can also inverse this procedure

$$\varphi(\mathbf{r} - \mathbf{R}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \varphi_{\mathbf{k}}(\mathbf{r}). \tag{23}$$

We can also write this in bra-ket notation

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |\mathbf{R}\rangle \quad \text{and} \quad |\mathbf{R}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} |\mathbf{k}\rangle. \tag{24}$$

We now want to understand what the Hamiltonian looks like in this new basis set. Let us first rewrite the Hamiltonian in bra-ket notation in real space. Note that

$$|\mathbf{R}_i\rangle\langle\mathbf{R}_j| = \begin{matrix} \\ i \rightarrow \end{matrix} \begin{pmatrix} 0 \\ \cdot \\ \cdot \\ 0 \\ 1 \\ 0 \\ \cdot \end{pmatrix} \begin{matrix} \\ (0, 0, \cdots, 0, 1, 0, \cdots) \\ \uparrow \\ j \end{matrix} = \begin{matrix} \\ i \rightarrow \end{matrix} \begin{pmatrix} & \cdot & \cdot & \cdot & \\ \cdots & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 1 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & \cdots \\ & \cdot & \cdot & \cdot & \end{pmatrix} \begin{matrix} \\ \\ \\ \\ \\ \uparrow \\ j \end{matrix} \tag{25}$$

using this we can rewrite the matrix in Eqn. (18)

$$H = \sum_{\mathbf{R},\mathbf{R}'} |\mathbf{R}'\rangle\langle\mathbf{R}'|H|\mathbf{R}\rangle\langle\mathbf{R}| = -t \sum_{\mathbf{R}\boldsymbol{\delta}} |\mathbf{R} + \boldsymbol{\delta}\rangle\langle\mathbf{R}|, \tag{26}$$

where $\boldsymbol{\delta}$ is a vector connecting $\mathbf{R}$ to its nearest neighbors (the atoms left and right of the atom in a chain). The Fourier transform can be made by inserting the definitions into the Hamiltonian:

$$H = = -t \sum_{\mathbf{R}\boldsymbol{\delta}} \frac{1}{N} \sum_{\mathbf{k},\mathbf{k}'} e^{-i\mathbf{k}\cdot(\mathbf{R}+\boldsymbol{\delta})} |\mathbf{k}\rangle\langle\mathbf{k}'| e^{i\mathbf{k}'\cdot\mathbf{R}} \tag{27}$$

$$= -t \sum_{\mathbf{k},\mathbf{k}'} \left(\frac{1}{N} \sum_{\mathbf{R}} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}} \right) \left(\sum_{\boldsymbol{\delta}} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \right) |\mathbf{k}\rangle\langle\mathbf{k}'| \tag{28}$$

$$= \sum_{\mathbf{k},\mathbf{k}'} \delta_{\mathbf{k},\mathbf{k}'} \varepsilon_{\mathbf{k}} |\mathbf{k}\rangle\langle\mathbf{k}'|. \tag{29}$$

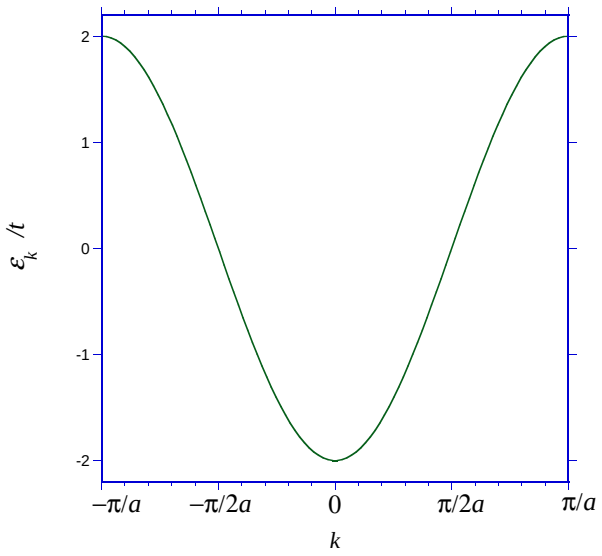


FIG. 3: The eigenenergies for a single tight-binding band $\varepsilon_k = -2t\cos k$ as a function of k.

We see that the Hamiltonian is diagonal in $\mathbf{k}$ due to the delta function. The diagonal matrix elements (which are directly the eigenvalues) are given by

$$\varepsilon_{\mathbf{k}} = -t\sum_{\boldsymbol{\delta}} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}}. \tag{30}$$

The nearest-neighbor vectors for a chain in the x-direction are given by $\delta = \pm a\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ is a unit vector in the x-direction.

$$\varepsilon_{\mathbf{k}} = -t(e^{ika} + e^{-ika}) = -2t\cos ka, \tag{31}$$

where $\mathbf{k} = k\hat{\mathbf{x}}$. Since goes from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$, the eigenvalues lie on a cosine between $-2t$ and $2t$, see Fig. 3.

V. NEARLY FREE-ELECTRON MODEL

AM Chapter 9

In free space in the Schrödinger equation is given by

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{32}$$

The solution is well known and the eigenfunction are simple plane waves

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{33}$$

where V is the size of the system. The eigenvalues are

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2\mathbf{k}^2}{2m} \tag{34}$$

Again, we can apply periodic boundary condition, see Eqn. (21), giving

$$k_i = \pm\frac{2\pi n}{L} \quad \text{with } n \text{ integer.} \tag{35}$$

Note that so far there is no restriction on the k values to the range $[-\frac{\pi}{a}, \frac{\pi}{a}]$. The only thing we have done so far is put the particles in a box, which is not yet a solid. The system becomes a solid by introducing the potential $U(r)$ due

to the nuclei that are arrange in a periodic structure. In general, we can express any arbitrary potential in a Fourier series

$$U(\mathbf{r}) = \sum_{\mathbf{k}} U_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{36}$$

However, we want to impose that the potential satisfies the periodicity of the lattice. Therefore, the potential should be equivalent when moving to a different lattice site by the vectors $\mathbf{R}$ that indicate the lattice sites:

$$U(\mathbf{r}+\mathbf{R}) = \sum_{\mathbf{k}} U_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{k}\cdot\mathbf{R}} U(\mathbf{r}). \tag{37}$$

This is not going to work for any arbitray wavevector $\mathbf{k}$. The vectors $\mathbf{K}$ that satisfy this are known as reciprocal lattice vectors

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1. \tag{38}$$

These vectors return again and again since they are intimately related to the translational symmetry of the crystal. We will discuss in more detail later on how to obtain these reciprocal lattice vectors and discuss various cases for different crystals. (and you might remember them from 566/666 or x-ray diffraction). Let us just satisfy ourselves that these vectors exist and only consider the case of one dimension

$$e^{iKa} = 1 \quad \Rightarrow \quad K = \pm\frac{2\pi n}{a}. \tag{39}$$

Note that since a is much smaller than L, the K are much larger the separation between the k values. In general, the periodic potential is therefore given by

$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}. \tag{40}$$

The matrix elements between different running waves are given by

$$\langle \mathbf{k}'|U|\mathbf{k}\rangle = \sum_{\mathbf{K}} \frac{1}{V}\int dx e^{-i\mathbf{k}'\cdot\mathbf{r}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\mathbf{K}} U_{\mathbf{K}} \frac{1}{V}\int d\mathbf{r} e^{-i(\mathbf{k}'-\mathbf{K}-\mathbf{k})\cdot\mathbf{r}} = \sum_{\mathbf{K}} U_{\mathbf{K}}\delta_{\mathbf{k}',\mathbf{k}+\mathbf{K}}. \tag{41}$$

In bra-ket notation, we can write the potential as

$$U = \sum_{\mathbf{kK}} U_{\mathbf{K}} |\mathbf{k}+\mathbf{K}\rangle\langle\mathbf{k}| \tag{42}$$

This has the importance consequence that a running wave with wavevector k is coupled to the running waves with wavevectors $k \pm 2\pi n/a$ with $n = 0, 1, 2, 3, \cdots$, see Fig. 4. However, this also means that k is no longer a good quantum number. The periodic potential reduces the k values that are good quantum numbers. Although we are free to choose the k values, generally the region $[-K/2, K/2] = [-\pi/a, \pi/a]$ is chosen. The wavevectors inside this region do not couple to each other with the periodic potential. In addition, any wavevector outside this region is coupled to one inside by a reciprocal lattice vector K. The allowed k values are therefore equivalent to those found in Eqn. (21) when discussing the tight-binding model.

Since only the $\mathbf{k}$ values separated by a reciprocal lattice vector $\mathbf{K}$ couple, we can write the eigenfunctions as a linear combination of these running waves

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}, \tag{43}$$

where $c_{\mathbf{k}-\mathbf{K}}$ is a coefficient. For each $\mathbf{k}$, we find a set of coupled equations

$$\varepsilon_{\mathbf{k}-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}+\mathbf{K}'} = E c_{\mathbf{k}-\mathbf{K}}. \tag{44}$$

Note that this reproduces to $E = \varepsilon_{\mathbf{k}-\mathbf{K}}$ in the absence of a periodic potential.

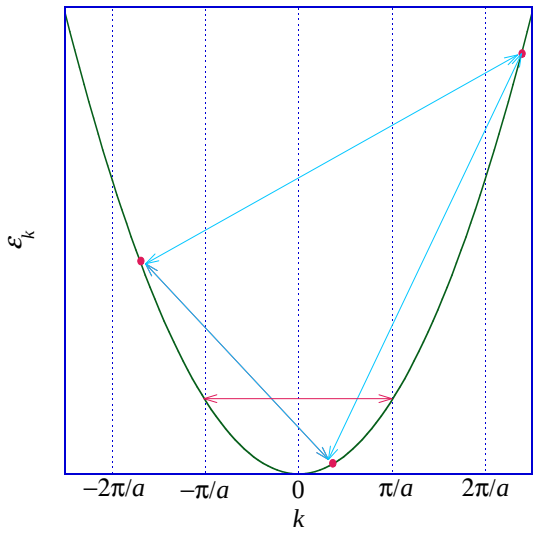


FIG. 4: The scattering of electrons between different running waves e^{ikx} due to a periodic potential resulting from nuclei in a chain at a distance a from each other. The potential couples k values with each other that are $K = \pm 2\pi n/a$ apart. The blue arrows show this scattering for an arbitrary k value (Note that only three k points are included). The red arrow shows the particular case for $k = \pm\frac{\pi}{a}$. This is a Bragg reflection and the electrons scatters to $k = \mp\frac{\pi}{a}$ which has exactly the same energy ε_k.

This model is known as the nearly-free electron model and is generally use only in the case the the periodic potential is weak (such as K, Na, and Al metals). However, even a weak potential can have a large influence if the energy separation of the states that if couples is small (or even zero). For the energy difference to be zero we require

$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}-\mathbf{K}} \quad \Rightarrow \quad k^2 = (\mathbf{k}-\mathbf{K})^2 = k^2 - 2\mathbf{k}\cdot\mathbf{K} + K^2, \tag{45}$$

or

$$\mathbf{k}\cdot\mathbf{K} = \frac{1}{2}K^2. \tag{46}$$

Some of you might recognize this as the Laue condition for x-ray diffraction (which, of course is equivalent to the Bragg condition). In principle, this should not be a surprise. X-rays are scattered by a lattice through repeated interaction with the nuclei. The same applies to electrons. In one dimension, $\mathbf{k}$ and $\mathbf{K}$ are either parallel or antiparallel and we find $k = \pm\frac{1}{2}K$.Let us consider $K = 2\pi/a$, for which $k = K/2 = \pi/a$ should have the same energy as $k - K = -\pi/a$, which is indeed correct. The effect are therefore strongest close to the k values indicated by the dotted lines in Fig. 4. In this region, we can neglect the coupling to other running waves if $|\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{K}}| \gg U$. We are then left with solving the determinant

$$\begin{vmatrix} \varepsilon_{\mathbf{k}} - E & U_{\mathbf{K}} \\ U^*_{\mathbf{K}} & \varepsilon_{\mathbf{k}-\mathbf{K}} - E \end{vmatrix} = 0. \tag{47}$$

This leads to the quadratic equation

$$(\varepsilon_{\mathbf{k}} - E)(\varepsilon_{\mathbf{k}-\mathbf{K}} - E) - |U_{\mathbf{K}}|^2 = 0, \tag{48}$$

which has the solutions

$$E = \frac{\varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{k}-\mathbf{K}}}{2} \pm \sqrt{\left(\frac{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}-\mathbf{K}}}{2}\right)^2 + |U_{\mathbf{K}}|^2}. \tag{49}$$

In the limit that $\varepsilon_{\mathbf{k}} \cong \varepsilon_{\mathbf{k}-\mathbf{K}}$, we obtain

$$E = \varepsilon_{\mathbf{k}} \pm |U_{\mathbf{K}}|. \tag{50}$$

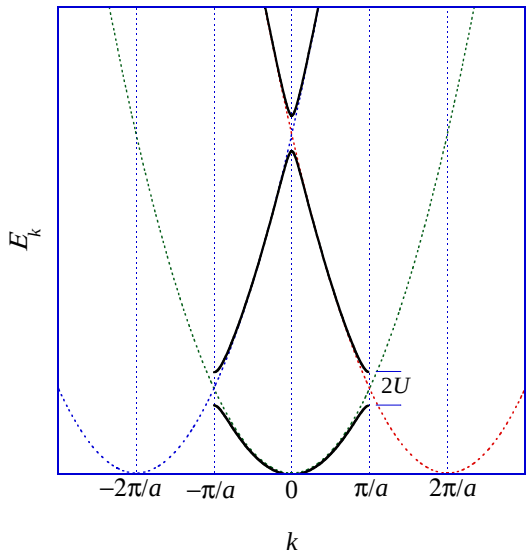


FIG. 5: Calculation of the bands in a nearly-free electron model. Shown are the energies ε_k and ε_{k+K} with $K = \pm\frac{2\pi}{a}$. The calculated nearly-free electron bands are shown for the region $[-K/2, K/2] = [-\frac{\pi}{a}, \frac{\pi}{a}]$

We see that an energy gap opens at the $k = \pm\frac{1}{2}K$. We can also verify that in this limit

$$\frac{\partial E}{\partial \mathbf{k}} = \frac{\hbar^2}{m}(\mathbf{q} - \frac{1}{2}\mathbf{K}), \tag{51}$$

i.e. the derivative is zero on the Bragg planes and the bands are therefore flat. (Not entirely surprising since we just demonstrated that a gap opens, so the bands must be either in a maximum or a minimum).

We can extend this procedure to include additional reciprocal lattice vectors K. Let us consider the situation in one dimension for $K = 0$ and $K_\pm = \pm\frac{\pi}{a}$. We can also use the following properties of the potential. Since the potential is real, we have

$$U_{-\mathbf{K}} = U^*_{\mathbf{K}}. \tag{52}$$

If in addition, we have inversion symmetry (meaning that the system is unchanged when $\mathbf{r} \to -\mathbf{r}$, which is the case for a linear chain), we also have

$$U_{-\mathbf{K}} = U_{\mathbf{K}} = U^*_{\mathbf{K}}. \tag{53}$$

Using this we can write down the Hamiltonian.

$$H = \begin{pmatrix} \varepsilon_k & U_K & U_K \\ U_K & \varepsilon_{k-K_-} & U_{2K} \\ U_K & U_{2K} & \varepsilon_{k-K_+} \end{pmatrix}. \tag{54}$$

The results are given in Fig. 5. Note that the energies $\varepsilon_{k-K_\pm} = \hbar^2(k - K_\pm)^2/2m$ look in the region $[-K/2, K/2]$ as parabolas centered around $K_\pm$. The eigenvalues of H can be easily solved numerically. The values for E_{kn}, where $n = 1, 2, 3$ is the bandindex are plotted in the region $[-K/2, K/2]$. We have taken $U_K = U_{2K}$. This is known as the reduced-zone scheme, see AM Fig. 9.4). This is the scheme commonly used is the scientific literature. Figure 9.4 also shows the extended-zone scheme and the repeated-zone scheme. In particular, the extended-zone scheme looks natural at first. It looks like the original parabola with gaps opened at the reciprocal lattice vectors K. However, this clings too much to the free-electron like picture and in some sense is slightly misleading. It is important to note that in a chain of N atoms, there are only N k-values that are good quantum numbers. Convention dictates that these N k-values are chosen in the region $[-K/2, K/2]$. This region is known as the first Brillouin zone. All the other k-values are not good quantum number. For example, $k = 2.3\pi/a$ is not a good k value since it is coupled by the periodic potential to $k = 0.3\pi/a$. This directly implies that we have more eigenstates than k-values. This is why there is another quantum number, the band index n. All eigenstates $E_{\mathbf{k}n}$ are identified by the value of k in

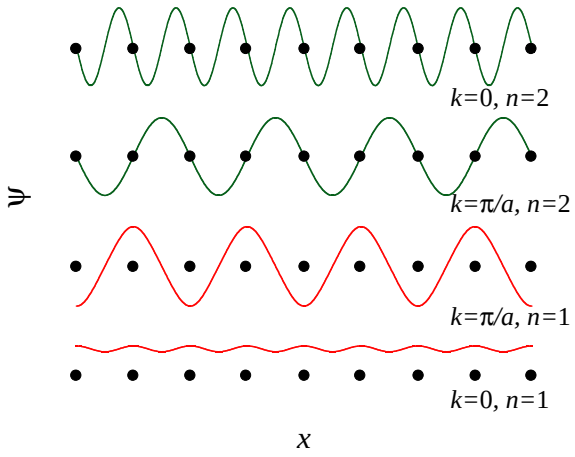


FIG. 6: The wavefunction of the nearly-free electron eigenstates for four eigenvalues $E_{0,1}$, $E_{\frac{\pi}{a},1}$, $E_{\frac{\pi}{a},2}$, and $E_{0,2}$. We have assumed $U_K < 0$ and $U_{2K} > 0$.

the region $[-K/2, K/2]$ and the band index n. Because of the mixing, we can no longer identify eigenstates with the free-electron bands. Even at $k = 0$, we have, for the lowest eigenfunction in Fig. 5,

$$|E_{k=0,1}\rangle = a|k\rangle - \sqrt{1-a^2}(|k-K_-\rangle + |k-K_+\rangle), \tag{55}$$

where $a \cong 1$ (actually $a = 0.9978$ for the example in the figure). Indeed close to $|k\rangle$, but still mixed with $|k \pm K_\pm\rangle$. The repeated-zone scheme has its uses from time to time, as long as you keep in mind that it just repeats the same information as is already contained in the first Brillouin zone and nothing new is added.

VI. COMPARISON OF RESULTS FOR TIGHT-BINDING AND NEARLY-FREE ELECTRON MODEL

In this section, we will compare the results from tight-binding and the nearly-free electron model. At first, this looks like a pointless excersize. For tight-biding we find a single band given $E_k = -2t\cos ka$. For the nearly-free electron model we have several bands which originate from free electron parabolas. Although, we are not going to make the claim that the two are exactly equivalent, they have more in common that you might think at first sight. The tight-binding model starts from atomic states which include the potential of the nucleus fully and then starts adding the kinetic energy due to the delocalization of the electrons when the solid is formed. The nearly-free electron model starts from completely delocalized electron and starts adding the effect of the potential of the nuclei. Somewhere along the way to two must have something in common. (They will never be entirely equivalent, since the treatment of the potential in the nearly-free electron is somewhat oversimplified. The inclusion of only two Fourier compoments, U_K and U_{2K}, is obviously insufficient to describe the much more complicated shape of the potential.

Let us start by looking at the eigenfunctions in the nearly-free electron model. Let us start with the one with the lowest energy. The eigenfunction is given in Eqn. (55). This gives a wave in real space for $k = 0$ and $n = 1$,

$$\psi_{0,1}(x) = \frac{1}{\sqrt{L}}(a - 2\sqrt{1-a^2}\cos Kx). \tag{56}$$

In the case that $a = 1$ (i.e., the limit $U = 0$), we just obtain that $psi_{0,1} = \frac{1}{\sqrt{L}}$ constant throughout the system. The higher-order oscillation are a result of the (small) mixing in of the $K_\pm$ terms.

Effect are more drastic around $k = K_\pm/2$. Let us take $k = K_+/2 = \frac{\pi}{a}$. Here we obtain mixing of the free-electron states ε_k and $\varepsilon_{k-K_+/2}$, as we have solved in Eqn. (47) (we can neglect $\varepsilon_{k+K/2}$ which is at higher-energies). The wavefunction are

$$\psi_{\frac{\pi}{2},i}(x) = \frac{1}{2\sqrt{L}}(e^{i\frac{\pi}{a}x} \mp \mathrm{sgn}(U_K)e^{i\frac{\pi}{a}x}). \tag{57}$$

with $i = 1, 2$. The wavefunctions depend on the sign of the coupling. Let us consider the situation $U_K < 0$, shown in

Fig. 116, which gives

$$\psi_{\frac{\pi}{2},i}(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\frac{\pi}{a}x \\ i\sqrt{\frac{2}{L}}\sin\frac{\pi}{a}x \end{cases} \tag{58}$$

We see that $\psi_{\frac{\pi}{2},1}(x)$ has extrema on the positions of the nuclei, whereas $\psi_{\frac{\pi}{2},2}(x)$ has nodes on the positions of the nuclei. This is reminescent of atomic physics: s orbitals have their maxima at the nucleus, whereas, for example the p_x orbital has a node at the nucleus. From this we can understand one origin of the discrepance between our tight-binding and nearly-free electron calculation. In our tight-binding calculation, we only included s orbitals, so we only get one bandw hich resembles the lowest band of the nearly-free electron calculation, but not the higher-lying band. On the other hand, we also see that the effect of folding the free-electron bands is to create "orbital-like" structure related to the nuclei. For the highest energy of the second band ($n = 2$), the wavefunction has nodes not only at the nuclei, but also between the nuclei, see Fig. 116.

However, we see that we can create a better connection between the two approaches by including p type orbitals. Let us try to extend our tight-binding approach, following the approach by Slater and Koster, Phys. Rev. B **94**, 1498 (1954). We adjust Eqn. (22) to allow the inclusion of more orbitals

$$\varphi_{\mathbf{k},s}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\varphi_s(\mathbf{r}-\mathbf{R}). \tag{59}$$

The dispersion for these states, we found to be

$$\varepsilon_k^{ss} = 2(ss\sigma)\cos k \qquad \text{with} \qquad (ss\sigma) = \int d\mathbf{r}\varphi_s(\mathbf{r}-\mathbf{R}')H\varphi_s(\mathbf{r}-\mathbf{R}) \tag{60}$$

where $\mathbf{R}$ and $\mathbf{R}'$ are nearest neigbors and $(ss\sigma) = -t$ (using the notation by Slater and Koster indicating that the matrix element is between two s orbitals; the σ indicates the type of bonding. There are also π and δ bonding, but that is not relevant for the discussion here). We can repeat this approach for p orbitals giving

$$\varphi_{k,p}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\varphi_p(\mathbf{r}-\mathbf{R}) \tag{61}$$

with energies

$$\varepsilon_{\mathbf{k}}^{pp} = 2(pp\sigma)\cos k. \qquad \text{with} \qquad (pp\sigma) = \int d\mathbf{r}\varphi_p(\mathbf{r}-\mathbf{R}')H\varphi_p(\mathbf{r}-\mathbf{R}) \tag{62}$$

This looks similar, but there is an important difference. For typical Hamiltonians H, the matrix elements are negative when the positive lobes are pointing to each other. This is always the case for the s orbital which is positive everywhere

$$\cdots(+)(+)(+)(+)(+)(+)(+)(+)\cdots, \tag{63}$$

where $(+)$ schematically indicates an s orbital at a certain site. This is the state found for $k = 0$ (and energy $\varepsilon_k = 2(s\sigma) < 0$). Note that this is positive everywhere just as the nearly-free electron wavefunction for $k = 0$ and $n = 1$ in Fig. 116. For $k = \frac{\pi}{a}$ (and energy $\varepsilon_k = -2(s\sigma) > 0$), the exponential changes sign at each site, giving

$$\cdots(+)(-)(+)(-)(+)(-)(+)(-)\cdots. \tag{64}$$

This has nodes between the nuclei, just as the wavefunction for $k = \frac{\pi}{a}$ and $n = 1$.

The p orbital on the other hand have a node

$$\cdots(-+)(-+)(-+)(-+)(-+)(-+)(-+)(-+)\cdots \tag{65}$$

The convention we choose is that the postive lobe of the p orbital $(-+)$ is in the positive x direction (we can choose any convention that we like, but in the end it should lead to the same results). In this convention, we see that the positive lobes are pointing towards the negative lobes. The matrix elements are therefore negative. This also has as a consquence that the solution with the lowest energy is the one where the sign changes for each sites, i.e.

$$\cdots(-+)(+-)(-+)(+-)(-+)(+-)(-+)(+-)\cdots \tag{66}$$

However, this looks nice since the positive lobes are pointing towards the positive lobes and the negative lobes are pointing towards the negative lobes. This is essentially the bonding state with no nodes between the nuclei. This corresponds well with the lowest $n = 2$ nearly-free electrons solution for $k = \frac{\pi}{a}$ (alternating signs), which also has no nodes between the nuclei. The state with the higher energy is given in Eqn. (65), where there are nodes between the nuclei, comparable to the nearly-free electron wavefunction for $k = 0$ and $n = 2$ in Fig. 116.

We can also compare the dispersion. In order to do this, we need to overcome one more hurdle, namely the matrix elements between s and p are not zero,

$$(sp\sigma) = \int d\mathbf{r}\varphi_s(\mathbf{r} - \mathbf{R}')H\varphi_p(\mathbf{r} - \mathbf{R}). \tag{67}$$

The dispersion does not follow a cosine dependence since an s orbital, in our convention, couples differently to the left and the right

$$\cdots(-+)(+)(-+), \tag{68}$$

a problem that did not arise when dealing with just s orbitals. Following Eqns. (30) and (31), we find

$$\varepsilon_k^{sp} = (sp\sigma)(e^{ika} - e^{-ika}) = 2i(sp\sigma)\sin ka. \tag{69}$$

We now have a basis $(\psi_{k,s}, \psi_{k,p})$ giving a matrix

$$H = \begin{pmatrix} \varepsilon_k^{ss} & \varepsilon_k^{sp} \\ (\varepsilon_k^{sp})^* & \varepsilon_k^{pp} \end{pmatrix} \tag{70}$$

Figure 7 gives a comparison between the lowest two bands ($n = 1, 2$) in the nearly-free electron model and the s and p tight-binding model. The fit has been done by eye. Although a perfect fit cannot be expected due to the different approximations, it is clear that they are giving comparable physics.

Although, at first sight, it might seem surprising that similar physics comes out of a model starting with free electrons and a model starting from atomic orbitals. A comparison between tight-binding and nearly-free electron model can be given as follows:

	tight binding	**nearly free electronmodel**
starting point	atomic properties	kinetic energy of the electrons
basis functions	atomic orbitals	plane waves
$k = \pm n\frac{2\pi}{L}$	periodic boundary conditions	periodic boundary conditions
$k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$	N atoms give N k values or $\frac{N}{2}\frac{2\pi}{L} \leq k \leq \frac{N}{2}\frac{2\pi}{L}$	periodic potential couples k values that differ by $K = n\frac{2\pi}{a}$
number of bands	equals number of atomic orbitals	equal number of reciprocal lattice vectors
approximations	neglect orbitals	$U_K = 0$ for large K

(71)

However, when you think more of it, in principle it should not make a difference. The starting wavefunctions are just a basis. If my basis is complete (i.e. you can express any arbitrary wavefunction in your basis, a statement you might remember from Fourier analysis) then solving the same Hamiltonian should give the same eigenfunction and eigenenergies, regardless of the basis we started with. Differences do arise because we start making approximations along the way:

- The free-electron model is beautiful as a basis (exponentials are the foundation of Fourier analysis): they are orthogonal and complete. The tight-binding basis set is more problematic. In principle, the solutions of the Hydrogen atom form a complete basis which is orthogonal. However, this is not what we are doing. We are taking the solution and putting them on different sites. This basis set is not even orthogonal.

- The potential of the nuclei is much better treated in the tight-binding model. There is one important caveat: in general we are not dealing with Hydrogen atom. The potential is treated much more poorly in the nearly-free electron model. So far, we have included only two Fourier terms. Obviously, this will give a sinosoidal potential and not the $1/r$ potential that one would expect from the nuclei. However, in principle nothing prevents us from including all Fourier components. Then again, this defeats the purpose of a nearly-free electron model.

Summarizing, although the nearly-free electron usually takes pride of place in most textbooks over the tight-binding model (in that it is usually treated in an earlier chapter), the tight-binding model wins out in practicality. Tight-binding is often used in the scientific literature. The electronic structure is nowadays generally calculated with complex

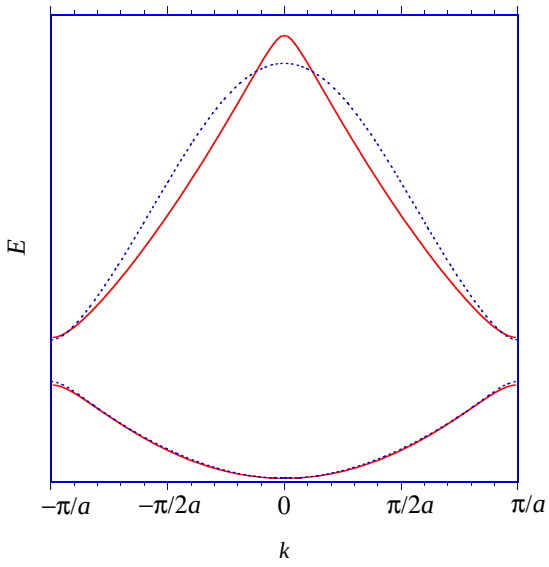


FIG. 7: Comparison of the two bands lowest in energy ($n = 1, 2$) in a nearly-free electron with a tight-binding calculation including an s and a p orbital.

codes that have been developed over many years. However, one often would like to use the output of such calculations as the input for other calculations (for the experts, for example, many-body calculations or molecular dynamics). This is usually done by making a tight-binding fit to the more sophisticated electronic structure calculations. Nearly-free electron models are used much less often (typing in tight-binding on Physical Review online yielded more 3500 papers, whereas nearly-free electron gave less than 300 papers). One of the reasons is that it works well for only a few systems, usually involving s and sometimes p orbitals. One might actually wonder why it works at all. One needs that the nucleus is very well screened. One has to realize that most electrons in a solid are very strongly bound to the nucleus and only the electrons in the outer shells really form bands. However, this inner shell electrons can effectively screen the nucleus. They are effectively a negative charge compensating the positive charge of the nucleus.

VII. FORMALIZATION: BLOCH THEOREM

AM Chapter 8

In the chaper on the nearly-free electron model we saw that the wavefunction can be written as, copying Eqn. (43),

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}. \tag{72}$$

Since the exponentials form a complete basis set (which means we should be able to express any function in them), this is a general statement. We can therefore express all eigenstates with eigenenergies $E_{n\mathbf{k}}$ in this fashion. We also saw that $\mathbf{k}$ is a good quantum number in a crystal. Let us therefore separate the part related to $\mathbf{k}$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{K}} c^n_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad u_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c^n_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}. \tag{73}$$

This shows that the eigenfunction can be expressed in a plane-wave part $e^{i\mathbf{k}\cdot\mathbf{r}}$ and a function $u_{n\mathbf{k}}(\mathbf{r})$. The interesting property of the latter is that it has the periodicity of the lattice

$$u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = \sum_{\mathbf{K}} c^n_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot(\mathbf{r}+\mathbf{R})} = u_{n\mathbf{k}}(\mathbf{r}), \tag{74}$$

since $e^{-i\mathbf{K}\cdot\mathbf{R}} = 1$. This is related to the orbital structure that we obtained when folding k values back into the first Brillouin zone (in one dimension, the region $[-K/2, K/2]$. An alternative way of expressing Bloch's theorem is

$$\psi_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R})} u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n\mathbf{k}}(\mathbf{r}). \tag{75}$$

That is nice you might say, but what does it physically mean? Let us consider free space. We know that the solutions are given by plane waves

$$\psi_{\mathbf{k},\text{free}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{76}$$

Free space is uniform. Therefore, we expect that the probability of finding an electron is equal everywhere. This is the case since $|\psi_{\mathbf{k},\text{free}}|^2 = 1/V$ everywhere (some of you might say that the probability does not have to be constant: we can make wavepackages. This is correct, but you might also remember that wave packages are not eigenstates in free space). However, even though the probability is constant, the wavefunction can still pick up a phase. Under a displacement $\boldsymbol{\tau}$, we have

$$\psi_{\mathbf{k},\text{free}}(\mathbf{r}+\boldsymbol{\tau}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot(\mathbf{r}+\boldsymbol{\tau})} = e^{i\mathbf{k}\cdot\boldsymbol{\tau}} \psi_{\mathbf{k},\text{free}}(\mathbf{r}). \tag{77}$$

In a solid, we do not expect the probability to be uniform in space. On the contrary, it is very natural to expect that the probability is higher closer to the nuclei where the electron feel and attractive potential. So we do not expect something for an arbitrary vector $\boldsymbol{tau}$. However, we do expect that the probability is exactly the same when we displace ourselves by a lattice vector $\mathbf{R}$. After all, the solid looks exactly the same again. This is the underlying physics of Eqn. (75). In a solid, under displament of $\mathbf{R}$, the only change to the wavefunction can be a phase factor.

Does the Bloch theorem also hold for tight-binding wavefunctions that look different from Eqn. (72), see Eqn. (22). Let us check

$$\begin{aligned} \varphi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}') &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \varphi(\mathbf{r}+\mathbf{R}'-\mathbf{R}) \\ &= \frac{1}{\sqrt{N}} e^{i\mathbf{k}\cdot\mathbf{R}'} \sum_{\mathbf{R}-\mathbf{R}'} e^{i\mathbf{k}\cdot(\mathbf{R}-\mathbf{R}')} \varphi(\mathbf{r}+\mathbf{R}'-\mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}'} \varphi_{\mathbf{k}}(\mathbf{r}), \end{aligned} \tag{78}$$

which is Bloch's theorem.

VIII. CRYSTAL STRUCTURES

AM Chapters 4-7

In this section, we will briefly repeat some of the important aspects of the crystal structure. This has been treated extensively in 566. In the previous sections, we studied a simple one-dimensional chain consisting of one type of atom. Taking this chain along the x-direction, we can build up this chain by taking multiples of a primitive vector that gives the vector needed to go from lattice site into another

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \quad \Rightarrow \quad \mathbf{R} = n\mathbf{a}_1 \quad \text{with} \quad n = \cdots, -2, -1, 0, 1, 2, \cdots \tag{79}$$

However, more important for our considerations of the periodic potential was not so much the real space position of the atoms, but their effect on reciprocal space. This is directly related to the fact that momentum $\mathbf{k}$ is a good quantum number. Translational symmetry of the potential imposed, reproducing Eqn. (82),

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1. \tag{80}$$

In one dimension this gives reciprocal lattice vectors, which again can be expressed in a unit vector

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}} \quad \Rightarrow \quad \mathbf{K} = n\mathbf{b}_1 \quad \text{with} \quad n = \cdots, -2, -1, 0, 1, 2, \cdots \tag{81}$$

It is easy to see that $\mathbf{R}$ and $\mathbf{K}$ satisfy the condition $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$. In condensed-matter physics, one is dealing more often with three-dimensional systems. Again, we can built up a crystal starting from the primitive vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$. For a simple cubic system, these are given by $\mathbf{a}_1 = a\hat{\mathbf{x}}$, $\mathbf{a}_2 = a\hat{\mathbf{y}}$, and $\mathbf{a}_3 = a\hat{\mathbf{z}}$. Often however the crystal structures are more complicated, such as face-centered cubic or body-centered cubic. (This is for a large part related to the fact that simple cubic is not close packed. Try obtaining a simple cubic lattice by throwing marbles in a box ...). The crystal structures that are built up are called Bravais lattices. Often the primitive vectors are insufficient to generate the crystal lattice and instead of having one atom at the positions $\mathbf{R}$, one has several. Simple examples

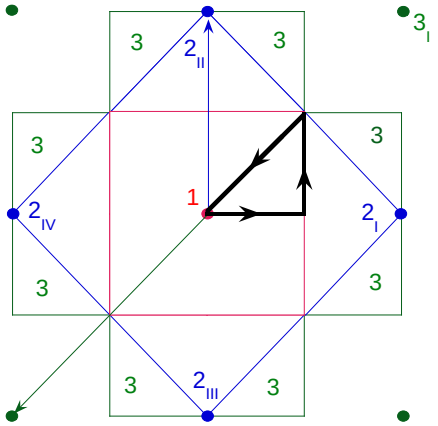


FIG. 8: The first three Brillouin zones for a square lattice.

are graphite, which has a honeycomb lattice and Si and diamond, which have a diamond lattice. However, despite their added complexity, one still needs to satisfy the condition $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$. This can be done by defining the primitive vectors

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}. \tag{82}$$

The vectors $\mathbf{b}_2$ and $\mathbf{b}_3$ can be obtained by cyclic rotation, i.e $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$. Note tha $\mathbf{a}_2 \cdot \mathbf{b}_1 = 0$ and $\mathbf{a}_3 \cdot \mathbf{b}_1 = 0$, since the outer product makes $\mathbf{b}_1$ perpendicular to $\mathbf{a}_2$ and $\mathbf{a}_3$. In addition, $\mathbf{a}_1 \cdot \mathbf{b}_1 = 2\pi$, and therefore the condition $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ is satisfied. It is important to remember that for the electronic structure, the most dramatic effects due to the periodic potential do not happen at the reciprocal lattice vectors $\mathbf{K}$ but at the points in reciprocal space where the Bragg condition, see Eqn. (46)

$$\mathbf{k} \cdot \mathbf{K} = \frac{1}{2}K^2, \quad \text{or} \quad \mathbf{k} \cdot \hat{\mathbf{K}} = \frac{1}{2}K, \tag{83}$$

where is $\hat{\mathbf{K}}$ is a unit vector in the direction of $\mathbf{K}$, is satisfied.

IX. FREE ELECTRON IN TWO DIMENSIONS

Let us consider the nearly-free electron model in two dimensions for a square lattice. A square lattice can be generated by the primitive vectors

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \quad \text{and} \quad \mathbf{a}_2 = a\hat{\mathbf{y}} \quad \Rightarrow \quad \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2. \tag{84}$$

The reciprocal lattice vectors satisfying $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ are also easily obtained

$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}} \quad \text{and} \quad \mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}} \quad \Rightarrow \quad \mathbf{K} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2. \tag{85}$$

We will be calculating the electronic structure in the first Brillouin zone. Although we will consider the other Brillouin zones to try to connect to the free-electron model, it is important to get used to working in the first Brillouin with only the $\mathbf{k}$ vectors that are good quantum numbers for the system. Virtually all sophisticated electronic structure programs work only in the first Brillouin zone. For the one-dimensional chain, the first Brillouin zone was the region $[-\frac{\pi}{a}, \frac{\pi}{a}]$, where the k-points $\pm\frac{\pi}{a}$ satisfy the Bragg condition $k = \frac{1}{2}K$, see Eqn. (83). To find the first Brillouin zone in two dimensions, we need to find the k points that satisfy the Bragg condition. Obviously, we need to unclude the reciprocal lattice vector $\mathbf{K} = 0$. The next reciprocal lattice vectors are $\pm\frac{2\pi}{a}\hat{\mathbf{x}}$ and $\pm\frac{2\pi}{a}\hat{\mathbf{y}}$. This leads to the following Bragg condition in the x-direction

$$\mathbf{k} \cdot (\pm\hat{\mathbf{x}}) = \frac{1}{2}\frac{2\pi}{a} \quad \Rightarrow \quad k_x = \pm\frac{\pi}{a}. \tag{86}$$

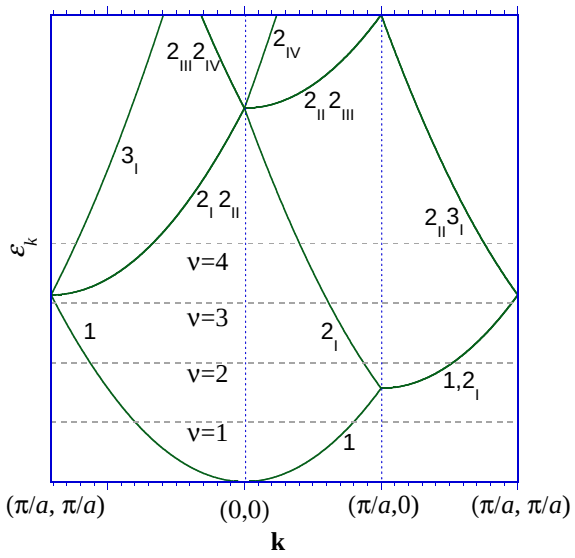


FIG. 9: The free-electron bands in two dimensions along particular directions indicated in Fig. 8.

Note that there is no restriction on k_y. The Bragg condition is therefore satisfied for all points $(0, \pm\frac{\pi}{a})$. This point is more general. The condition $\mathbf{k}\cdot\hat{\mathbf{K}} = \frac{1}{2}K$ always corresponds to a line perpendicular to $\hat{\mathbf{K}}$ that crosses the vector $\mathbf{K}$ at half of its length. The next reciprocal lattice vectors are $(\pm\frac{2\pi}{a}\hat{\mathbf{x}}, \pm\frac{2\pi}{a}\hat{\mathbf{y}})$ and $(\pm\frac{2\pi}{a}\hat{\mathbf{x}}, \mp\frac{2\pi}{a}\hat{\mathbf{y}})$. The resulting lines where the Bragg condition is satisfied are shown in Fig. 8. The first Brillouin zones is the area around $\mathbf{K} = 0$ up to the first line that satisfies a Bragg condition. Note that for a square lattice the first Brillouin zone is determined by the four shortest reciprocal lattice vectors (in general, it is not only determined by the shortest). We then calculate the values of the energies

$$\varepsilon_{\mathbf{k}-\mathbf{K}} = \frac{\hbar^2}{2m}(\mathbf{k}-\mathbf{K})^2 \tag{87}$$

inside the first Brillouin zone. In two dimensions, it is no longer practical to show the values for all k points. One therefore usually shows the bands in particular directions. A typical choice for two dimensions is $(\frac{\pi}{a}, \frac{\pi}{a}) \to (0,0) \to (\frac{\pi}{a}, 0)$. The energies can be expressed in terms of $\overline{\varepsilon} = \frac{\hbar^2}{2m}\frac{\pi^2}{a^2}$. Let us first consider the direction from $(0,0) \to (0, \frac{\pi}{a})$. The energy $\varepsilon_{\mathbf{k}}$ goes from 0 to $\overline{\varepsilon}$. The energies of $\varepsilon_{\mathbf{k}-\mathbf{K}}$ with $\mathbf{K}$ equal to $\pm\frac{2\pi}{a}\hat{\mathbf{x}}$ and $\pm\frac{2\pi}{a}\hat{\mathbf{y}}$ are all equal at $(0,0)$ (often known as the Γ point). The energy is given by $4\overline{\varepsilon}$. These degeneracies are directly related to the high symmetry of the Γ point. Moving away from the Γ, the bands split: $\varepsilon_{\mathbf{k}-\frac{\pi}{a}\hat{\mathbf{x}}}$ decreases to $\overline{\varepsilon}$ and $\varepsilon_{\mathbf{k}+\frac{\pi}{a}\hat{\mathbf{x}}}$ increases to $9\overline{\varepsilon}$. The bands $\varepsilon_{\mathbf{k}\pm\frac{\pi}{a}\hat{\mathbf{y}}}$ remain degenerate and increase to $5\overline{\varepsilon}$. The point $(\frac{\pi}{a}, \frac{\pi}{a})$ is again a special point in the Brillouin zone at the same distance from $(0,0)$, $(\frac{2\pi}{a}, \frac{2\pi}{a})$, $(\frac{2\pi}{a}, 0)$, and $(0, \frac{2\pi}{a})$. The lowest four bands are therefore degenerate with an $2\overline{\varepsilon}$. Moving towards $(0,0)$, with $k_x = k_y$, $\varepsilon_{\mathbf{k}}$ decreases to zero. $\varepsilon_{\mathbf{k}-\frac{2\pi}{a}(\hat{\mathbf{x}}+\hat{\mathbf{y}})}$ increases to $8\overline{\varepsilon}$. The band $\varepsilon_{\mathbf{k}-\frac{2\pi}{a}\hat{\mathbf{x}}/\hat{\mathbf{y}}}$ are degenerate and increase to $4\overline{\varepsilon}$.

Density of states.– For many physical quantities the exact dispersion is not important and one is more interested in the number of states at a particular energy. This is known as the density of states, which was introduced in 566.

technical intermezzo: Although, this density of states could have been calculated easily analytically, it was actually done numerical (useful when moving away from the free-electron model). How do you do this. There are several procedure to do this, some of them more efficient than others. Basically one discretizes the first Brillouin zone in a grid with a total of N_k points. and calculates the eigenvalues for each point (since the matrix is diagonal ($U = 0$), this is trivial). One could have produced a simple histrogram. This works wonders in case of a square density of states, but does not quickly produce nice results in other cases. Instead each k point has been broadened by a Gaussian

$$w(E) = \frac{\sqrt{\pi}}{N_k\sigma}e^{\left(\frac{E-\varepsilon_{\mathbf{k}}}{\sigma}\right)^2}, \tag{88}$$

and all the Gaussians are added together. The Gaussian is normalized to give a weight of $1/N_k$. We have taken $\sigma = 0.022\overline{\varepsilon}$. The effect of broadening is visible at the edge of the density of states ($E = 0$). In addition, we have used

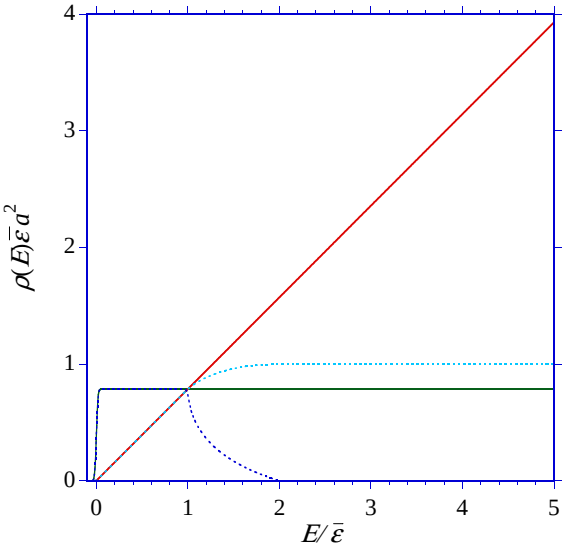


FIG. 10: The green line gives the density of states as a function of energy. The red line gives the integrated density of states. The dotted dark-blue line gives the density of states of the band from the first Brillouin zone (indicated by 1 in Fig. 9). The dotted light-blue gives it integral.

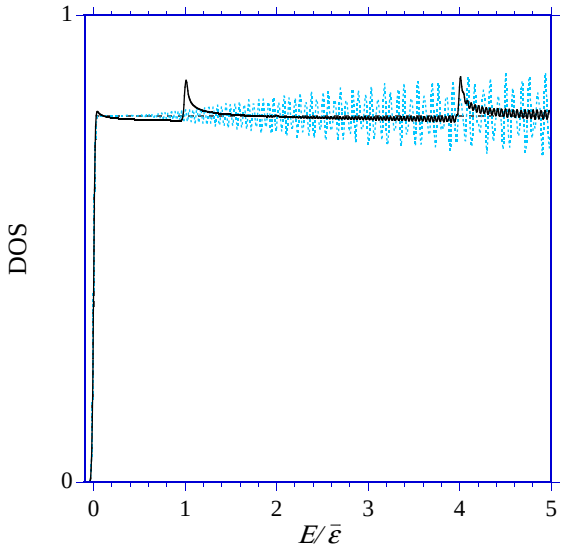


FIG. 11: Typical numerical problems in calculating the density of states. Dashed blue line: insufficient k points taken into account in the calculation. Black line: improper treatment of the edges of the Brillouin zone.

$N_k = 200^2$, which gives a nice smooth result. When $N_k = 50$ is taken, one observes oscillations, see Fig. 11, due to the undersampling of the Brillouin zone. The black line in Fig. 11 shows the effect of an improper treatment of the edges of the Brillouin zone. The calculation uses only a quarter of the Brillouin zone (only positive k), since the other parts are equivalent. In fact, we really only need 1/8 of the whole Brillouin zone due to symmetry. However, the k points at the edges are shared by different regions. For example, the k points at the edge of the first Brillouin zone lie for one half in the first and for the other half in the second Brillouin zone. When this is not taking into account properly (i.e. by scaling these k points by a factor of $\frac{1}{2}$, one observes spikes in the density of states, see the black line in Fig. 11. Obviously, these would become irrelevant when $N_k \to \infty$, by for $N_k = 100^2$ they are clearly visible. There exist more advanced and efficient methods to calculate the density of states (for example, the tetrahedron method, which effectively interpolates between the different k-points), but for a simple two-dimensional problem this works well enough.

The results are shown in Fig. 10. The end result looks simple: the density of states is constant. Obviously, we

could have derived this more easily. However, in general this cannot be done, so this is certainly a useful check to see whether this routine works properly. Let us derive this density of states analytically. We ignore the spin of the electron for the moment. Although we have a discrete number of k states, the density is always large enough that we can approximate this by a continuous function. The amount of k space occupied by one k point is $A_1 = \left(\frac{2\pi}{L}\right)^2$ following from the periodic boundary conditions in Eqn. (21) appplied in both x and y directions. The number of k states in a certain are can then be obtained by dividing the are by A_1. For a free-electron model where the energy is given by $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$, the areas of constant energy are circles. The number of electron inside the circle is given by

$$N(k) = \pi k^2 / A_1 = \pi k^2 \left(\frac{L}{2\pi}\right)^2 = \frac{A}{4\pi} k^2, \tag{89}$$

where A is the area (i.e. the size) of the system. This number can be easily written in terms of energy

$$N(E) = \frac{A}{4\pi}\frac{2m}{\hbar^2}E \quad \text{or} \quad n(E) = \frac{N(E)}{A} = \frac{1}{4\pi}\frac{2m}{\hbar^2}E, \tag{90}$$

where $n(E)$ is the density of electrons. Often we are also interested in what the density is for a certain energy $dn(E) = \rho(E)dE$. This gives the density of states

$$\rho(E) = \frac{dn(E)}{dE} = \frac{1}{4\pi}\frac{2m}{\hbar^2}. \tag{91}$$

which is indeed a constant. The plot uses some normalizations. The energy is normalized to the value at $(0, \frac{\pi}{a})$, i.e., $\overline{\varepsilon} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2$. Figure 10 also shows the integrated intensities. Furthermore, if we had one electron per site, the electron density would be $1/a^2$. However, it is more convenient to think about 1 el/site, so let us multiply times a^2.

$$\rho(E)a^2\overline{\varepsilon} = a^2\overline{\varepsilon}\frac{1}{4\pi}\frac{2m}{\hbar^2}\left(\frac{a}{\pi}\right)^2\left(\frac{\pi}{a}\right)^2 = \frac{\pi}{4} \cong 0.785, \tag{92}$$

which is the value of the constant density of states in the figure. It is interesting to look at only the band in the first Brillouin zone (see the dotted lines). Note that the density of states is no longer constant. You can easily observe this by drawing circles around the Γ point. For values of $k > \frac{\pi}{a}$ these turn into arcs, up to $k = \sqrt{2}\frac{\pi}{a}$ (with energy $2\overline{\varepsilon}$), where only one point at the edge of the Brillouin zone is left (actually, there are four points, but since al four points are shared by four Brillouin zones there is only 1 point). The integral over the first Brillouin zone goes to one. The number of states in the first Brillouin zone can be easily calculated

$$N_{\text{first}} = \left(\frac{2\pi}{a}\right)^2\left(\frac{L}{2\pi}\right)^2 = \frac{L^2}{a^2} = \frac{A}{a^2} = N. \tag{93}$$

Or exactly one state per site. This is not too much different from the tight-binding model we saw earlier. There we started from one state per site and filled up the entire first Brillouin zone (in one dimension). Again, by imposing the periodicity of the lattice, we are effectively creating orbitals on each site.

However, we have not applied any potential yet, so we are not going to fill up this orbital but fill up the free-electron bands. The k-value for ν electrons per site is determined by

$$\nu N = 2\pi k^2 \left(\frac{L}{2\pi}\right)^2 \quad \Rightarrow \quad k_\nu = 2\sqrt{\frac{\nu}{2\pi}}\frac{\pi}{L}\sqrt{N} = \sqrt{\frac{2\nu}{\pi}}\frac{\pi}{a} \tag{94}$$

where the factor 2 takes acount of the fact that each state has spin-up and a spin-down component. The corresponding energy is given by

$$E_\nu = \frac{\hbar^2}{2m}k_\nu^2 = \frac{2\nu}{\pi}\overline{\varepsilon}. \tag{95}$$

The maximum energy in the system (at least at $T = 0$) is known as the Fermi energy E_F. For $\nu = 1$ (1 electron per site), the Fermi energy is $0.637\overline{\varepsilon}$ with a corresponding Fermi wavevector of $0.798\frac{\pi}{a}$. The lies well inside the first Brillouin zone. This means that only the lowest band cross the Fermi level, see Fig. 9. This is essentially the Sommerfeld model, since the presence of nuclei can be essentially neglected. For $\nu = 2$, $E_F = 1.27\overline{\varepsilon}$. The corresponding wavevector $k = 1.13\frac{\pi}{a}$ lies outside the first Brillouin zone. Although the pictures are easily constructed by drawing a circle through the different Brillouin zones in Fig. 8, it is important to learn to think in the first

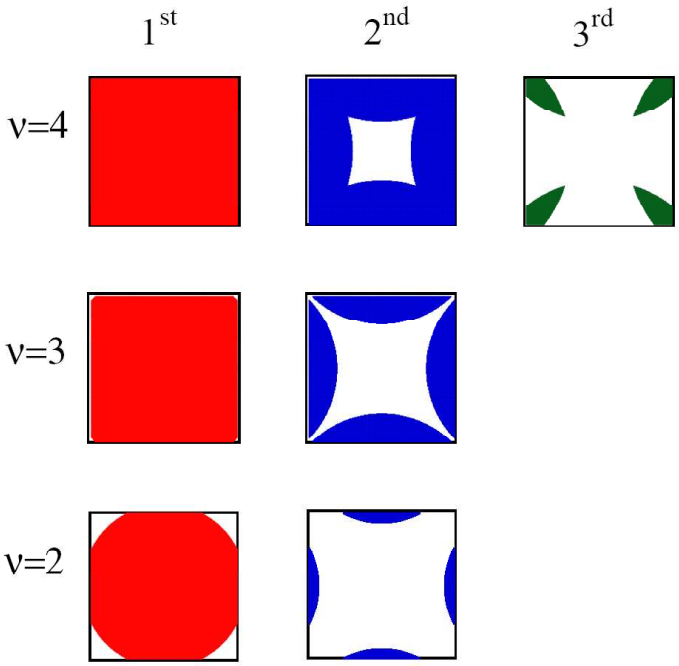


FIG. 12: The Fermi surfaces for different number of electrons ν per site. The 1^{st}, 2^{nd}, and 3^{rd} indicate from which Brillouin zone the bands originate.

Brilllouin zone, since no state-of-the-art calculations use free-electron approximations anymore. Things become more obvious when we compare the Fermi surfaces in Fig. 8 with the bands in Fig. free2D. For $\mathbf{k}$ from $(0,0)$ to $(\frac{\pi}{a},0)$, we see that the band from the first Brillouin zone is entirely below E_F for $\nu = 2$. In Fig. 8, we see that in this direction there is no Fermi surface in for the bands coming from the first Brillouin zone (red), but we do see a Fermi surface in the bands coming from the second Brillouin zone (blue). However, when going from $(0,0)$ to $(\frac{\pi}{a},\frac{\pi}{a})$, we see that it is the band from the first Brillouin zone that crosses the Fermi level and we see that we have a Fermi surface in this direction. When going to three electrons per site ($\nu = 3$), the part of the Fermi surface related to the bands from the second Brillouin zone increases, but the rest remain similar. Note that along the $(0,0) \rightarrow (\frac{\pi}{a},\frac{\pi}{a})$, there is still a Fermi surface since $\sqrt{\frac{6}{\pi}} < \sqrt{2}$. When going to $\nu = 4$, we also start involving the band coming from the third Brillouin zone. Note that along the $(0,0) \rightarrow (\frac{\pi}{a},\frac{\pi}{a})$, first the band from the second Brillouin zone crosses the Fermi level and then the band from the third Brillouin zone. Therefore in the direction, we have two Fermi surfaces (blue and green). However, along the $(0,0) \rightarrow (\frac{\pi}{a},0)$ direction, there is only the band from the second Brillouin zone crossing the Fermi level.

X. NEARLY-FREE ELECTRON IN TWO DIMENSIONS

So far, we have shown how the free-electron bands are folded back into the first Brillouin zone when the proper crystal symmetry is applied. However, in the end, this does not change anything. Without potential, you will simply end up with the Sommerfeld model. You cannot fool nature, you can pretend there are atoms, but without potential they are still free electrons. Obviously, there are potentials and even if they are small, they will have an effect close to the Bragg planes (okay, Bragg lines in two dimensions). For any finite U gaps will open up when the Bragg condition is satisfied. However, when U is small the effects will be small as well and the Fermi surfaces will not be too much different from the free-electron ones in Fig. 12. Let us consider a larger U value and a density of one electron per site ($n = 1$). We directly observe a substantial change in the band structure. Degeneracies are lifted and gaps open up, Fig. 13. Since the band structure is more complicated, we can no longer easily determine the values of E_F and k_F. However, we can calculate them numerically, by determining the density of states $\rho(E)$, see Fig. 14. E_F is the energy for which the integral of $\rho(E)$ with respect to energy equals the number of electrons (note that the density of states is plotted for one spin degree of freedom (up spin or down spin), so we need to integrate up to 0.5). The density of states is substantially different from the free electron one. First, we observe sharp peaks. The are called van Hove

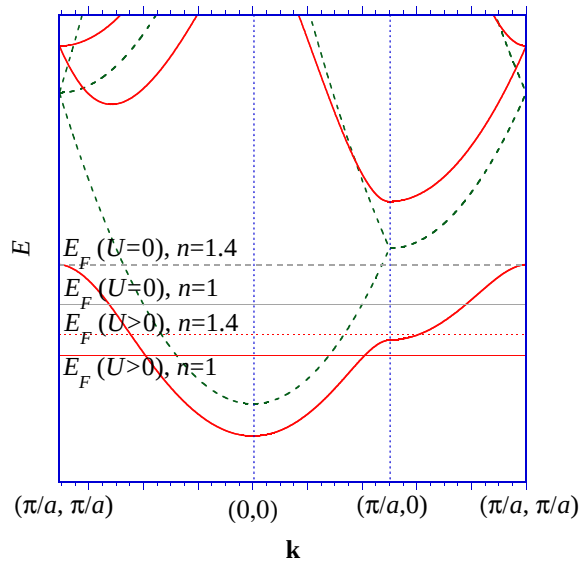


FIG. 13: The dashed lines show the free-electron model in two dimensions. The red lines indicate the effect of applying a potential U. The horizontal lines indicate the Fermi levels for 1.7 electrons per site.

singulaties. They are related to flat-band regions. The van Hove singularity just below the Fermi surface for $U > 0$ is a result of the flat-band in the lowest band around $(\frac{\pi}{a}, 0)$. In addition, we observe gaps in the density of states. For those energies there are no states in the band structure. Note that the band structure is only given for particular directions. It is difficult to see from the bands if there is a gap for any $\mathbf{k}$. However, $\rho(E)$ clearly shows the absence of states. The integrate intensity of $\rho(E)$ up to the gap equals one (or two, if we take both spin degrees of freedom into account). Therefore, if there were two electrons per site in the system, the material would be a semiconductor. Figure 15 shows the Fermi surfaces for $U = 0$ and $U > 0$ with a density of $n = 1$. Note that they look very similar. The surface for $U > 0$ has some slight distortion but it is close to a circle despite the relatively large value of U. The reason for that is that the states that are at the Fermi level are not close to satisfying the Bragg condition. This is the key ingredient for the surprising success of the Sommerfeld model for various materials. Let us see what happens if the Fermi was close to the states at the edges of the Brillouin zone by changing the number of free electrons to 1.4 per site. (This could be done with doping. However, the goal of this excersize is to demonstrate an effect that occurs in noble metals, where $3d$ bands play an important role). As expected, when increasing U, gaps open up, see Fig. 13. However, let us consider 1.4 electrons per site. Figure 15 shows that for $U = 0$, the Fermi sphere is circular (as we would have expected). However, for $U > 0$, the Fermi surfaces touches the edges of the Brillouin zone (of course, the example is specifically chosen that this happens). At first, this looks comparable to what happens for the bands coming from the first Brillouin zone (red) in Fig. 12 for $\nu = 2$. You might expect a picture of the surface for bands coming from the second Brillouin zone (blue in 15). However, there is none. The trick to understand this is to follow the Fermi energy in different directions. Along the $(0, 0) \rightarrow (\frac{\pi}{a}, 0)$ directions for $U = 0$, we cross the free-electron band centered around $(0, 0)$ for a filling of 1.4 electrons per site, see Fig. 13. For $U > 0$, a gap opens up and this band is pushed below the Fermi level. For two electrons per site, the E_F is larger, see $\nu = 2$ in Fig. 9, and the Fermi level crosses the free-electron band centered around $(\frac{2\pi}{a}, 0)$, i.e. there is a Fermi surface for bands coming from the second Brillouin zone, see Fig. 12. On the other hand, the second band for $U > 0$ is at higher enegy due to the opening of a gap, see Fig. 13. We can no longer identify this as the band coming from the second Brillouin zone, since the free-electron bands from the first and second Brillouin zone are mixed by the periodic potential U. Let us now look along the $(\frac{\pi}{a}, 0) \rightarrow (\frac{\pi}{a}, \frac{\pi}{a})$ direction. For a filling of 1.7 electrons per site, the Fermi level does not cross a band, see Fig. 13. Since the Fermi surface lies entirely inside the first Brillouin zone, , see Fig. 15, we do not expect a crossing since the direction $(\frac{\pi}{a}, 0) \rightarrow (\frac{\pi}{a}, \frac{\pi}{a})$ lies at the edge of the Brillouin zone. For a filling of 2 electrons per site, see $\nu = 2$ in Fig. 12, we do cross a band. In fact, two bands are crossed since the bands coming from the reciprocal lattice vectors $\mathbf{K} = (0, 0)$ and $(\frac{2\pi}{a}, 0)$ are degenerate along the $(\frac{\pi}{a}, 0) \rightarrow (\frac{\pi}{a}, \frac{\pi}{a})$ direction. This can be understood by noting that both $\mathbf{K}$ are always at the same distance from the line $(\frac{\pi}{a}, 0)$ and $(\frac{\pi}{a}, \frac{\pi}{a})$. Note that there is a Fermi surface in this direction for bands coming from the first (red) and second (blue) Brillouin zones in Fig. 12. For a finite U, this degeneracy is lifted, see Fig. 13. The Fermi level for a filling of 1.7 electrons per site just crosses the lowest band and the Fermi surface therefore lies entirely inside the first Brillouin zone. For the $(0, 0)$ and $(\frac{\pi}{a}, \frac{\pi}{a})$ direction, the situation is still very similar for $U = 0$ and $U > 0$, see Fig. 13.

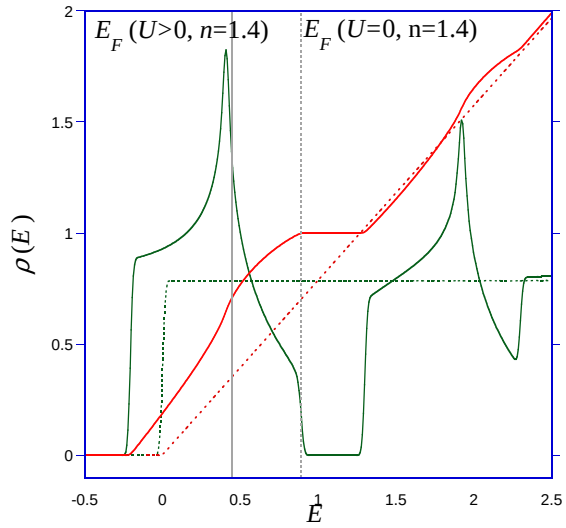


FIG. 14: The density of states $\rho(E)$ (green) without (dotted) and with U (solid) in the (nearly) free electron model. The red lines give their integrated intensity. The vertical lines indicate the Fermi level for 1.4 electrons per site. Since the density of states is shown for only one spin degree of freedom, they occur when the integrated density of states equals 0.7. The density of states is shown for the same energy region as the band structure in Fig. 13.

XI. TIGHT-BINDING IN TWO DIMENSIONS

The derivation of the tight-binding dispersion in two-dimension is very similar to that in one dimension in Eqn. (30)

$$\varepsilon_{\mathbf{k}} = -t \sum_{\boldsymbol{\delta}} e^{i\mathbf{k}\cdot\boldsymbol{\delta}} = -t(e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a}) = -2t(cosk_x a + cosk_y a). \tag{96}$$

We can plot this curve by hand. Along the $(0,0) \rightarrow (\frac{\pi}{a},0)$, we have $-2t\cos k_x a$, equivalent to the one-dimensional dispersion; along the $(\frac{\pi}{a},0) \rightarrow (\frac{\pi}{a},\frac{\pi}{a})$, we obtain $-2t(1+\cos k_y a)$; and along $(0,0) \rightarrow (\frac{\pi}{a},\frac{\pi}{a})$, the dispersion is $-4t\cos ka$ with $k = k_x = k_y$, see Fig. 16. The density of states $\rho(E)$ is shown in Fig. 17. Since the band is made up of n $1s$ electron per site, the total band can accomodate two electrons (taking spin into account). The density of states is also symmetric around $E = 0$. This might not be directly obvious by looking at the dispersion curves in Fig. 16. However, displacing k by (π,π) has as result that $\varepsilon_{\mathbf{k}} \rightarrow -\varepsilon_{\mathbf{k}}$. This directly implies that the Fermi level for one electron per site is at $E = 0$. The inset in Fig. 16 shows that the Fermi surface is a square. This can be easily understood since $E = 0$ implies $\cos k_x + \cos k_y = 0$, which is satisfied, for example when $k_y = \pi - k_x$ and all the other straight lines on the Fermi surface.

Another interesting thing to not is the remarkable similarity between the tight-binding dispersion in Fig. 16 and the lowest band in the two-dimension nearly-free electron model in Fig. 13. Despite the entirely different starting

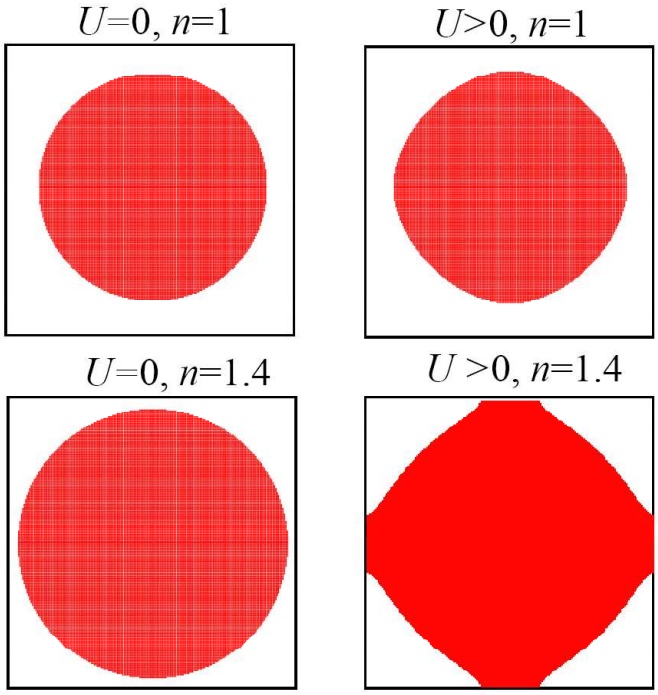


FIG. 15: The Fermi spheres for the band structures in Fig. 13 without (left) and with U (right).

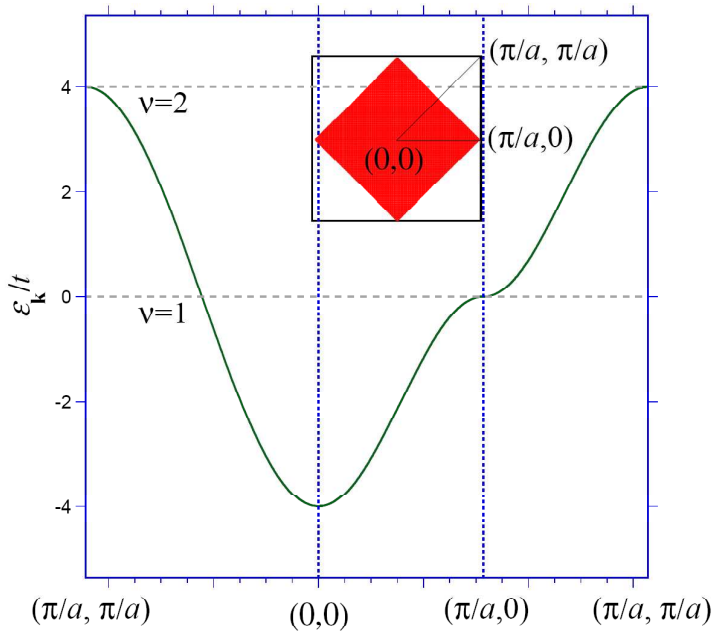


FIG. 16: The tight-binding dispersion $\varepsilon_{\mathbf{k}}$ for a two-dimensional square lattice along particular directions in the Brillouin zone. The inset shows the Fermi surface in for a filling of one electron per site.

points, the resulting physics is very similar.

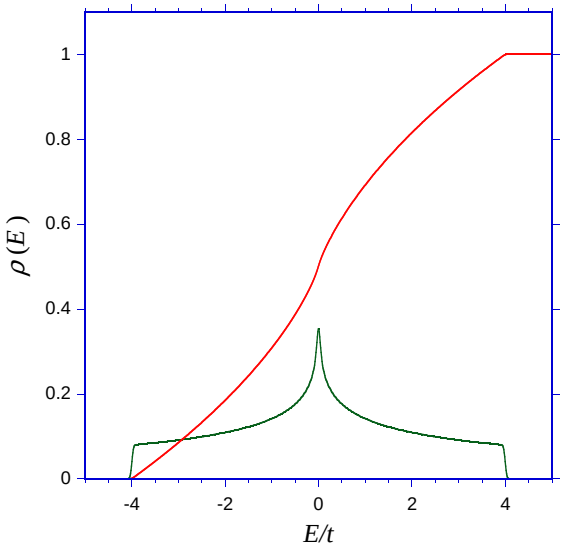


FIG. 17: The density of states $\rho(E)$ for tight-binding dispersion $\varepsilon_{\mathbf{k}}$, shown in green. The red line shows its integral.

XII. THE PERIODIC TABLE

Up to now, we have seen discussed the nearly-free electron and the tight-binding approach to the electronic structure of solids. In the end, we found similar results even though we started from opposite points of view. We now would like to discuss the electronic structure of several elements. Even starting from a free-electron model, we noticed the formation of atomic-like structure around the nuclei in the solid. Let us briefly recapitulate some of the results from atomic physics. The eigenfunctions for the Hydrogen atom were obtained by solving the Schrödinger equation

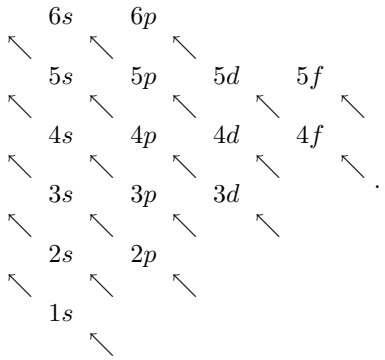
$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}), \tag{97}$$

is the potential from the nucleus. This was solved by separation of variables leading to eigenfunctions that can be written as

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_{lm}(\theta,\varphi), \tag{98}$$

where R_{nl} are Laguerre polynomials and $Y_{lm}(\theta,\varphi)$ spherical harmonics. The quantum numbers are given by $n = 1, 2, 3, \cdots, l = 0, 1, \cdots, n-1$, and $m = -l, -l+1 \cdots, l$. The orbitals are commonly denoted as s, p, d, f for $l = 0, 1, 2, 3$, respectively. Although the solution is exact for Hydrogen, the interactions between the electrons does not allow us to obtain exact solutions for larger atomic numbers. There are two approaches. We can try to do our best to treat the electron-electron interactions as well as possible. This leads to typical atomic physics (Hund's rule, local moments etc, see lecture notes from 560/1). However, this is many-body problem treating all the electrons explicitly and not a feasible approach for solid-state physics. The other approach is to assume that the electron only feels an average potential as a result of the presence of other electrons. This effectively modifies the potential $V(\mathbf{r})$. For example, one can easily understand stand that the $3s$ electron does not feel the potential of the eleven protons in the nucleus (a Na^{11+} ion), but an effective potential due to the nucleus plus all the strongly bound electrons in the $1s$, $2s$, and $2p$ shells. However, we might not be able to calculate the exact shape of the potential and therefore the radial wavefunction $R_{nl}(r)$.

A phenemenological scheme of filling the orbitals is



(99)

How this works out for the periodic table is shown in Fig. 19.

When we look at solids, we can still observe the atomic character of the orbitals although often orbitals get mixed and we find states with, for example, both s and p character. Also, in solids we cannot easily determine the radial wavefunction R_{nl} without doing extensive calculations. However, some symmetry aspects still remain. For example, the $1s$ and $2s$ orbitals have the same spherical part of the wavefunction ($Y_{00}(\theta,\varphi) = 1/\sqrt{4\pi}$). However, we know that ψ_{100} and ψ_{200} have to be orthogonal. This directly implies that the radial wavefunction of the $2s$ orbital R_{20} must have a node (and positive and negative parts), since R_{10} does not have a node. This nodes make the orbitals more extended in space. This leads us to another simple rule of thumbs. The first orbitals of its kind are small. This means the $1s$, $2p$, $3d$, and $4f$. Of particular importance for condensed-matter physics are the compounds where the valence band contain $3d$ and $4f$ orbitals. Since the orbitals are small Coulomb interactions are important and we expect the nearly-free electron model to work less well.

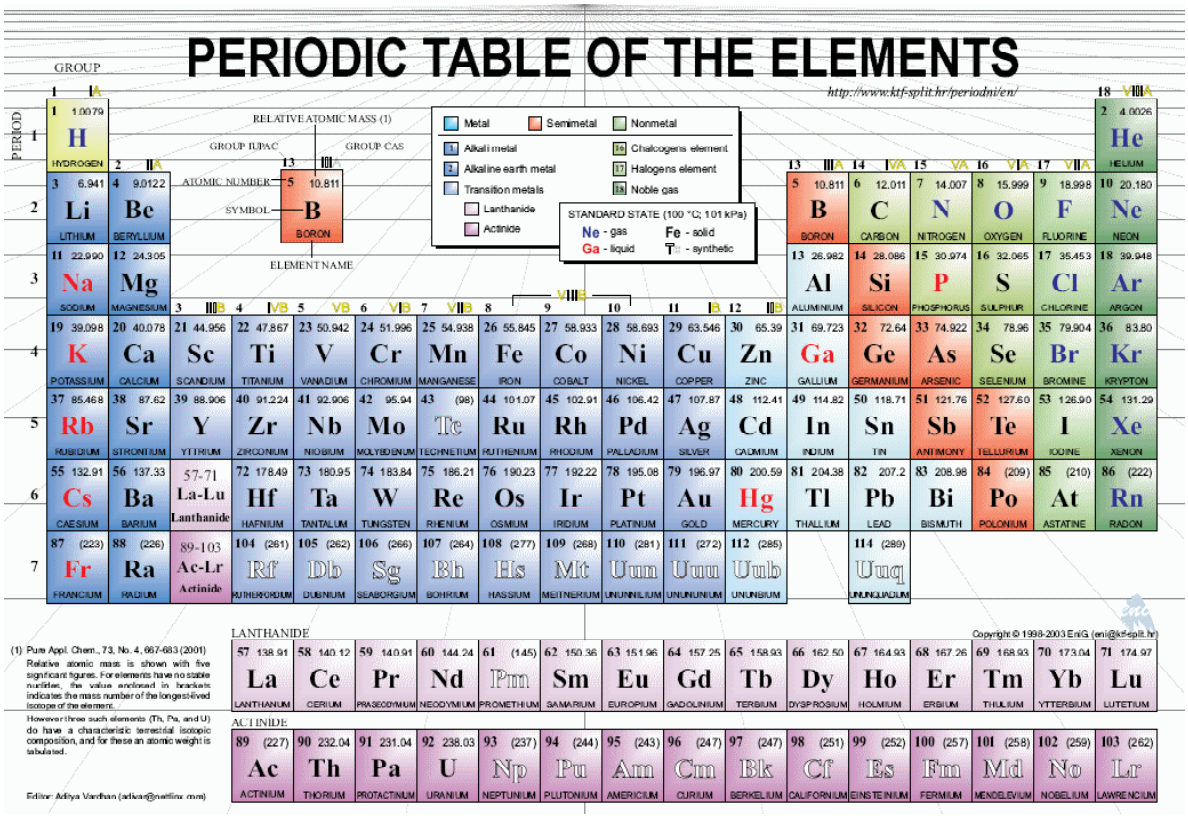


FIG. 18: The periodic table of elements.

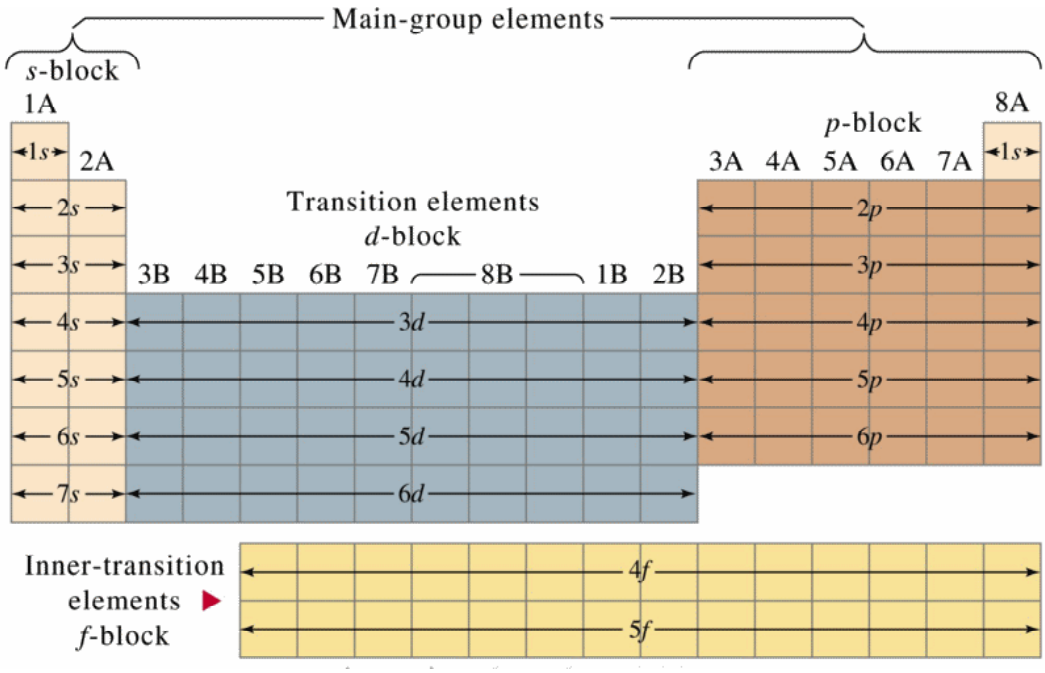


FIG. 19: The table shows which shell are being filled when going through the periodic table.

XIII. BAND STRUCTURE OF SELECTED MATERIALS: SIMPLE METALS AND NOBLE METALS

Let us first look at the situation of simple metals. Where can we find those in the periodic table? First, we do not want small orbitals, because then strong electron-electron interactions play an important role. This rules out all transition-metals (such as iron and cobalt), and all the rare earths. We want materials with s and p electrons. However, some of these are usually only present as gases (such as He) often in the form of molecules (such as H_2, N_2, and O_2). Certain combinations of s and p electrons have the tendency to form sp hybrids (for example in Si and carbon compounds such as graphene and diamond), which will be discussed later. We are therefore left with elements from groups 1A (Na, K, Rb), 2A (Mg, Ca), and 3A (Al). Let us consider Aluminum.

Al has a face-centered cubic lattice (fcc), see Fig. 20. This lattice type was treated in 566/666. The lattice vectors

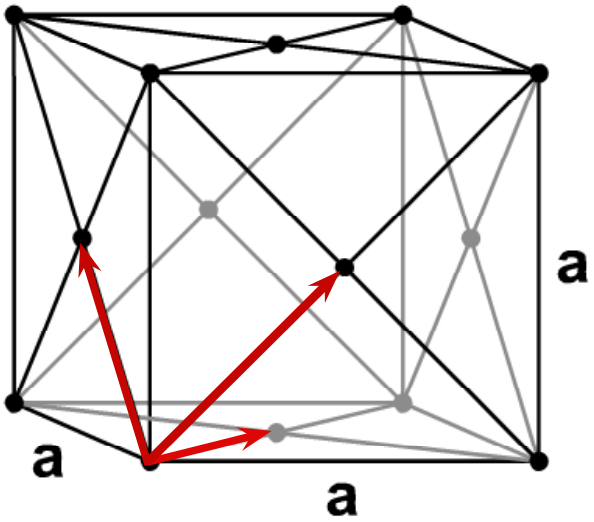


FIG. 20: The face-centered cubic lattice.

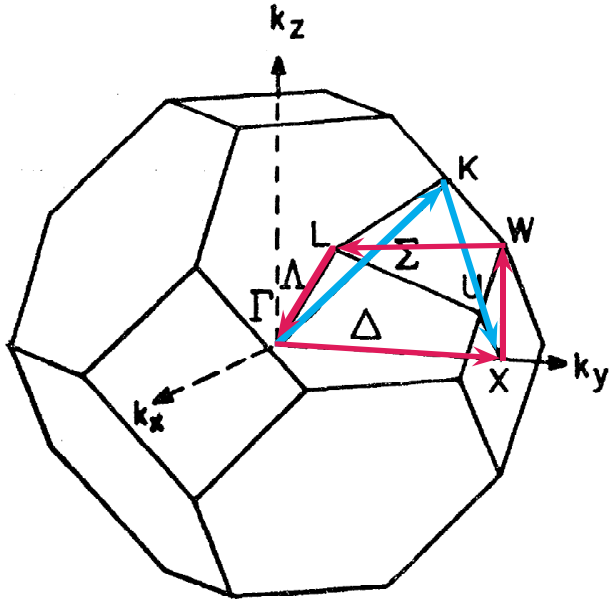


FIG. 21: The first Brillouin zone for Aluminum. Since Al is fcc, the reciprocal lattice vectors form a bcc lattice. The lines indicate the directions taken in plotting the electronic structure in Fig. 22.

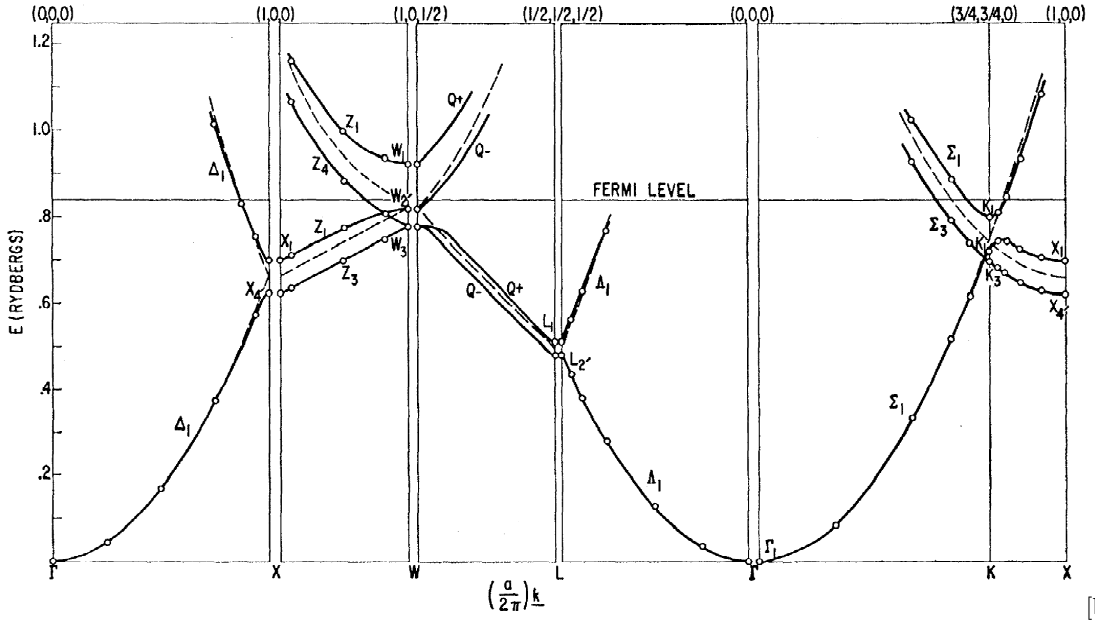


FIG. 22: The electronic structure of Aluminum along several directions. The dashed lines indicate the results for the free-electron model. From Segall, Phys. Rev. **124**, 1797 (1961).

are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}). \tag{100}$$

The reciprocal lattice vectors can be obtained using Eqn. (82)and are

$$\mathbf{b}_1 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}), \quad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}), \tag{101}$$

which corresponds to the lattice vectors of a body-centered cube (bcc). The first Brillouin is shown in Fig. 21. Bragg reflection occurs in planes perpendicular to the reciprocal lattice vectors at half the length of the vector. The

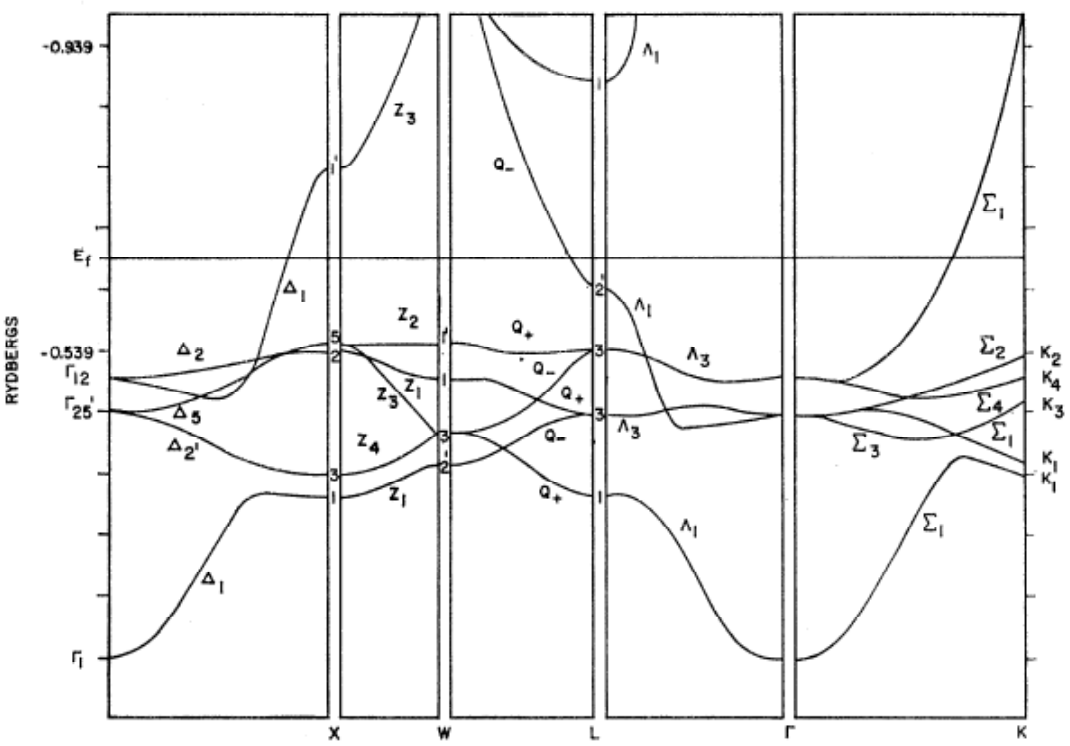


FIG. 23: The electronic structure of copper along several directions. The dashed lines indicate the results for the free-electron model. From Burdick, Phys. Rev. **129**, 138 (1963).

nearest-neighbors in reciprocal space are at the centers of the cube along the (111) directions, giving rise to the largest planes in the first Brillouin zone. The next-nearest neighbors are along the sides of the cube in the (100) directions. The electronic structure is shown in Fig. 22, where is is compared to a free-electron model. The periodic potential is smaller than we chose for the two-dimensional example. The gap at point X in reciprocal space is less the 0.1 Ry or of the order of one electron volt. We also observe (for example, along the XW direction), the lifting of degeneracies due to the periodic potential. However, despite the added complexity of dealing with a fcc lattice, the (nearly) free electron model is surprisingly successful.

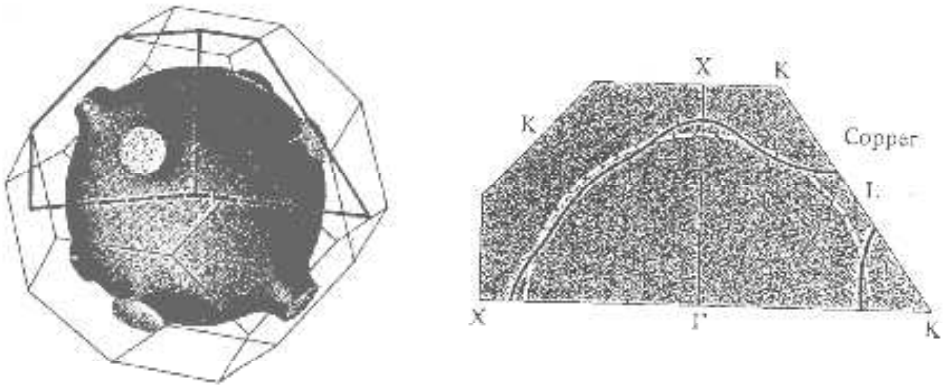


FIG. 24: The Fermi surface of copper (AM page 290). The left shows the Fermi surface in three dimensions. The right shows the Fermi surface along particular cuts through the First Brillouin zone. The dashed line shows the free-electron result.

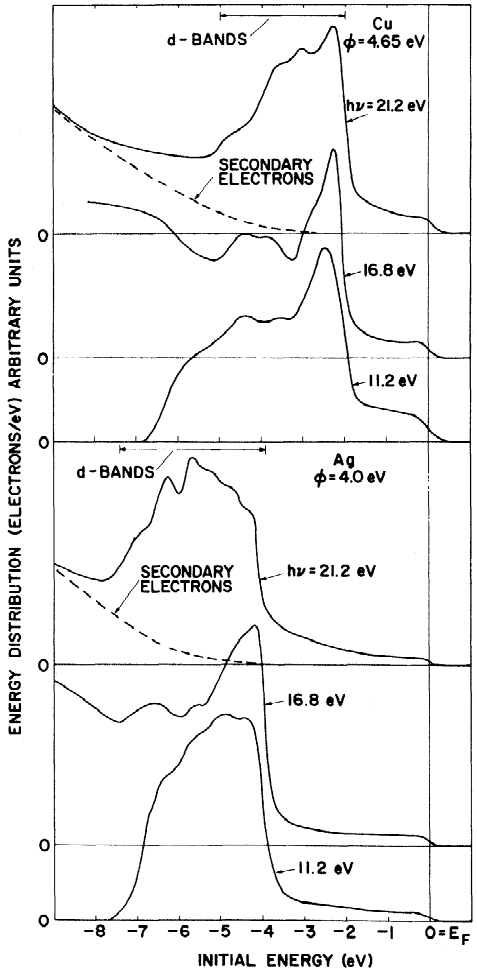


FIG. 25: Valence band photoemission of copper and silver from Eastman and Cashion, Phys. Rev. Lett. **24**, 310 (1970) using different energies for the incoming photon. Note the onset of the d band at 2 and 4 eV below the Fermi level for Cu ($3d$) and Ag ($4d$), respectively. The bands crossing the Fermi level are the $4sp$ and $5sp$ bands, respectively.

There is another class of compounds, where the free-electron model is useful. These are the noble metals. Although transition metals, the d shell is full for the noble metals. For example, the atomic structure of copper is $[\mathrm{Ar}]3d^{10}4s^1$, where [Ar] indicates the same shell as the noble element argon. These shells ($1s$ to $3p$) are all full and deep-lying core levels. The relevant shells are the $3d$ and $4s$ levels. Note that even for atomic copper, the $3d$ shell if full. This is an exception to the phenomenological diagram that indicate that the $4s$ shell is filled first. This is true for all the other $3d$ transition metals that have a configuration $3d^n4s^2$. However, the filled $3d$ shell is so stable, that it effectively "steals" an electron from the $4s$ shell. Note that the next element, zinc, has a $[\mathrm{Ar}]3d^{10}4s^2$ configuration, again with the $3d$ shell filled. When looking the electronic structure of copper, see Fig. 23, we expect significantly more bands due to the presence of the $3d$ states. Since copper also has an fcc structure, we can try to compare it to Al, see Fig. 22. The first notable difference is the cluster of bands with relatively narrow dispersion. These are the five $3d$ bands (sometimes we see fewer bands due to degeneracies along particular directions). The $3d$ bands are below the Fermi level, corresponding to the fact that the $3d$ states are full. There is also one band which has a large dispersion (indicated by Δ_1 in the figure. This corresponds to the $4s$ states. The difference is due to the hybridization matrix elements. The dd matrix elements are much smaller due to the smaller radial extent of the $3d$ orbitals compared to the $4s$ orbitals. However, the band related to the $4s$ does not simply cross the $3d$ bands. Along the ΓX direction, it more or less looks like the $4s$ band merges with the $3d$ bands, and then reemerges at higher energies. This is a result of the finite matrix elements between the $4s$ and $3d$ orbitals. The dispersion of the $4s$ band is similar to the band indicated by Δ_1 for Al, see Fig. 22.

A good technique to determine the density of states is photoemission. Photoemission uses the photoelectric effect. The kinetic energy E_{kin} of the outgoing photoelectrons is measured and can be directly related to their binding

energies E_b via

$$E_{\rm kin} = \hbar\omega - E_b, \tag{102}$$

where $\hbar\omega$ (or $h\nu$) is the energy of the photon. The spectra for copper and silver are given in Fig. 25. Different photon energies are used. The spectra look different due to changes in the matrix elements as a function of photon energy. What is clear is the strong emission from the d bands. The onset of is around 2 eV for copper and 4 eV for silver. The band width for copper is smaller than that of silver (this is most clearly seen in the spectra taken at 21.2 eV). This is in agreement with our notion that the $3d$ bands are smaller and therefore more localized than the $4d$ bands. The density of states at the Fermi level is rather small and due to the *sp* bands.

Another interesting effect occurs at the L point in the Brillouin zone. The Fermi surface lies just above the band at the edge of the Brillouin zone. This situation is very similar to our example for the nearly-free electron model in two dimensions for $n = 1.4$ electrons per site, see Fig. 13 (in three dimensions, the ΓL direction is (111), whereas in two dimensions the $(0, 0)$ (Γ in two dimensions) to $(\frac{\pi}{a}, \frac{\pi}{a})$ direction is $(1, 1)$. Note that the plot directions are opposite). We saw that in two dimensions a neck was formed touching the edge of the Brillouin zone. A comparable effect occurs in three dimension, see Fig. 24, where we find "neck" formation along the (111) directions.

XIV. OPTICAL SPECTROSCOPY

In a regular course on electricity and magnetism, the electronic structure is treated in a very approximate way (this section will, unlike AM, follow SI units). The assumption is that an external electric field induces a polarization $\mathbf{P}$ counteracting the external field. The external field is given by the displacement $\mathbf{D}$ which can be related to external charges that create the external field. The external field and the polarization together produce the electric field inside the solid

$$\mathbf{E} = \frac{1}{\varepsilon_0}(\mathbf{D} - \mathbf{P}), \tag{103}$$

where ε_0 is the permittivity of free space (vacuum). We know from Gauss's law that $\nabla \cdot \mathbf{E} = \rho/\varepsilon_0$, where ρ is the charge density. Taking the divergence of the above equation gives

$$\varepsilon_0 \nabla \cdot \mathbf{E} = \nabla \cdot \mathbf{D} - \nabla \cdot \mathbf{P} \quad \Rightarrow \quad \rho = \rho_{\rm free} + \rho_{\rm ind}, \tag{104}$$

where we have used $\nabla \cdot \mathbf{D} = \rho_{\rm free}$ and $\nabla \cdot \mathbf{P} = -\rho_{\rm ind}$, giving the free and induced charges, respectively. The assumption is now that the polarizability is directly proportional to the electric field

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E}, \tag{105}$$

where χ is known as the electric susceptibility. This quantity is supposed to represent all the electronic structure of the solid. Often the solid is represented as a simple electron gas. Although this assumption works often surprisingly well (it explains for example why light is reflected from metals, giving them the mirror-like appearance), it does not work well when considering more details (for example, why is copper reddish, silver silver, and gold yellow). To obtain some understanding about these details, we have to understand the interaction between light and solids in terms of transitions in the electronic structure. However, let us first continue with the standard E&M approach.

Inserting Eqn. (105) into (103), gives

$$\mathbf{E} = \frac{1}{\varepsilon_0}(\mathbf{D} - \varepsilon_0 \chi \mathbf{E}) \quad \Rightarrow \quad \mathbf{E} = \frac{1}{\varepsilon_0(1+\chi)}\mathbf{D} = \frac{\mathbf{D}}{\varepsilon_0 \varepsilon_r} = \frac{\mathbf{D}}{\varepsilon}, \tag{106}$$

where we have introduced the relative permittivity $\varepsilon_r = 1 + \chi$, also known as the dielectric constant. We see that once we have found χ, we can also directly relate the electric field inside the solid to the externally applied field.

The Lorentz oscillator.– Let us first consider the example of a Lorentz oscillator. This classical model is useful since it can be related to quantum-mechanical interband transitions in a solid. We can also reduce it to the Drude model which quantum mechanically includes all intraband transitions (i.e. no scattering with reciprocal lattice vectors). The quantum-mechanical theory can therefore be seen as an extension of its classical analog. We start by considering Newton's equation for an electron in an electric field

$$\sum \mathbf{F} = m\mathbf{a} \quad \Rightarrow \quad -e\mathbf{E} - m\Gamma\mathbf{v} - m\omega_0^2\mathbf{r} = m\mathbf{a}. \tag{107}$$

Classically, this means that the electron feels an electric force $-e\mathbf{E}$. It is held in its place by an effective spring force $-m\omega_0^2\mathbf{r}$ from the nucleus. In addition, it feels a viscous damping $-m\Gamma\mathbf{v}$. Quantum mechanically, we will see that $\hbar\omega_0$ corresponds to the energy of inter/intraband transtions. The damping is due to scattering giving a finite lifetime (and therefore a broadening Γ) to the electronic states. Eqn. (107) leads to a differential equation

$$\frac{d^2\mathbf{r}}{dt^2} + \Gamma\frac{d\mathbf{r}}{dt} + \omega_0^2\mathbf{r} = -\frac{e}{m}\mathbf{E}. \tag{108}$$

If the local electric field varies as $e^{-i\omega t}$, then $\mathbf{r}\ e^{-i\omega t}$ has a similar time dependence. Since $\mathbf{r}$ gives the displacement of the electron with respect to the nucleus, this gives an induced dipole moment

$$\mathbf{r} = -\frac{e\mathbf{E}}{m}\frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega} \quad \Rightarrow \quad \mathbf{p} = -e\mathbf{r} = \alpha(\omega)\mathbf{E} \quad \text{with} \quad \alpha(\omega) = \frac{e^2}{m}\frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega}. \tag{109}$$

The total polarization per unit volume is given by

$$\mathbf{P} = \frac{N}{V}\mathbf{p} = n\alpha(\omega)\mathbf{E} \equiv \varepsilon_0\chi\mathbf{E} \quad \Rightarrow \quad \chi = \frac{n\alpha(\omega)}{\varepsilon_0}, \tag{110}$$

where $n = N/V$ is the electron density. This gives for the dielectric constant

$$\varepsilon_r = 1 + \chi = 1 + \frac{n\alpha(\omega)}{\varepsilon_0} = 1 + \frac{ne^2}{m\varepsilon_0}\frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega}. \tag{111}$$

We can reduce this to the Drude result by realizing that the Drude model excludes the attractive potential of the nuclei ($\omega_0 = 0$) and does not include scattering (Γ). This gives

$$\varepsilon_r = 1 - \frac{ne^2}{m\varepsilon_0}\frac{1}{\omega^2} = 1 - \frac{\omega_p^2}{\omega^2}, \tag{112}$$

where $\omega_p^2 = ne^2/\varepsilon_0 m$ is the plasma frequency. This result basically has the electron gas moving along with the electric field.

Let us see what a typical value is for the plasma frequency. Let us consider aluminum. Al is face-centered cubic with a lattice constant $a = 4.05$ Å. Since this is fcc there are four atoms in the cube, see Fig. 20 (eight at the corners that count for 1/8 and six at the sides that count for a 1/2). Al has a $3s^2 3p$ configuration, so each Al atom contributes three electrons. This gives a density $n = 4 \times 3/(4.05 \times 10^{-10})^3 = 1.8 \times 10^{29}$ m^{-3}. Inserting the numbers gives $\omega_p = 2.4 \times 10^{16}$ s^{-1} or in energy $\hbar\omega = 99$ eV. This is undoubtedly going to be too high since we know that the Drude model neglects the Fermi-Dirac statistics and therefore overestimates n.

Interaction of light with a solid.– This is all nice, but how does this affect the interaction of light with a solid, i.e. the optical properties of a solid? Let us go back to Maxwell equations. Two of them include the divergence of the electric and magnetic fields

$$\nabla\cdot\mathbf{D} = \rho_{\text{free}} \quad \rightarrow \quad \nabla\cdot(\varepsilon_R\mathbf{E}) = \rho_{\text{free}} = 0, \tag{113}$$

in the absence of an applied electric field. Some care should be taken here with the permittivity. We use here a real permittivity $\varepsilon_R = \text{Re}[\varepsilon]$. As we will see the complex part will be related to the currents. Furthermore, we also have for the magnetic induction $\nabla\cdot\mathbf{B} = 0$. The other two involve the rotation of the magnetic and electric fields.

$$\nabla\times\mathbf{E} + \frac{\partial\mathbf{B}}{\partial t} = 0 \quad \text{and} \quad \nabla\times\mathbf{H} - \frac{\partial\mathbf{D}}{\partial t} = \mathbf{J}_{\text{free}}, \tag{114}$$

where $\mathbf{J}_{\text{free}}$ is the current due to the free charges. Since we are interested in the propagation of a wave in a solid, we want to transform these equations into a wave equation. This can be done by taking the rotation as follows

$$\nabla\times\nabla\times\mathbf{E} = \nabla(\nabla\cdot\mathbf{E}) - \nabla^2\mathbf{E} = -\nabla\times\frac{\partial\mathbf{B}}{\partial t}. \tag{115}$$

In an isotropic medium, we have the relation $\mathbf{B} = \mu\mathbf{H}$ (similar to the relation $\mathbf{D} = \varepsilon\mathbf{E}$). Since $\nabla\cdot\mathbf{E} = 0$, we obtain with the use of the other Maxwell equation

$$\nabla^2\mathbf{E} = \mu\nabla\times\frac{\partial\mathbf{H}}{\partial t} = \mu\frac{\partial}{\partial t}(\nabla\times\mathbf{H}) = \varepsilon_R\mu\frac{\partial^2\mathbf{E}}{\partial t^2} + \mu\frac{\partial\mathbf{J}_{\text{free}}}{\partial t}. \tag{116}$$

For the current, we have apply Ohm's law: $\mathbf{J} = \sigma\mathbf{E}$, where σ is the conductivity. This gives us the wave equation

$$\nabla^2\mathbf{E} - \varepsilon_R\mu\frac{\partial^2\mathbf{E}}{\partial t^2} = \mu\sigma\frac{\partial\mathbf{E}}{\partial t}. \tag{117}$$

The term with σ is related to the optical conductivity related to optical transitions accompanying photon absorption. Remember that the wave equation in free space is given by

$$\nabla^2\mathbf{E} - \varepsilon_0\mu_0\frac{\partial^2\mathbf{E}}{\partial t^2} = 0, \tag{118}$$

where $\varepsilon_0\mu_0 = 1/c^2$, where c is the speed of light in vacuum. We will now look for solution of the electric field in a solid of the form

$$\mathbf{E} = \mathbf{E}_0 e^{i\mathbf{q}\cdot\mathbf{r} - i\omega t}. \tag{119}$$

Inserting into Eqn. (116) gives

$$-q^2 + \varepsilon_R\mu\omega^2 = -i\mu\sigma\omega \quad \Rightarrow \quad q^2 = \frac{\mu_r\varepsilon_1}{c^2}\omega^2 + i\mu_r\mu_0\sigma\omega = \mu_r\frac{\omega^2}{c^2}\left(\varepsilon_1 + i\frac{c^2\mu_0\sigma}{\omega}\right) = \mu_r\frac{\omega^2}{c^2}\left(\varepsilon_1 + i\frac{\sigma}{\varepsilon_0\omega}\right), \tag{120}$$

where $\varepsilon_R \equiv \varepsilon_0\varepsilon_1$ and $\mu_r = 1$ in a nonmagnetic solid. We can only find a solution if the wavevector is complex, which means we allow for evanescent waves. Let us define a complex diffractive index $\hat{n}$,

$$q = \frac{\omega}{c}\hat{n} = \frac{\omega}{c}(n + i\kappa), \tag{121}$$

where n is the refractive index and κ is the extinction coefficient (many books use k or K here, but this notation is a bit confusing). Substituting gives

$$\frac{\omega^2}{c^2}(n + i\kappa)^2 = \frac{\omega^2}{c^2}(n^2 - \kappa^2 + 2in\kappa) \equiv \mu_r\frac{\omega^2}{c^2}\left(\varepsilon_1 + i\frac{\sigma}{\varepsilon_0\omega}\right), \tag{122}$$

or

$$\varepsilon_1 = \frac{n^2 - \kappa^2}{\mu_r} \quad \text{and} \quad \frac{\sigma}{\varepsilon_0\omega} = \frac{2n\kappa}{\mu_r}. \tag{123}$$

Often this is written as a complex dielectric function

$$\varepsilon_r = \varepsilon_1 + i\varepsilon_2 = \frac{\hat{n}^2}{\mu_r}, \tag{124}$$

giving

$$\varepsilon_1 = \varepsilon = \frac{n^2 - \kappa^2}{\mu_r} \quad \text{and} \quad \varepsilon_2 = \frac{\sigma}{\varepsilon_0\omega} = \frac{2n\kappa}{\mu_r}. \tag{125}$$

Let us consider nonmagnetic systems from now on, for which we have

$$\varepsilon_1 = \varepsilon = n^2 - \kappa^2 \quad \text{and} \quad \varepsilon_2 = 2n\kappa. \tag{126}$$

We can also invert these equations to find the expressions for n and κ in terms of ε_1 and ε_2. Writing

$$n^2 - \left(\frac{\varepsilon_2}{2n}\right)^2 - \varepsilon_1 = 0 \quad \Rightarrow \quad n^4 - \varepsilon_1 n^2 - \left(\frac{\varepsilon_2}{2}\right)^2 = 0 \tag{127}$$

This is a cubic equation in n^2, where the roots are given by

$$n^2 = \frac{1}{2}\varepsilon_1 + \frac{1}{2}\sqrt{\varepsilon_1^2 + 4\left(\frac{\varepsilon_2}{2}\right)^2}, \tag{128}$$

or

$$n = \sqrt{\frac{1}{2}\varepsilon_1 + \frac{1}{2}\sqrt{\varepsilon_1^2 + \varepsilon_2^2}}. \tag{129}$$

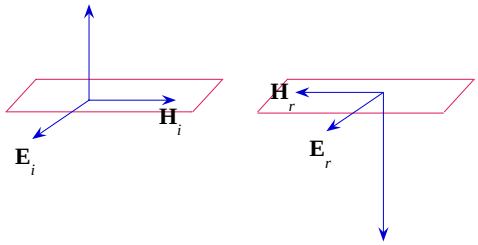


FIG. 26: The reflectance of light at the surface of a solid.

Similarly, we can find

$$\kappa = \sqrt{-\frac{1}{2}\varepsilon_1 + \frac{1}{2}\sqrt{\varepsilon_1^2 + \varepsilon_2^2}}. \tag{130}$$

We can split the dielectric constant that we obtained before into a real and imaginary part

$$\varepsilon_r = 1 + \frac{ne^2}{m\varepsilon_0}\frac{1}{\omega_0^2 - \omega^2 - i\Gamma\omega}. = 1 + \frac{ne^2}{m\varepsilon_0}\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2} + i\frac{ne^2}{m\varepsilon_0}\frac{\Gamma\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}. \tag{131}$$

which gives

$$\varepsilon_1 = 1 + \frac{ne^2}{m\varepsilon_0}\frac{\omega_0^2 - \omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2} \quad \text{and} \quad \varepsilon_2 = \frac{ne^2}{m\varepsilon_0}\frac{\Gamma\omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}. \tag{132}$$

As we will see later on, ε_2 is related to the absorption. Note that the function is like a Lorentzian (it is plotted in Fig. 32), with a width related to Γ. Note that in the limit $\Gamma \to 0$ this function becomes a δ-function, going to zero for $\omega \neq \omega_0$ and having a value of $1/\omega\Gamma \to \infty$ for $\omega = \omega_0$. This means that the solid can only absorb light with energy $\hbar\omega_0$. Obviously, few solids have only one resonance frequency. However, we can easily generalize the Lorentz oscillator problem for many oscillators. Let us take n_j the density of electrons bound with resonance frequency ω_j

$$\varepsilon_r = 1 + \sum_j \frac{n_j e^2}{m\varepsilon_0}\frac{1}{\omega_j^2 - \omega^2 - i\Gamma_j\omega}, \tag{133}$$

with $\sum_j n_j = n$.

Drude model and intraband transitions.– Although the Drude model fails in a quantitative description of a solid (by grossly overestimating the number of electrons relevant for the conductivity and other properties, due to the neglect of Fermi-Dirac statistics), the idea that the conduction is determined by electrons that behave almost freely works rather well. This implies that $\omega_0 = 0$ The value of Γ is can be related to the inverse of the mean free time between collisions, $\Gamma = 1/\tau$. This gives for the dielectric functions

$$\varepsilon = 1 - \frac{\omega_p^2\tau}{\omega(\omega\tau + i)} \quad \Rightarrow \quad \varepsilon_1 = 1 - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2} \quad \text{and} \quad \varepsilon_2 = \frac{\omega_p^2\tau}{\omega(1 + \omega^2\tau^2)} \tag{134}$$

Reflectance.– Although there are many different types of optical spectroscopies, one of the most intuitive ones is the reflectance. Let us consider an wave coming in perpendicular, see Fig. 26. Let us take the incident electric field along the x-direction,

$$\mathbf{E}_i = E_i e^{i\hat{q}z - i\omega t}\hat{\mathbf{x}}, \tag{135}$$

where $\hat{q}$ can be complex. We can find the magnetic field from the Maxwell equation

$$\nabla \times \mathbf{E} = -\mu\frac{\partial \mathbf{H}}{\partial t} = i\mu\omega\mathbf{H}. \tag{136}$$

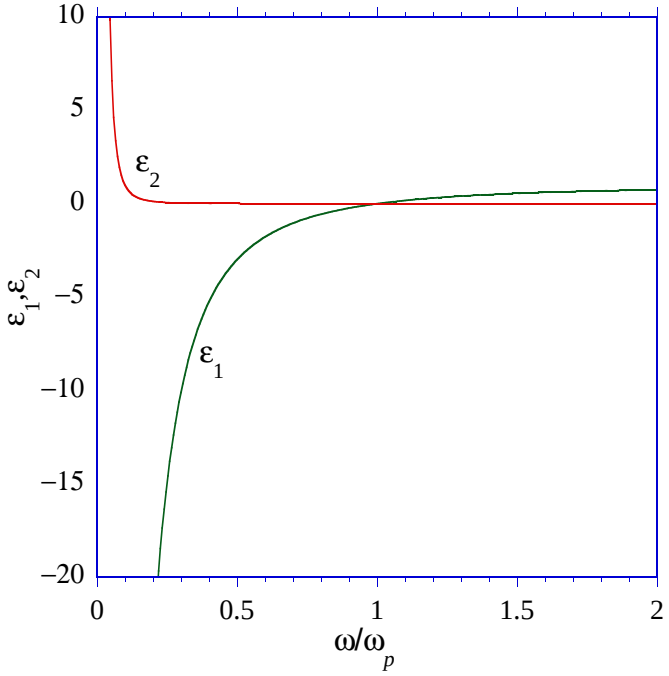


FIG. 27: The dependence of ε_1 and ε_2 as a function of ω (normalized to the plasma frequency ω_p) of the Drude model. The scattering is small, i.e. $\Gamma = \tau^{-1} \ll \omega_p$.

The rotation can be obtained from

$$\nabla \times \mathbf{E} = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ E_x & 0 & 0 \end{vmatrix} = \frac{\partial E_x}{\partial z}\hat{\mathbf{y}} = i\hat{q}E_x\hat{\mathbf{y}} \tag{137}$$

This gives

$$\mathbf{H}_i = \frac{\hat{q}}{\mu\omega}E_i e^{i\hat{q}z-i\omega t}\hat{\mathbf{y}}, \tag{138}$$

which means $\mathbf{H}$ is perpendicular to $\mathbf{E}$ (as it should be). At the surface part of the wave is reflected and part of it is transmitted. However, the other Maxwell equations impose continuity of the electric field

$$E_i + E_r = E_t, \tag{139}$$

where r and t stand for reflected and transmitted, respectively. For the magnetic field, we must satisfy

$$H_i - H_r = H_t, \tag{140}$$

where we should take care the the direction of the magnetic field changes for the reflected light, see Fig. 26. We can relate this to the electric field by

$$\frac{\hat{q}_1}{\mu_1\omega}(E_i - E_r) = \frac{\hat{q}_2}{\mu_2\omega}E_t, \tag{141}$$

Using that $\hat{q} = \omega\hat{n}/c$ and that medium 1 is the vacuum for which we have $\hat{n}_1 = 1$ and $\mu_1 = \mu_0$ and, in addition, taking the solid nonmagnetic, which gives $\mu_2 = \mu_0$, we obtain

$$E_i - E_r = \hat{n}E_t. \tag{142}$$

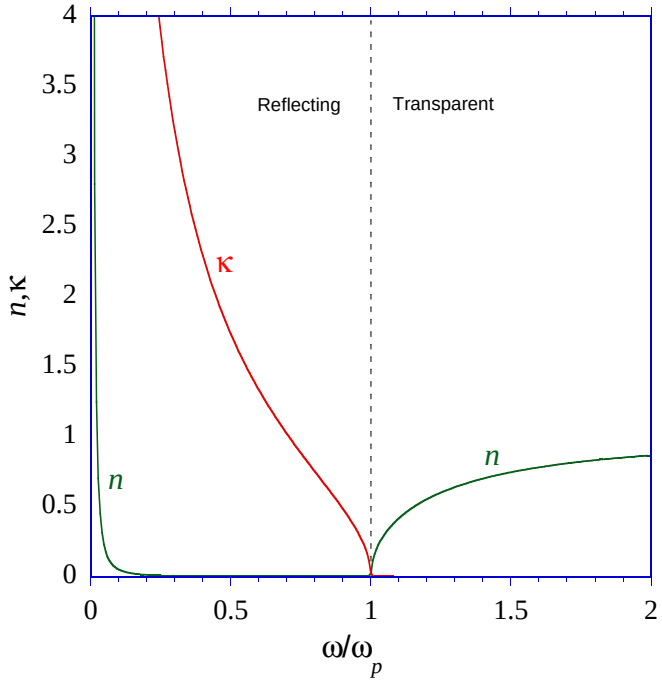


FIG. 28: The dependence of n and κ as a function of ω (normalized to the plasma frequency ω_p) for the Drude model. Same Γ as in Fig. 27.

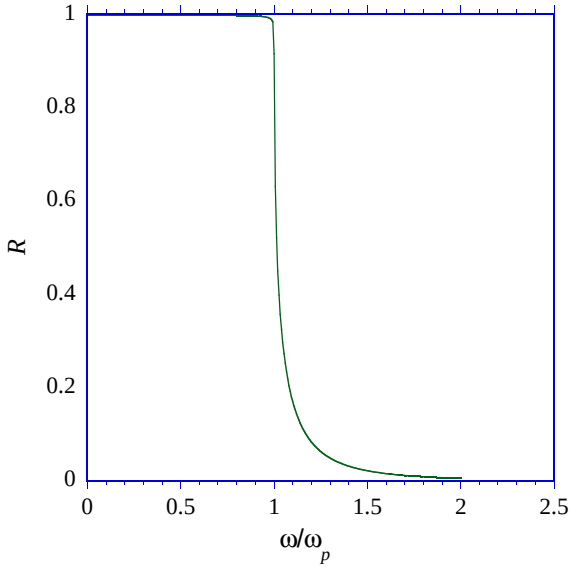


FIG. 29: The dependence of the reflectivity R as a function of ω (normalized to the plasma frequency ω_p) for the Drude model. Same Γ as in Fig. 27.

Combining this with Eqn. (139) gives

$$(\hat{n}-1)E_i + (1+\hat{n})E_r = 0 \quad \Rightarrow \quad r = \frac{E_r}{E_i} = \frac{1-\hat{n}}{1+\hat{n}}. \tag{143}$$

The reflectivity is then given by

$$R = r^* r = \left|\frac{1-\hat{n}}{1+\hat{n}}\right|^2 = \frac{(1-n)^2+\kappa^2}{(1+n)^2+\kappa^2} \tag{144}$$

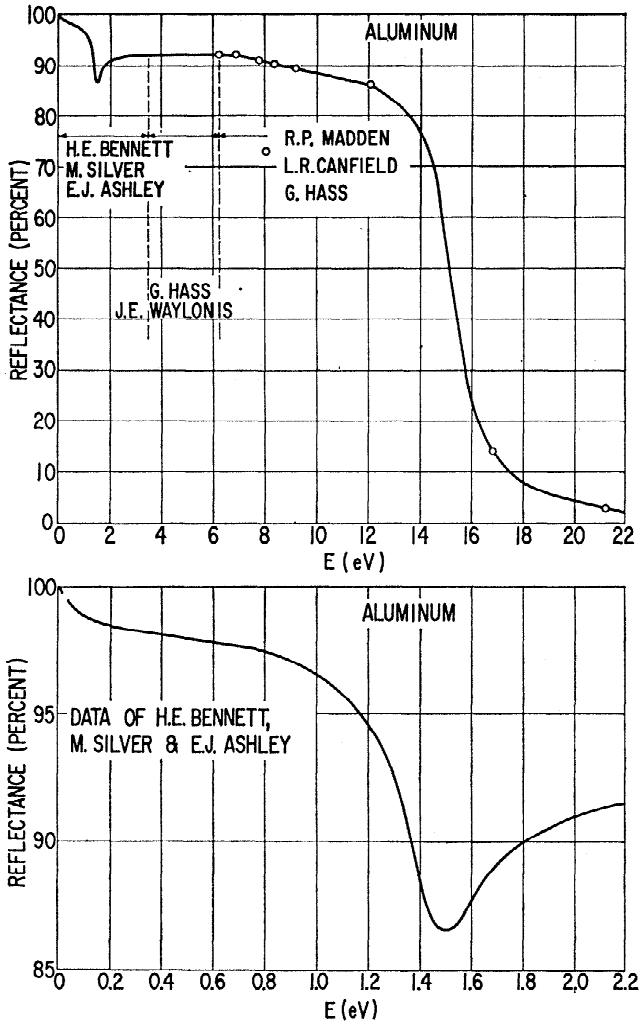


FIG. 30: The reflectance of aluminum. The plasma frequency is given by $\hbar\omega_p = 14.7$ eV. The decrease in reflectance around 1.4 eV is due to a weak interband transition.

Given the expressions for ε_1 and ε_2, see Fig. 27, for the Drude model, it is straightforward to calculate the index of refraction $\hat{n} = n + i\kappa$ and the reflectivity, see Fig. 28 and 29. Let us first look at the most intuitive one: the reflectivity, see Fig. 29. In the Drude, we see that the reflectivity is close 100% up to the plasma frequency ω_p. How does this work out for our "prototype" nearly-free electron system Al? Figure 30 shows that there is a remarkable agreement in the reflectivity. Close to 90% of the light is reflected up to the plasma frequency. The wavelength of visible light ranges from 380 (violet) to 750 (red) nm. This corresponds to an energy of 1.66-3.27 eV. The value of $\hbar\omega_p$ for Al is 14.7 eV. Therefore all the visible light is reflected, explaining why aluminum foil has the mirror-like look. The difference in the two sides of the aluminum foil has to do with the manufacturing process. Since aluminum foil is so thin, two sheet of foil are placed on top of each other in the final rolling. When separated after rolling the inside is duller than the outside due to different surface roughness. The reflectance is 88% for the shiny side and 80% for the dull side. There is a decrease in reflectance deviating from the Drude-like behavior around 1.4 eV due to weak interband transitions. The plasma frequency is $\omega_p = 3.5$ s^{-1}. This corresponds to a density of $n = 3.9 \times 10^{27}$ m^{-3}. So when neglecting the Fermi-Dirac distribution, we overestimate n by a factor 50. (As you might remember from 566, two order of magnitude was roughly the overestimation of the conductivity in the Drude model, which is given by $\sigma = ne^2\tau/m$, where τ is the time between scattering events. However, even though the model completely misses the actual value of ω_p, it gives a very nice description of the reflectivity.

The reflectance for frequencies less than the plasma frequency also manifests itself in other quantities. For $\omega < \omega_p$, the extinction coefficient is finite, indicating that light does not penetrate the solid. For $\omega > \omega_p$ we obtain no extinction and obtain a finite index of refraction. Thus aluminum will become transparent in the ultraviolet. We also observe a

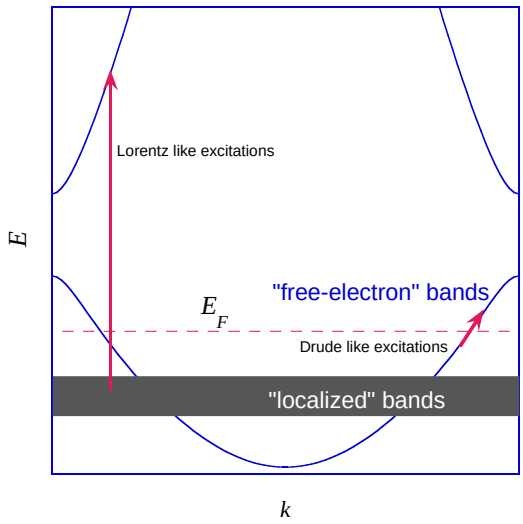


FIG. 31: Schematic figure of the possible transitions. The Drude model describes intraband transition. For free electron like systems and noble metals that would be in the free electron like bands that cross the Fermi level. The minimum energy needed for these transitions is zero. However, for noble metals, one also has to consider interband transitions from the more localized $3d$ bands. These occur at a finite energy.

finite refractive index n close to $\omega = 0$. This is due to absorption related to the fact that $\omega_0 = 0$ for the Drude model.
Lorentz oscillators and interband transitions.–

However, the Drude model appears to fail for noble metals, such as copper (reddish) and gold (yellow), although it works reasonably well for silver. The electron density of copper is $n = 4 \times 1/(3.61 \times 10^{-10})^3 = 8.5 \times 10^{28}$ m^{-3}. This about a factor two smaller than that of aluminum (although the absolute densities fail to predict the plasma frequency, your first order guess for the ratio of the plasma frequencies would be the ratio of the electron densities). Naively one can expect the plasma frequency to be about a factor $\sqrt{2}$ smaller. This would be of the order of 10 eV, sufficiently high to reflect all visible light. However, to obtain absorption in the visible light we need a plasma frequency around 2 eV, about seven times smaller. Since $\omega_p \sim \sqrt{n}$, this would correspond to an electron density which is about a factor 50 smaller. Although we might be willing to swallow a factor two, this is a bit too much. To understand the difference one needs to take a closer look at the electronic structure. The Drude model describes intraband transition. For free electron like systems like aluminum, these occur in the bands that cross the Fermi level. The minimum energy needed for these transitions is zero. However, for noble metals, one also has to consider interband transitions from the more localized d bands. These occur at a finite energy.

Let us therefore return to the original expressions for ϵ, see Eqn. (111). The real and imaginary part of the dielectric function, ε_1 and ε_2 are plotted in Fig. 32. The refractive index n, extinction coefficient κ, and the reflectivity R are shown in Fig. 33 for $\omega_0 = \omega_p/2$. Again, let us first look at the reflectivity. In the limit that $\Gamma \to 0$, we see again that a decrease in reflectivity around ω_p. This transition occurs when $\varepsilon_1 = 0$, or, for $\Gamma = 0$,

$$\varepsilon_1 = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2} = 0 \quad \Rightarrow \quad \omega = \sqrt{\omega_p + \omega_0^2}. \tag{145}$$

This gives or our example $\omega_p \sqrt{1 + \left(\frac{1}{2}\right)^2} \cong 1.12\ \omega_p$. Above this energy, the solid is transparent. Below this energy the solid is reflecting down to the energy ω_0. Below that energy, the system becomes transparent again. This situation is very comparable to what is found for semiconductors or insulators. For a wide-band insulator (for example, diamond, see Fig. 34) an optical transition occurs at a finite energy, i.e. the energy needed to excite an electron from the valence band into the conduction band. Below that energy, the system becomes transparent. For diamond, the minimum excitation energy is greater than 5 eV, larger than the energy of visible light. This makes diamond transparent for visible light giving it a glass light appearance. However, the reflectance is not entirely zero and some of the light will therefore be reflected. Diamonds can also have a color. This is due to impurities. These impurities create energy states inside the insulating gap. In Fig. 33, the optical properties are divided into four regions. These regions roughly indicate the dominant aspect of the material. For ω less than roughly $0.4\omega_0$, the material is mainly transparent with

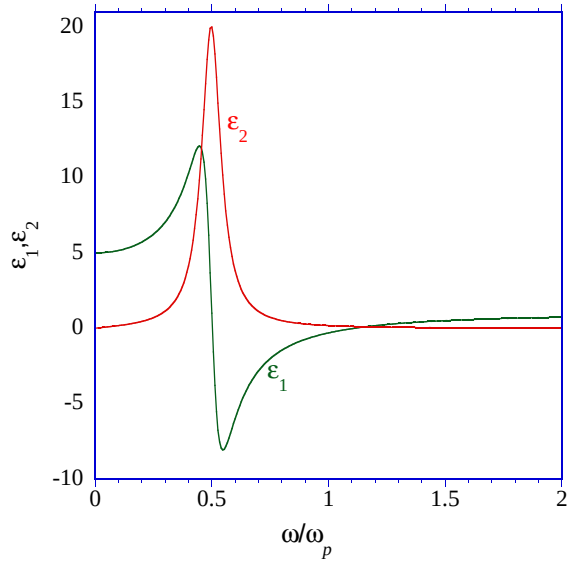


FIG. 32: The coefficients ε_1 and ε_2 as a function of ω/ω_p with $\omega_0 = \omega_p/2$ and $\Gamma = 0.1\omega_p$.

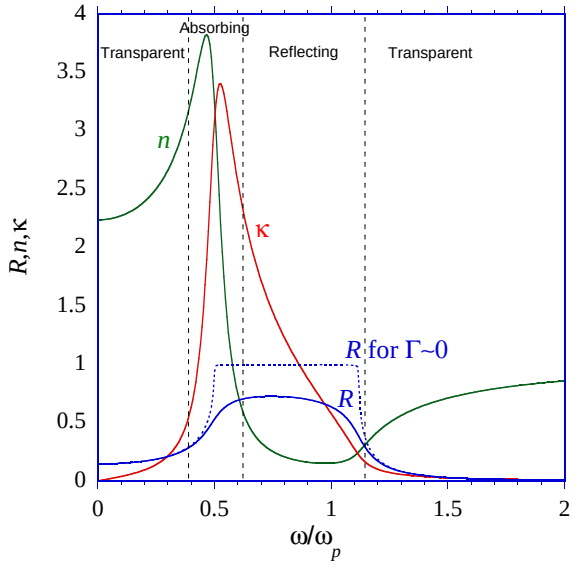


FIG. 33: The refractive index n, extinction coefficient κ, and the reflection coefficient R for a Lorentz oscillator as a function of ω/ω_p with $\omega_0 = \omega_p/2$ and $\Gamma = 0.1\omega_p$.

a finite refractive index n and a small extinction coefficient κ. Around ω_0, the material is predominantly absorbing, where the incoming light causes transitions of energy $\hbar\omega$. Between $0.6\hbar\omega_0$ and ω_p, the system is reflecting with a large R. For energies greater than ω_p, we again observe transparent behavior.

When considering the reflectance of noble metal such as copper and silver, see Fig. 35, one has to consider a combination of both Drude and Lorentz excitations. The Drude excitations related to excitations in the $4sp$ bands crossing the Fermi level dominate the reflectance for low energies. However at approximately 2 and 4 eV for Cu and Ag, respectively, we observe Lorentz-like excitations related to transitions from the occupied $3d$ band into the empty $4sp$ states, see also Fig. 25. To describe the reflectance we cannot consider a single Lorentz oscillator, but we have to take into account a large number of Lorentz oscillators of different energy. This causes a sharp drop in reflectance. For Ag, this hardly affects the reflectance in the visible light, since 4 eV is in the ultraviolet. However, for copper, the decrease in reflectance occur in the visible region, cutting of the blue part of the spectrum, giving copper its reddish

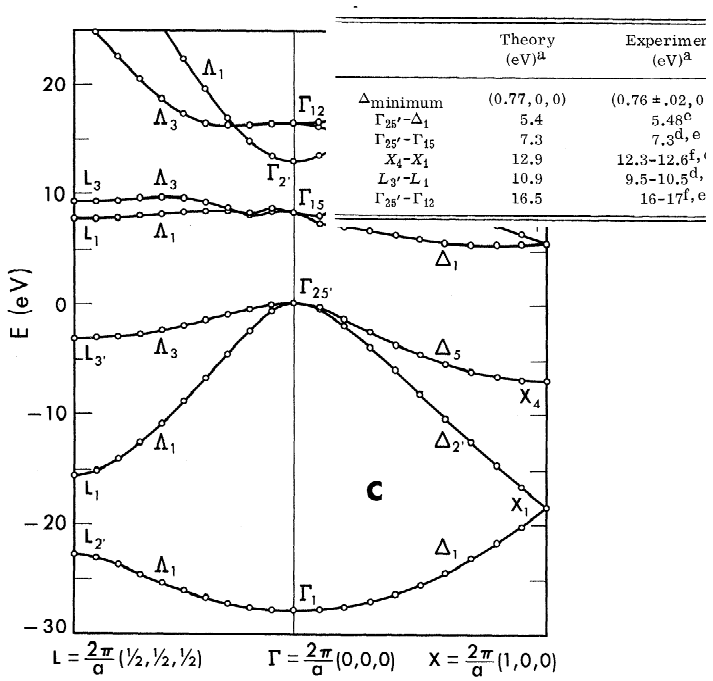


FIG. 34: The band structure of diamond after Saslow, Bergstresser, and Cohen, Phys. Rev. Lett. **16**, 354 (1966). The inset shows the values of several optical transitions.

color. Note that another drop of occurs at higher energies, clearly visible in Ag around 7-8 eV. This drop-off is related to the plasma frequency at an energy about half that in Al, in agreement with our simple estimate of the relative plasma frequencies of Al and Ag/Cu.

XV. QUANTUM-MECHANICAL TREATMENT OF OPTICAL SPECTROSCOPY

We now want to interpret optical spectroscopy in term of quantum mechanics and relate the Lorentz oscillators to interband and intraband transitions. We can write our eigenstates in the absence of light as

$$H_0 = |\mathbf{k}n\rangle = E_{\mathbf{k}n}|\mathbf{k}n\rangle, \tag{146}$$

where H_0 is the Hamiltonian describing the solid and $E_{\mathbf{k}n}$ are the eigenenergies that describe the electronic structure. We want to study how the solid reacts to light and we therefore add a time-dependent perturbation to the Hamiltonian,

$$H = H_0 + H'(t). \tag{147}$$

The wave function as a function of time can now be found from the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = [H_0 + H'(t)]|\psi(t)\rangle. \tag{148}$$

The question is now, what states are involved in the wavefunction $|\psi(t)\rangle$? We have to make some approximations here. Obviously, we want to include the ground state, which is the Fermi sea, i.e. all the states filled up to the Fermi level following Pauli's principle (we assume that $T = 0$ K). For the Fermi sea, which we denote by $|0\rangle$, we have

$$H_0|0\rangle = E_0|0\rangle \quad \text{with} \quad E_0 = \sum_{E_{\mathbf{k}n}\leq E_F} E_{\mathbf{k}n}. \tag{149}$$

Let us now consider the excited states. To lowest order, the light will create electron-hole pair excitations with respect to the Fermi sea. Let us denote these states by

$$|m\rangle = |\mathbf{k}'n'; \underline{\mathbf{k}n}\rangle \tag{150}$$

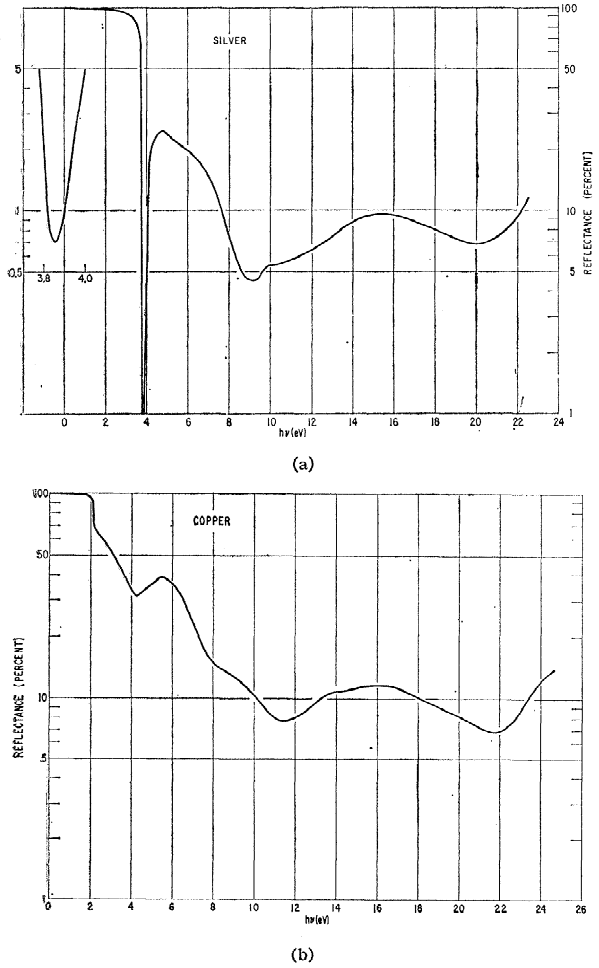


FIG. 35: The reflectance of copper and silver, see Ehrenreich and Philipp, Phys. Rev. **128**, 1622 (1962).

where the state $|\mathbf{k}'n';\underline{\mathbf{k}n}\rangle$ indicates a Fermi sea, but with an electron with wave vector $\mathbf{k}'$ and band index n' above the Fermi level and a hole (or missing electron) with wavevector $\mathbf{k}$ and band index n below the Fermi level. The energy of this state is given by

$$H_0|m\rangle = E_m|m\rangle = (\hbar\omega_m + E_0)|m\rangle \quad \text{with} \quad \hbar\omega_m = E_{\mathbf{k}'n'} - E_{\mathbf{k}n}. \tag{151}$$

We can now write the time-dependent wavefunction as

$$|\psi(t)\rangle = \sum_m a_m(t)e^{-iE_m t/\hbar}|m\rangle. \tag{152}$$

Inserting this into the Schrödinger equation gives

$$i\hbar\sum_m \left\{\frac{da_m(t)}{dt} - \frac{i}{\hbar}E_m a(t)\right\} e^{-iE_m t/\hbar}|m\rangle = \sum_m \left\{E_m + H'(t)\right\} a_m(t)e^{-iE_m t/\hbar}|m\rangle. \tag{153}$$

We see that the terms with E_m cancel, giving

$$i\hbar\sum_m \frac{da_m(t)}{dt}e^{-iE_m t/\hbar}|m\rangle = \sum_m H'(t)a_m(t)e^{-iE_m t/\hbar}|m\rangle. \tag{154}$$

We can multiply this on the left by $\langle m'|e^{iE_m t/\hbar}$, giving

$$i\hbar\frac{da_{m'}(t)}{dt} = \sum_m \langle m'|H'(t)|m\rangle a_m(t)e^{i(E_{m'}-E_m)t/\hbar}. \tag{155}$$

If we take the system to be initially in the ground state,

$$a_m = \delta_{m,0}, \qquad t = 0, \tag{156}$$

we obtain $E_{m'} - E_m = E_{m'} - E_0 = \hbar\omega_m$. Using

$$H'_{m'} = \langle m'|H'(t)|0\rangle = \int d\mathbf{r}\varphi^*_{\mathbf{k}'n'}H'\varphi_{\mathbf{k}n}, \tag{157}$$

we can write, in first order approximation theory,

$$i\hbar\frac{da_{m'}(t)}{dt} = H'_{m'}e^{i\omega_{m'}t}. \tag{158}$$

Note that the summation has disappeared since we only consider one transition, from the ground state $|0\rangle$ to and excited state $|m'\rangle$.

So far we have not really specified the pertubation $H'(t)$. For a classical oscillator, we can write

$$H'(t) = e\mathbf{E}(t)\cdot\mathbf{r}. \tag{159}$$

We are concerned with the situation that the wavelength of the light is much larger than the dimension of the atom. So we can therefore approximate the electric field by its value at the nucleus. Let us consider monochromatic light with a cosine dependence (we can always express other light in these components),

$$\mathbf{E}(t) = \mathbf{E}\cos\omega t = \frac{1}{2}\mathbf{E}(e^{i\omega t} + e^{-i\omega t}). \tag{160}$$

We can then express

$$H(t) = \frac{1}{2}e\mathbf{E}\cdot\mathbf{r}(e^{i\omega t} + e^{-i\omega t}) \quad \Rightarrow \quad H'_m = \frac{1}{2}e\mathbf{E}\cdot\langle\mathbf{r}\rangle_m(e^{i\omega t} + e^{-i\omega t}), \tag{161}$$

where

$$\langle\mathbf{r}\rangle_m = \langle m|\mathbf{r}|0\rangle = \int d\mathbf{r}\varphi_{\mathbf{k}'n'}r\varphi_{\mathbf{k}n} \tag{162}$$

is the dipole matrix element, which follows the usual dipole selection rules Let us drop the prime in Eqn. (158) and integrate the time from $t = 0$ to a particular time t

$$a_m(t) = \frac{1}{i\hbar}\frac{1}{2}e\mathbf{E}\cdot\langle\mathbf{r}\rangle_m\int_0^t dt'\left[e^{i(\omega_m+\omega)t'} + e^{i(\omega_m-\omega)t'}\right] \tag{163}$$

$$= \frac{e\mathbf{E}\cdot\langle\mathbf{r}\rangle_m}{2\hbar}\left[\frac{1-e^{i(\omega_m+\omega)t}}{\omega_m+\omega} + \frac{1-e^{i(\omega_m-\omega)t}}{\omega_m-\omega}\right]. \tag{164}$$

We are interested in comparing the classical with the quantum-mechanical dielectric function. We obtained the classical dielectric function by studying the induced dipole moment due to the electric field. Let us consider calculate the induced dipole moment which can be directly related to the expectation value of $\mathbf{r}$,

$$\mathbf{p} = -e\langle\psi(t)|\mathbf{r}|\psi(t)\rangle. \tag{165}$$

However, we just obtained the expression for $|\psi(t)\rangle$ within first-order perturbation theory. Using this, we have

$$\mathbf{p} = -e\sum_{m,m'}a^*_{m'}(t)a_m(t)\langle m'|\mathbf{r}|m\rangle e^{i(E_{m'}-E_m)t/\hbar}. \tag{166}$$

However, we expect that the coefficients a_m with $m \neq 0$ are relatively small. Therefore, the major contributions will come from the terms where either $m = 0$ or $m' = 0$. Renaming one of the dummy arguments gives

$$\mathbf{p} = -e\sum_m\left[a^*_m(t)\langle m|\mathbf{r}|0\rangle e^{i\omega_m t} + a_m(t)\langle 0|\mathbf{r}|m\rangle e^{-i\omega_m t}\right] = -e\sum_m\left[a^*_m(t)\langle\mathbf{r}\rangle_m e^{i\omega_m t} + a_m(t)\langle\mathbf{r}\rangle^*_m e^{-i\omega_m t}\right] \tag{167}$$

Let us now also assume that the excited states have a finite lifetime. This means that they obtain a complex frequency

$$\omega_m \to z_m = \omega_m + \frac{i}{2}\Gamma_m, \tag{168}$$

giving a time dependence $e^{i\omega t - \frac{1}{2}\Gamma_m t}$, showing a decay of the wavefunction. In the remainder, we neglect the m dependende of Γ. We are now dealing with terms

$$a_m(t)e^{-iz_m t} = \frac{e\mathbf{E}\cdot\langle\mathbf{r}\rangle_m}{2\hbar}\left[\frac{e^{-iz_m t}-e^{i\omega t}}{z_m+\omega}+\frac{e^{-iz_m t}-e^{-i\omega t}}{z_m-\omega}\right] \to -\frac{e\mathbf{E}\cdot\langle\mathbf{r}\rangle_m}{2\hbar}\left[\frac{e^{i\omega t}}{z_m+\omega}+\frac{e^{-i\omega t}}{z_m-\omega}\right], \tag{169}$$

where in the last step we have used the fact that only the terms with the same frequency as the driving force remain whn taking a time average. Let us for simplicity also take the electric field along the x direction, with $\mathbf{E} = E\hat{\mathbf{x}}$. This gives also a dipole moment p_x along the x direction. Using $x_m = \langle m|x|0\rangle$, we find for the dipole moment

$$p = \sum_m \frac{e^2E|x_m|^2}{2\hbar}(z_m + z_m^*)\left[\frac{e^{i\omega t}}{(z_m+\omega)(z_m^*-\omega)}+\frac{e^{-i\omega t}}{(z_m-\omega)(z_m^*+\omega)}\right], \tag{170}$$

where $z_m + z_m^* = 2\omega_m$ and

$$\begin{aligned}(z_m \pm \omega)(z_m^* \mp \omega) &= (\omega_m + \frac{i}{2}\Gamma \pm \omega)(\omega_m - \frac{i}{2}\Gamma \mp \omega) &(171)\\ &= (\omega_m \pm \omega)(\omega_m \mp \omega) + \frac{i}{2}\Gamma[\omega_m \mp \omega - (\omega_m \pm \omega)] - \frac{1}{4}\Gamma^2 &(172)\\ &= \omega_m^2 - \omega^2 - \frac{1}{4}\Gamma^2 \mp i\Gamma\omega \to \omega_m^2 - \omega^2 \mp i\Gamma\omega, &(173)\end{aligned}$$

where in the last step we assumed that the broadening is small relatively to the excitation energy ω_m. This gives for the dipole moment

$$p = \sum_m \frac{e^2E|x_m|^2}{\hbar}\left[\frac{\omega_m e^{i\omega t}}{\omega_m^2-\omega^2-i\Gamma\omega}+\frac{\omega_m e^{-i\omega t}}{\omega_m^2-\omega^2+i\Gamma\omega}\right]. \tag{174}$$

The polarization is then given by

$$P = \frac{N}{V}p = \sum_m \frac{2e^2n|x_m|^2}{\hbar}\left[\frac{\omega_m(\omega_m^2-\omega^2)}{(\omega_m^2-\omega^2)^2+\Gamma^2\omega^2}\cos\omega t + \frac{\omega_m\Gamma\omega}{(\omega_m^2-\omega^2)^2+\Gamma^2\omega^2}\sin\omega t\right]E. \tag{175}$$

In order to relate this to the dielectric function, we need to look at the response to a cosine wave. We know that for an electric field $\mathbf{E}\ e^{-i\omega t}$, the polarization is given by $\mathbf{P} = \chi(\omega)\varepsilon_0\mathbf{E}$. To construct a cosine, we also need $\chi(-\omega)$. From Eqn. (111), we can see that replacing ω by $-\omega$ gives $\varepsilon(-\omega) = \varepsilon^*(-\omega)$. We therefore have for a cosine

$$\begin{aligned}\mathbf{P} = \frac{1}{2}\varepsilon_0 E(\chi e^{-i\omega t} + \chi^* e^{i\omega t}) &= \frac{1}{2}\varepsilon_0 E\left[(\varepsilon_1 - 1)(e^{-i\omega t}+e^{i\omega t}) + i\varepsilon_2(e^{-i\omega t}-e^{+i\omega t})\right] &(176)\\ &= \varepsilon_0(\varepsilon_1-1)E\cos\omega t + \varepsilon_0\varepsilon_2 E\sin\omega t. &(177)\end{aligned}$$

This means that the cosine term is related to ε_1,

$$\varepsilon_1 = 1 + \sum_m \frac{2e^2n|x_m|^2}{\varepsilon_0\hbar}\frac{\omega_m(\omega_m^2-\omega^2)}{(\omega_m^2-\omega^2)^2+\Gamma^2\omega^2} \tag{178}$$

and the sine term to ε_2,

$$\varepsilon_2 = \sum_m \frac{2e^2n|x_m|^2}{\varepsilon_0\hbar}\frac{\omega_m\Gamma\omega}{(\omega_m^2-\omega^2)^2+\Gamma^2\omega^2}. \tag{179}$$

We can also write this in its complex form

$$\varepsilon_r = 1 + \frac{ne^2}{m\varepsilon_0}\sum_m \frac{f_m}{\omega_m^2-\omega^2-i\Gamma\omega}, \tag{180}$$

with the oscillator strength given by

$$f_m = \hbar\omega_m\frac{2m}{\hbar^2}|x_m|^2. \tag{181}$$

XVI. RELATION TO ABSORPTION

Earlier it was mentioned that ε_2 was related to absoprtion. This might not be directly obvious. We are used to righting absorption and emission in terms of Fermi's Golden Rule

$$I(\omega) \sim \sum_m |\langle m|H'|0\rangle|^2 \delta(\omega - \omega_m), \tag{182}$$

where $I(\omega)$ is the absorption intensity. However, we want rewrite the δ-function. Using

$$-i\int_0^\infty e^{i(\omega-\omega_m)t-\eta t}dt = \frac{1}{\omega-\omega_m+i\eta} = \frac{\omega-\omega_m}{(\omega-\omega_m)^2+\eta^2} - i\frac{\eta}{(\omega-\omega_m)^2+\eta^2} \tag{183}$$

Note that the imaginary part works as a δ-function in the limit $\eta \to 0$, when it is zero for $\omega \neq \omega_m$ and $1/\eta \to \infty$ for $\omega = \omega_m$. The integral over this function, known as a Lorentzian, is equal to π. Normalizing the δ-function to unity, we have

$$\delta(\omega-\omega_m) = \frac{1}{\pi}\frac{\eta}{(\omega-\omega_m)^2+\eta^2} = -\frac{1}{\pi}\mathrm{Im}\frac{1}{\omega-\omega_m+i\eta}. \tag{184}$$

The function $(\omega-\omega_m+i\eta)^{-1}$ is also known as a Green's function. Therefore we can also write Fermi's golden fule as

$$I(\omega) \sim -\frac{1}{\pi}\sum_m |x_m|^2 \mathrm{Im}\frac{1}{\omega-\omega_m+i\eta} = -\frac{1}{\pi}\sum_m |x_m|^2 \mathrm{Im}\frac{1}{\omega-z_m^*}, \tag{185}$$

where we have used $x_m = \langle m|H'|0\rangle$. We can also do the inverse process and emit a photon

$$I(\omega) \sim \sum_m |\langle 0|H'|m\rangle|^2 \delta(\omega_m+\omega). \tag{186}$$

This term requires some closer consideration. The conservation of energy says that we start we an initial state and end up with an excitation with energy $\hbar\omega_m$ and a photon with energy $\hbar\omega$. Since energy is conserved this implies that $\hbar\omega = -\hbar\omega_m$. Since the photon energy is always positive, this implies that $\hbar\omega_m < 0$. However,we saw before that the $\hbar\omega_m$ corresponded to an electron-hole pair excitation, which is always positive. However, we can have this term if there are excitations in the initial state, which can be present at finite temperature or due to laser excitations. Then the energy $\hbar\omega_m$ corresponds to the deexcitation of an electron-hole pair. We can also rewrite this in an integral form

$$i\int_{-\infty}^0 e^{i(\omega_m+\omega)t+\eta t}dt = -\frac{1}{\omega_m+\omega+i\eta} = -\frac{1}{\omega+z_m} \tag{187}$$

The gives for the intensity

$$I(\omega) \sim -\frac{1}{\pi}\sum_m |x_m|^2 \mathrm{Im}\frac{1}{\omega+z_m}, \tag{188}$$

Adding the two terms together gives

$$\frac{1}{\omega-z_m^*} - \frac{1}{z_m+\omega} = -\frac{z_m+z_m^*}{(\omega-z_m^*)(\omega+z_m)}, \tag{189}$$

which reproduces the $e^{i\omega t}$ term in Eqn. (173).

XVII. THOMAS-FERMI SCREENING

As we have seen in the previous sections, the electrons respond to an externally applied electric field. In the same way, one can envision the electron cloud corresponding to the electric field produced by an electron. This is called screening. We can understand screening physically by noting that the electrons cloud reacts to the electron and will move as a result of the potential created by the electron. However, in a system in equilibrium we assume that the

chemical potential $\mu = E_F(\mathbf{r}) - U(\mathbf{r})$ remains constant. Thus the change in potential has to be compensated by a change in number of electrons

$$\frac{dE_F}{dn}\Delta n - U = 0. \tag{190}$$

In a free electron model, the Fermi energy is given by

$$N = 2\frac{V}{(2\pi)^3}\frac{4}{3}\pi k_F^3 \Rightarrow k_F = (3\pi^2 n)^{1/3} \Rightarrow E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi n)^{2/3}, \tag{191}$$

giving $dE_F/dn = \frac{2}{3}E_F/n$. The induced charge is therefore

$$\rho_{\text{ind}} = e\Delta n = \frac{3}{2}\frac{enU}{E_F} = \frac{3}{2}\frac{e^3 n}{E_F \epsilon_0 q^2} \tag{192}$$

where use has been made of Laplace's equation to calculate the potential from the point charge e: $\nabla^2 V = e/\epsilon_0$ (which also follows from Gauss's equation $\nabla \cdot \mathbf{E} = -e/\varepsilon_0$ and $\mathbf{E} = -\nabla V$. or in momentum space $-q^2 V = e/\varepsilon_0$ or $V = -e/\varepsilon_0 q^2$. The potential energy is then $U = -eV = e^2/\varepsilon_0 q^2$. An alternative way of obtaining the same result is to make a Fourier transform of the Coulomb potential

$$U(r) = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}. \tag{193}$$

The use of this alernative way becomes clear in a little while. The Fourier transform gives

$$U_q = \frac{e^2}{4\pi\varepsilon_0}\int_0^{2\pi} d\varphi \int_0^{\infty} dr \int_0^{\pi} d\theta r^2 \sin\theta e^{iqr\cos\theta}\frac{1}{r} \tag{194}$$

$$= \frac{e^2}{2\varepsilon_0}\int_0^{\infty} dr \int_{-1}^{1} d\cos\theta r e^{iqr\cos\theta} = \frac{e^2}{2iq\varepsilon_0}\int_0^{\infty} dr(e^{iqr} - e^{-iqr}) \tag{195}$$

Here we have a small problem with the convergence of the integration. This can be solved by making the oscillation damp out by $e^{-\lambda r}$, and in the end take $\lambda = 0$

$$U_q = \frac{e^2}{2iq\varepsilon_0}\int_0^{\infty} dr(e^{iqr} - e^{-iqr})e^{-\lambda r} = \frac{e^2}{2iq\varepsilon_0}\int_0^{\infty} dr(e^{i(q+i\lambda)r} - e^{-i(q-i\lambda)r}) = \frac{e^2}{2q\varepsilon_0}\left[\frac{1}{q+i\lambda} + \frac{1}{q-i\lambda}\right]$$
$$= \frac{e^2}{\varepsilon_0}\frac{1}{q^2+\lambda^2} \tag{196}$$

where a λ has been introduced to let the oscillations damp out slowly. In the limit $\lambda \to 0$, we obtain $U_q = e^2/\varepsilon_0 q^2$.

For the dielectric function we then find

$$\epsilon_r = 1 + \chi = 1 - \frac{\rho_{\text{ind}}}{\rho_{\text{free}}} = 1 - \frac{\rho_{\text{ind}}}{-e} = 1 + \frac{3e^2 n}{2E_F\varepsilon_0 q^2} = 1 + \frac{q_{TF}^2}{q^2} \tag{197}$$

with $q_{TF} = \sqrt{3ne^2/2\varepsilon_0 E_F}$. We therefore find an effective Coulomb potential

$$U_q = \frac{1}{\varepsilon}\frac{e^2}{q^2} = \frac{1}{\varepsilon + 0}\frac{e^2}{\varepsilon_r q^2} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{q^2 + q_{TF}^2}. \tag{198}$$

One might wonder to what potential this corresponds in real space. However, we see that the form is exactly the same as the form obtained in deriving the Fourier transform of the potential. We can therefore write the effective screened potential as

$$U(r) = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}e^{-q_{TF}r}, \tag{199}$$

which look like a Coulomb potential but with a reduced range.

XVIII. MANY-PARTICLE WAVEFUNCTIONS

In quantum mechanics, particles are indistinguishable. This means that we should be able to interchange two particles without seeing any effect on the probability function. We can distinguish two fundamentally different types of particles, namely those with a symmetric and antisymmetric wavefunction. Under permutation between particle i and j for a N particle wavefunction, one has the following possibilities

$$P_{ij}\psi^{\pm}_{n_1\cdots n_N}(\mathbf{r}_1,\cdots,\mathbf{r}_i,\cdots,\mathbf{r}_j,\cdots,\mathbf{r}_N) = \pm\psi^{\pm}_{n_1\cdots n_N}(\mathbf{r}_1,\cdots,\mathbf{r}_i,\cdots,\mathbf{r}_j,\cdots,\mathbf{r}_N) \tag{200}$$

where k_i means that a particle is in a certain quantum state n_i (for example a particle in a box where the quantum numbers are $n_i = n_x, n_y, n_z$, but it could also refer to the quantum numbers of an atom $n_i = nlm\sigma$). At first sight one might think it does not make any difference since the real properties are related to the square of the wavefunction and a plus or minus sign should not make too much of a difference. However, the sign has drastic consequences for the statistics. Let us look at the wavefunction for two particles:

$$\psi^{\pm}_{k_1,k_2}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}(\varphi_{k_1}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_2) \pm \varphi_{k_2}(\mathbf{r}_1)\varphi_{k_1}(\mathbf{r}_2)). \tag{201}$$

where ϕ_k are eigenfunctions of the Hamiltonian. The symmetric and antisymmetric wavefunctions give two fundamentally different particles. Particles whose wavefunction is symmetric are bosons, particles with antisymmetric wavefunctions are called fermions. Examples of bosons are photons, π and K mesons. These are particles with integral spin. Also the harmonic oscillator and lattice vibrations (also known as phonons) behave like a "boson"-like particle. Particles with half integral spin behave like fermions. Examples are electrons, protons, and neutrons. The antisymmetric wavefunctions have a very special characteristic. Let us take two particle in the same quantum state

$$\psi^{-}_{k,k}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}(\varphi_k(\mathbf{r}_1)\varphi_k(\mathbf{r}_2) - \varphi_k(\mathbf{r}_1)\varphi_k(\mathbf{r}_2)) = 0. \tag{202}$$

Therefore, it is impossible to have two fermions with the same quantum numbers. Note that the spin is also considered a quantum number. Therefore, we can have two electrons in the same wavefunction (say the same plane wave or the same atomic orbital), but with opposite spins. The occupation of each fermion state is therefore 0 or 1.

Let us now generalize the wavefunctions for an arbitrary number of particles. For bosons the general wavefunction is

$$\Psi_{k_1,\ldots,k_N} = \sqrt{\frac{\Pi_i n_{k_i}!}{N!}}\sum_P \psi_{k_1}(\mathbf{r}_1)\cdots\psi_{k_N}(\mathbf{r}_N), \tag{203}$$

where the summations runs over all the possible permutations of *different* indices k_i. This gives the normalization constant. n_{k_i} indicates how many k-values are k_i. Note that the $\sum_i n_{k_i} = N$. For two particles with $S = 0$, we have

$$\Psi_{k_1,k_2} = \frac{1}{\sqrt{2}}\left\{\psi_{k_1}(\mathbf{r}_1)\psi_{k_2}(\mathbf{r}_2) + \psi_{k_2}(\mathbf{r}_1)\psi_{k_1}(\mathbf{r}_2)\right\}. \tag{204}$$

For $k_1 = k_2 = k$, we find

$$\Psi_{k_1,k_2} = \sqrt{\frac{2!}{2!}}\psi_k(\mathbf{r}_1)\psi_k(\mathbf{r}_2) = \psi_k(\mathbf{r}_1)\psi_k(\mathbf{r}_2), \tag{205}$$

using the fact that $n_k = 2$. We see that it is possible to put two bosons in the same quantum state. In fact, we can put any arbitrary number of bosons in a particle quantum state. From a statistical point of view, we therefore have for the occupation numbers of a particular quantum state i

$$n_i = 0, 1 \quad \text{fermions} \tag{206}$$

$$n_i = 0, 1, 2, 3, \cdots \quad \text{bosons} \tag{207}$$

This is an important aspect that we have to include in our quantum statistics. Up till now the only aspect that we have used is the indistinguishability.

The situation for electrons (and other spin-1/2 particles) is fact a bit more complicated since the total wavefunction, i.e., orbital and spin, has to be asymmetric. This means $\psi_S(\mathbf{r}_1,\mathbf{r}_2)\xi_A(1,2)$ or $\psi_A(\mathbf{r}_1,\mathbf{r}_2)\xi_S(1,2)$, where $\xi(1,2)$ is the wavefunction for the spin. There are four ways to combine two spins $\xi_\uparrow(1)\xi_\uparrow(2)$, $\xi_\uparrow(1)\xi_\downarrow(2)$, $\xi_\downarrow(1)\xi_\uparrow(2)$, and $\xi_\downarrow(1)\xi_\downarrow(2)$.

$\xi_\uparrow(1)\xi_\uparrow(2)$ and $\xi_\downarrow(1)\xi_\downarrow(2)$ are clearly symmetric spin functions, since interchange of the particles does not change the sign of the wave function. These are the $\xi_{11}(1,2)$ and $\xi_{1,-1}(1,2)$ components of the triplet ($S=1$). Since $S_z = 1, 0, -1$ for $S=1$, there should also be a $S=0$ component. This can be obtained by using the step operator for the spin

$$S_-\xi_{11} = \sqrt{(1+1)(1-1+1)}\xi_{10} = \sqrt{2}\xi_{10} = \xi_\uparrow(1)\xi_\downarrow(2) + \xi_\downarrow(1)\xi_\uparrow(2) \tag{208}$$

$$\Rightarrow \qquad \xi_{10} = \frac{1}{\sqrt{2}}\left[\xi_\uparrow(1)\xi_\downarrow(2) + \xi_\downarrow(1)\xi_\uparrow(2)\right] \tag{209}$$

where we have used

$$S_\pm \xi_{SS_z} = \sqrt{(S \mp S_z)(S \pm S_z + 1)}\xi_{S,S_z\pm 1} \tag{210}$$

Note that this is also a symmetric wavefunction. The remaining wave function has to be orthogonal to the previous one

$$\xi_{00}(1,2) = \frac{1}{\sqrt{2}}\left[\xi_\uparrow(1)\xi_\downarrow(2) - \xi_\downarrow(1)\xi_\uparrow(2)\right] \tag{211}$$

which is antisymmetric. Since there is only one component (called a singlet), this has to be $S=0$. The four total wavefunctions for two electrons are therefore $\Psi_{1S_z}(\mathbf{r}_1,\mathbf{r}_2) = \psi_A(\mathbf{r}_1,\mathbf{r}_2)\xi_{1S_z}(1,2)$ with $S_z = 1, 0, -1$ and $\Psi_{00}(\mathbf{r}_1,\mathbf{r}_2) = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\xi_{00}(1,2)$. The $S=1$ and $S_z=1$ is given by

$$\Psi_{11}(\mathbf{r}_1,\mathbf{r}_2) = \psi_A(\mathbf{r}_1,\mathbf{r}_2)\xi_{11}(1,2) = \frac{1}{\sqrt{2}}\left[\varphi_{k_1}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_2) - \varphi_{k_2}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_1)\right]\xi_\uparrow(1)\xi_\uparrow(2) \tag{212}$$

$$= \frac{1}{\sqrt{2}}\left[\varphi_{k_1}(\mathbf{r}_1)\xi_\uparrow(1)\varphi_{k_2}(\mathbf{r}_2)\xi_\uparrow(2) - \varphi_{k_2}(\mathbf{r}_1)\xi_\uparrow(1)\varphi_{k_2}(\mathbf{r}_1)\xi_\uparrow(2)\right] \tag{213}$$

$$= \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1)\xi_\uparrow(1) & \varphi_{k_1}(\mathbf{r}_2)\xi_\uparrow(2) \\ \varphi_{k_2}(\mathbf{r}_1)\xi_\uparrow(1) & \varphi_{k_2}(\mathbf{r}_2)\xi_\uparrow(2) \end{vmatrix} \tag{214}$$

The $S=0$ and $S_z=0$ wavefunction is given by

$$\Psi_{00}(\mathbf{r}_1,\mathbf{r}_2) = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\xi_{00}(1,2) = \frac{1}{\sqrt{2}}\left[\varphi_{k_1}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_2) + \varphi_{k_2}(\mathbf{r}_1)\varphi_{k_2}(\mathbf{r}_1)\right]\frac{1}{\sqrt{2}}\left[\xi_\uparrow(1)\xi_\downarrow(2) - \xi_\downarrow(1)\xi_\uparrow(2)\right] \tag{215}$$

$$= \frac{1}{2}\left[\varphi_{k_1}(\mathbf{r}_1)\xi_\uparrow(1)\varphi_{k_2}(\mathbf{r}_2)\xi_\downarrow(2) - \varphi_{k_2}(\mathbf{r}_1)\xi_\downarrow(1)\varphi_{k_1}(\mathbf{r}_2)\xi_\uparrow(2)\right. \tag{216}$$

$$\left. -\varphi_{k_1}(\mathbf{r}_1)\xi_\downarrow(1)\varphi_{k_2}(\mathbf{r}_2)\xi_\uparrow(2) + \varphi_{k_2}(\mathbf{r}_1)\xi_\uparrow(1)\varphi_{k_1}(\mathbf{r}_2)\xi_\downarrow(2)\right] \tag{217}$$

Note that this can also be written as a combination of Slater determinants

$$\Psi_{00}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1)\xi_\uparrow(1) & \varphi_{k_1}(\mathbf{r}_2)\xi_\uparrow(2) \\ \varphi_{k_2}(\mathbf{r}_1)\xi_\downarrow(1) & \varphi_{k_2}(\mathbf{r}_2)\xi_\downarrow(2) \end{vmatrix} - \frac{1}{\sqrt{2}}\begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1)\xi_\downarrow(1) & \varphi_{k_1}(\mathbf{r}_2)\xi_\downarrow(2) \\ \varphi_{k_2}(\mathbf{r}_1)\xi_\uparrow(1) & \varphi_{k_2}(\mathbf{r}_2)\xi_\uparrow(2) \end{vmatrix}\right) \tag{218}$$

$$= \frac{1}{\sqrt{2}}[\psi_{k_1\uparrow,k_2\downarrow}(\mathbf{r}_1,\mathbf{r}_2) - \psi_{k_1\downarrow,k_2\uparrow}(\mathbf{r}_1,\mathbf{r}_2)] \tag{219}$$

Note that in general we can built up antisymmetric states from Slater determinants

$$\psi_{k_1\sigma_1,\ldots,k_N\sigma_N}(\mathbf{r}_1\cdots\mathbf{r}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1)\xi_{\sigma_1}(1) & \cdots & \varphi_{k_1}(\mathbf{r}_N)\xi_{\sigma_1}(N) \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \varphi_{k_N}(\mathbf{r}_1)\xi_{\sigma_N}(1) & \cdots & \varphi_{k_N}(\mathbf{r}_N)\xi_{\sigma_N}(N) \end{vmatrix} \tag{220}$$

where $\sigma_i = \uparrow, \downarrow$. As a result of the properties of the determinant, having two columns with the same k and σ implies that the determinant is zero, just as for the exclusion principle. Interchange of two columns also leads to a change in sign of the determinant, giving us directly the antisymmetry. This is obvious for the $S_z = 1, -1$ states of the triplet. For the $S_z = 0$ states, one needs a combination of Slater determinants

$$\Psi_{k_1k_2,00} = \frac{1}{\sqrt{2}}\left(\psi_{k_1\uparrow,k_2\downarrow} - \psi_{k_1\downarrow,k_2\uparrow}\right) \qquad \text{and} \qquad \Psi_{k_1k_2,10} = \frac{1}{\sqrt{2}}\left(\psi_{k_1\uparrow,k_2\downarrow} + \psi_{k_1\downarrow,k_2\uparrow}\right). \tag{221}$$

You may have noticed that dealing with the statistic of many particles using wavefunction is quite cumbersome. This is due to the fact that we have to permute all the different particles (or the different coordinates $\mathbf{r}_i$ over all the

different wavefunctions. The statistics for fermions and bosons can greatly simplify if we start out with something indistinguishable. This can be done by using operators. You probably remember that the analytical solution of the harmonic oscillator involved the step up/down operators $a^\dagger$ and a, which had the relations

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle \quad \text{and} \quad a|n\rangle = \sqrt{n}|n-1\rangle. \tag{222}$$

Now forget for the moment the relation of $a^\dagger$ with x and p, since this result is far more general. Note that $a^\dagger$ effectively put adds one to the quantum state, whereas a removes one from the quantum state. Let us now identify this with bosons. $a^\dagger$ creates a boson in the quantum state, whereas a removes a boson from the quantum state. Now the harmonic oscillator is only one quantum state. We can in principle have many different quantum states k in which we can put bosons. So we can generalize it to

$$a_k^\dagger|n_1, n_2, \cdots, n_k, \cdots\rangle = \sqrt{n_k+1}|n_1, n_2, \cdots, n_k+1, \cdots\rangle \quad \text{and} \tag{223}$$

$$a_k|n_1, n_2, \cdots, n_k, \cdots\rangle = \sqrt{n_k}|n_1, n_2, \cdots, n_k-1, \cdots\rangle. \tag{224}$$

These operators have some nice characteristics: they are indistinguishable. In addition, they are symmetric. This follows from the generalized commutation relations

$$[a_k, a_{k'}^\dagger] = \delta_{k,k'} \qquad \text{and} \qquad [a_k^\dagger, a_{k'}^\dagger] = 0 \qquad \text{and} \qquad [a_k, a_k'] = 0 \tag{225}$$

Thus for $k \neq k'$, we can write

$$a_k^\dagger a_{k'}^\dagger = a_{k'}^\dagger a_k^\dagger. \tag{226}$$

Therefore, interchange of two particles does not change the sign of the wavefunction.

The wavefunction for a single harmonic oscillator could be written as

$$|n\rangle = \frac{1}{\sqrt{N!}}(a^\dagger)^N|0\rangle. \tag{227}$$

For more than one k value, we can generalize the wavefunction as

$$|\{n_{k_i}\}\rangle = \frac{1}{\sqrt{\Pi_i n_{k_i}}}\Pi_i(a_{k_i}^\dagger)^{n_{k_i}}|0\rangle. \tag{228}$$

Let us look at the two-particle wavefunctions. If the two particles are in the same state (i.e. have the same quantum number) then the wavefunction should be similar to that of the harmonic oscillator:

$$|kk\rangle = \frac{1}{\sqrt{2}}a_k^\dagger a_k^\dagger|0\rangle. \tag{229}$$

This wavefunction is now properly normalized since

$$\langle kk|kk\rangle = \frac{1}{2}\langle 0|a_k a_k a_k^\dagger a_k^\dagger|0\rangle = \frac{1}{2}\langle 0|a_k(1+a_k^\dagger a_k)a_k^\dagger|0\rangle \tag{230}$$

$$= \frac{1}{2}\langle 0|a_k a_k^\dagger|0\rangle + \frac{1}{2}\langle 0|a_k a_k^\dagger a_k a_k^\dagger|0\rangle \tag{231}$$

$$= \frac{1}{2}\langle 0|(1+a_k^\dagger a_k)|0\rangle + \frac{1}{2}\langle 0|(1+a_k^\dagger a_k)(1+a_k^\dagger a_k)|0\rangle = 1 \tag{232}$$

$$\tag{233}$$

since $a_k|0\rangle = 0$. For two different wavevectors, we have

$$|k_1 k_2\rangle = a_{k_1}^\dagger a_{k_2}^\dagger|0\rangle. \tag{234}$$

This gives the right normalization since

$$\langle k_1 k_2|k_1 k_2\rangle = \langle 0|a_{k_1}a_{k_2}a_{k_2}^\dagger a_{k_1}^\dagger|0\rangle = \langle 0|a_{k_1}(1+a_{k_2}^\dagger a_{k_2})a_{k_1}^\dagger|0\rangle = \langle 0|a_{k_1}a_{k_1}^\dagger|0\rangle = \langle 0|(1+a_{k_1}^\dagger a_{k_1})|0\rangle = 1 \tag{235}$$

Working with Slater determinants becomes quite elaborate. We can however do the same trick with operators to account for the statistics as with bosons. The operator $c_k^\dagger$ creates a fermion in a certain quantum state k, whereas c_k removes it from this quantum state, i.e.

$$c_k^\dagger|0_k\rangle = |1_k\rangle \quad \text{and} \quad c_k|1_k\rangle = |0_k\rangle, \tag{236}$$

where $|0_k\rangle$ and $|1_k\rangle$ denote the states with 0 and 1 electron in quantum state k, respectively. However, unlike bosons that satisfy commutation relations, fermions satisfy anticommutation relations

$$\{c_k, c_{k'}^\dagger\} = \delta_{k,k'}, \qquad \{c_k^\dagger, c_{k'}^\dagger\} = 0, \qquad \{c_k, c_{k'}\} = 0, \tag{237}$$

where the term in braces is defined as

$$\{A, B\} = AB + BA. \tag{238}$$

However, we cannot put two particles in the same state, since

$$c_k^\dagger c_k^\dagger |0\rangle = \frac{1}{2}\{c_k^\dagger, c_k^\dagger\}|0\rangle = 0. \tag{239}$$

We can put them in different quantum states, thus for $k \neq k'$

$$c_k^\dagger c_{k'}^\dagger |0\rangle = -c_{k'}^\dagger c_k^\dagger |0\rangle. \tag{240}$$

Note that the operators directly take care of the antisymmetry of the wavefunctions. Including spin, we can write the wavefunctions $|k_1 k_2, SS_z\rangle$ for two particles in states labeled with quantum numbers k_1 and k_2 with different spin S and S_z as

$$|k_1 k_2, 11\rangle = c_{k_2\uparrow}^\dagger c_{k_1\uparrow}^\dagger |0\rangle \quad , \quad |k_1 k_2, 10\rangle = \frac{1}{\sqrt{2}}\left(c_{k_2\downarrow}^\dagger c_{k_1\uparrow}^\dagger + c_{k_2\uparrow}^\dagger c_{k_1\downarrow}^\dagger\right)|0\rangle \quad , \quad |k_1 k_2, 1, -1\rangle = c_{k_2\downarrow}^\dagger c_{k_1\downarrow}^\dagger |0\rangle \tag{241}$$

$$|k_1 k_2, 00\rangle = \frac{1}{\sqrt{2}}\left(c_{k_2\downarrow}^\dagger c_{k_1\uparrow}^\dagger - c_{k_2\uparrow}^\dagger c_{k_1\downarrow}^\dagger\right)|0\rangle. \tag{242}$$

In general, we can write the many-body Fermion wavefunction as

$$|\{n_{k_i}\}\rangle = \Pi_i (c_{k_i}^\dagger)|0\rangle. \tag{243}$$

Note, that the normalization is unity since we can never have more than one fermion in the same quantum state.

Summarizing, we have seen that the a symmetric and antisymmetric wavefunction corresponds to particles with completely different statistics. Bosons have a symmetric wavefunction that allows any number of bosons in a particular quantum state. Fermions have antisymmetric wavefunctions and the occupation numbers are restricted to 0 and 1. We also saw that these statistic can be closely related to operators and their corresponding commutation relationships. Bosons commute, whereas fermions anticommute.

XIX. PHONONS

A phonon is a lattice vibration. It is called a collective excitation, since atoms move at the same time. The easiest way to derive the phonon dispersion is to start from Newton's equation of motion. The potential between the atoms are considered to behave like springs. Or in other terms, the assumption is that the potential of the atom around its equilibrium position is given by a parabola. In one dimension, the equation of motion for atom at site $R = na$ where n is an integer and a the distance between the atoms. is then given by

$$M\frac{d^2 x_R}{dt^2} = K\left[(x_{R+a} - x_R) - (x_R - x_{R-a})\right] \tag{244}$$

$$= K(x_{R+a} + x_{R-a} - 2x_R), \tag{245}$$

We can look for normal modes of oscillation if we assume that

$$x_R \sim e^{ikR - i\omega t}. \tag{246}$$

Inserting gives

$$-\omega^2 M = K(e^{ika} + e^{-ika} - 2) = 2K(\cos ka - 1) \tag{247}$$

Using that $cos2x = 1 - 2\sin^2 x$ or $\sin^2 x = \frac{1}{2}(1 - \cos 2x)$, we find

$$\omega = \omega_m \sin\frac{1}{2}ka, \tag{248}$$

with $\omega_m = \sqrt{K/M}$.

Although this is the most convenient way to obtain the dispersion, it is often useful to derive this in a different fashion. Let us consider again the Hamiltonian.

$$H = \sum_n \frac{\mathbf{p}_{\mathbf{R}}^2}{2M} + V(\mathbf{r}_{\mathbf{R}_1}, \cdots, \mathbf{r}_{\mathbf{R}_N}), \tag{249}$$

where $\mathbf{r}_{\mathbf{R}_n}$ and $\mathbf{p}_{\mathbf{R}_n}$ are the position and momentum, respectively, of the n'th atom. We can expand the potential in a Taylor series around the equilibrium positions $\mathbf{r}_{\mathbf{R}_n} = 0$,

$$V(\mathbf{r}_{\mathbf{R}_1}, \cdots, \mathbf{r}_{\mathbf{R}_N}) = V(0, 0, \cdots) + \sum_{\mathbf{R}} \mathbf{r}_{\mathbf{R}} \cdot \nabla_{\mathbf{R}} V|_{\{\mathbf{r}_n = 0\}} + \frac{1}{2} \sum_{\mathbf{R},\mathbf{R}'} (\mathbf{r}_{\mathbf{R}'} \cdot \nabla_{\mathbf{R}'})(\mathbf{r}_{\mathbf{R}} \cdot \nabla_{\mathbf{R}}) V + \cdots \tag{250}$$

The first term is a simple shift of the energy, which we can ignore. The second term contains

$$\nabla_{\mathbf{R}} V = \frac{\partial V}{\partial x_{\mathbf{R}}} \hat{\mathbf{x}} + \frac{\partial V}{\partial y_{\mathbf{R}}} \hat{\mathbf{y}} + \frac{\partial V}{\partial z_{\mathbf{R}}} \hat{\mathbf{z}} \tag{251}$$

is zero, since we have taken $\mathbf{r}_{\mathbf{R}} = 0$ as the equilibrium position, i.e. V is in a minimum. The third term is a sum over second partial derivatives

$$\sum_{\mathbf{R},\mathbf{R}'} (\mathbf{r}_{\mathbf{R}'} \cdot \nabla_{\mathbf{R}'})(\mathbf{r}_{\mathbf{R}} \cdot \nabla_{\mathbf{R}}) V = \sum_{\mathbf{R},\mathbf{R}'} \sum_{\alpha,\alpha'=x,y,z} \alpha_{\mathbf{R}'} \frac{\partial^2 V}{\partial \alpha_{\mathbf{R}'} \partial \alpha_{\mathbf{R}}} \alpha_{\mathbf{R}}. \tag{252}$$

When we denote $V^{\alpha'\alpha}_{\mathbf{R}'\mathbf{R}} = \partial^2 V / \partial \alpha_{\mathbf{R}'} \partial \alpha_{\mathbf{R}}$, we can also write this in matrix form

$$V = \frac{1}{2} \sum_{\mathbf{R}'\mathbf{R}} \mathbf{r}^T_{\mathbf{R}'} V_{\mathbf{R}'\mathbf{R}}\ \mathbf{r}_{\mathbf{R}} = \frac{1}{2} \sum_{\mathbf{R}'\mathbf{R}} (x_{\mathbf{R}'}, y_{\mathbf{R}'}, z_{\mathbf{R}'}) \begin{pmatrix} V^{xx}_{\mathbf{R}'\mathbf{R}} & V^{xy}_{\mathbf{R}'\mathbf{R}} & V^{xz}_{\mathbf{R}'\mathbf{R}} \\ V^{yx}_{\mathbf{R}'\mathbf{R}} & V^{yy}_{\mathbf{R}'\mathbf{R}} & V^{yz}_{\mathbf{R}'\mathbf{R}} \\ V^{zx}_{\mathbf{R}'\mathbf{R}} & V^{zy}_{\mathbf{R}'\mathbf{R}} & V^{zz}_{\mathbf{R}'\mathbf{R}} \end{pmatrix} \begin{pmatrix} x_{\mathbf{R}} \\ y_{\mathbf{R}} \\ z_{\mathbf{R}} \end{pmatrix}. \tag{253}$$

Since we are dealing with a crystal, we obviously do not want to stay in real space, but make a Fourier transform over the positions of the nuclei in the solid to momentum space

$$\mathbf{r}_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}} \mathbf{r}_{\mathbf{q}} \quad \text{and} \quad \mathbf{p}_{\mathbf{R}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{R}} \mathbf{p}_{\mathbf{q}}. \tag{254}$$

The Hamiltonian then becomes

$$H = \sum_{\mathbf{q}} \frac{\mathbf{p}^\dagger_{\mathbf{q}} \mathbf{p}_{\mathbf{q}}}{2M} + \frac{1}{2} \sum_{\mathbf{q}} \mathbf{r}^\dagger_{\mathbf{q}} V_{\mathbf{q}} \mathbf{r}_{\mathbf{q}}, \tag{255}$$

where $\mathbf{r}_{\mathbf{q}}$ is a complex number so we need to take $\mathbf{r}^\dagger_{\mathbf{q}}$ as opposed to simply transposing it. The interaction matrix is now given by

$$V_{\mathbf{q}} = \begin{pmatrix} V^{xx}_{\mathbf{q}} & V^{xy}_{\mathbf{q}} & V^{xz}_{\mathbf{q}} \\ V^{yx}_{\mathbf{q}} & V^{yy}_{\mathbf{q}} & V^{yz}_{\mathbf{q}} \\ V^{zx}_{\mathbf{q}} & V^{zy}_{\mathbf{q}} & V^{zz}_{\mathbf{q}} \end{pmatrix}. \tag{256}$$

Note that whereas there are cross terms $V'_{\mathbf{R}}\mathbf{R}$ in real space (giving a double sum of $\mathbf{R}$ and $\mathbf{R}'$), the interaction is diagonal in $\mathbf{q}$, since it only depends on the $\mathbf{R} - \mathbf{R}'$,

$$V^{\alpha'\alpha}_{\mathbf{q}} = \sum_{\boldsymbol{\delta}'} e^{-i\mathbf{q}\cdot\boldsymbol{\delta}} V^{\alpha'\alpha}_{\mathbf{R}+\boldsymbol{\delta},\mathbf{R}}, \tag{257}$$

where $\boldsymbol{\delta}$ runs over the lattice sites around the site $\mathbf{R}$. Note that this is equivalent for each site $\mathbf{R}$. Let us go back to one dimension, to see what our next step is in solving the problem. In one dimension, the Fourier transform of the Hamiltonian

$$H = \sum_{\mathbf{R}} \frac{p_R^2}{2M} + \sum_{RR'} V_{R'R} x_{R'} x_R, \tag{258}$$

with $V_{R'R} = \frac{\partial^2 V}{\partial x_{R'} \partial x_R}$, becomes

$$H = \sum_q \left[\frac{p_q^\dagger p_q}{2M} + \frac{1}{2} m\omega_q^2 x_q^\dagger x_q \right], \tag{259}$$

with

$$\omega_q = \sqrt{\frac{V_q}{M}} \quad \text{with} \quad V_q = \sum_\delta e^{-iq\delta} V_{R+\delta,R}, \tag{260}$$

and the Fourier transforms

$$x_R = \frac{1}{\sqrt{N}} \sum_q e^{iqR} x_q \quad \text{and} \quad p_R = \frac{1}{\sqrt{N}} \sum_q e^{-iqR} p_q \quad \text{or, inversely} \quad x_q = \frac{1}{\sqrt{N}} \sum_R e^{-iqR} x_R \quad \text{and} \quad p_q = \frac{1}{\sqrt{N}} \sum_R e^{iqR} p_R$$

However, apart from the summation over q, we readily recognize Eqn. (259) as the Hamiltonian for a harmonic oscillator. We can diagonalize this by introducing the operators

$$a_q = \frac{1}{\sqrt{2M\hbar\omega_q}} (M\omega_q x_R + i p_q^\dagger) \quad \text{and} \quad a_q^\dagger = \frac{1}{\sqrt{2M\hbar\omega_q}} (M\omega_q x_R^\dagger - i p_q), \tag{261}$$

leading to

$$H = \sum_q \hbar\omega_q (a_q^\dagger a_q + \frac{1}{2}). \tag{262}$$

We would now like to determine the value of ω_q. Let us consider only nearest-neighbor interactions. The interaction is then

$$V = \sum_R \frac{1}{2} K (x_R - x_{R+a})^2 = \sum_R K(x_R^2 - x_R x_{R+a}) = K \sum_R x_R^2 - \frac{K}{2} \sum_R \sum_{\delta=\pm a} x_{R+\delta} x_R \tag{263}$$

Since this should be equivalent to $V = \frac{1}{2} \sum_{RR'} V_{RR'} x_{R'} x_R$, we have $V_{RR} = 2K$, $V_{R\pm a,R} = -K$, and $V_{R'R} = 0$ for $|R - R'| \geq 2a$. The Fourier transform is then

$$V_q = \sum_\delta e^{-iq\delta} V_{R+\delta,R} = 2K - K(e^{-iqa} + e^{iqa}) = 2K(1 - \cos qa) = 4K \sin^2 \frac{qa}{2}, \tag{264}$$

and

$$\omega_q = \sqrt{\frac{V_q}{M}} = 2\sqrt{\frac{K}{M}} \sin \frac{qa}{2} = \omega_m \sin \frac{qa}{2}, \tag{265}$$

with $\omega_m = \sqrt{\frac{K}{M}}$. reproducing the result at the beginning of the chapter. We can also express the position and momentum in terms of the step operators

$$x_q = \sqrt{\frac{\hbar}{2M\omega_q}} (a_{-q}^\dagger + a_q) \quad \text{and} \quad p_q = i\sqrt{\frac{2M\omega_q}{\hbar}} (a_q^\dagger - a_{-q}), \tag{266}$$

making use of the relations $x_q^\dagger = x_{-q}$ and $p_q^\dagger = p_{-q}$ and $\omega_q = \omega_{-q}$.

Let us now return to three dimensions, where life is complicated by the fact that the interaction between the nuclei is now a matrix, see Eqn. (256). However, we can turn this effectively into three independent one-dimensional problems by diagonalizing $V_{\mathbf{q}}$. This gives three eigenvalues $V_{\mathbf{q}}^s$. There are three mutually perpendicular eigenvectors. We can write those as unit vectors $\hat{\mathbf{e}}_1$, $\hat{\mathbf{e}}_2$, and $\hat{\mathbf{e}}_3$ in real space. These vectors are known as polarization vectors. The direction of these vectors depend on the wavevectors which we omit here. If one of the polarization vectors is parallel to $\mathbf{q}$ then there are longitudinally polarized phonons. Since the other two vectors are orthogonal, we also have two

transversely polarized phonons. However, this usually only occurs when $\mathbf{q}$ is along certain symmetry direction in the crystal. Equation (255) then becomes

$$H = \sum_{\mathbf{q}s} \left[\frac{p^\dagger_{\mathbf{q}s} p_{\mathbf{q}s}}{2M} + \frac{1}{2} V^s_{\mathbf{q}} r^\dagger_{\mathbf{q}s} r_{\mathbf{q}s} \right], \tag{267}$$

where the subscript s indicated that we are dealing with the component along a particular polarization vectors, i.e. $r_{\mathbf{q}s} = \mathbf{r}_{\mathbf{q}s} \cdot \hat{\mathbf{e}}_s$ and $p_{\mathbf{q}s} = \mathbf{p}_{\mathbf{q}s} \cdot \hat{\mathbf{e}}_s$. The frequencies are given by

$$\omega_{\mathbf{q}s} = \sqrt{\frac{V^s_{\mathbf{q}}}{M}}. \tag{268}$$

The step operators are given by

$$a_{\mathbf{q}s} = \frac{1}{\sqrt{2M\hbar\omega_{\mathbf{q}s}}} (M\omega_{\mathbf{q}s}\mathbf{r}_{\mathbf{q}} + i\mathbf{p}_{\mathbf{q}}) \cdot \hat{\mathbf{e}}_s \tag{269}$$

$$a^\dagger_{\mathbf{q}s} = \frac{1}{\sqrt{2M\hbar\omega_{\mathbf{q}s}}} (M\omega_{\mathbf{q}s}\mathbf{r}_{\mathbf{q}} - i\mathbf{p}_{\mathbf{q}}) \cdot \hat{\mathbf{e}}_s \tag{270}$$

leading to the Hamiltonian

$$H = \sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s} (a^\dagger_{\mathbf{q}s} a_{\mathbf{q}s} + \frac{1}{2}). \tag{271}$$

XX. ELECTRON-PHONON INTERACTION

In this section, we discuss the electron phonon interaction. The electrons are treated as a simple electron gas feeling the potential of the nuclei. The unperturbed Hamiltonian is given by

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s} a^\dagger_{\mathbf{q}s} a_{\mathbf{q}s}. \tag{272}$$

We then add the potential of the atoms. Unlike what we considered before (as in the free-electron model), the nuclei. We assume that the potential of the ion depends only on the distance from the equilibrium position of the ion. The periodic potential is then described in second quantization as

$$H_U = \frac{1}{N} \sum_{\mathbf{k}\mathbf{k}'\mathbf{R}} \langle \mathbf{k}' | U(\mathbf{r} - \mathbf{R} - \mathbf{r}_{\mathbf{R}}) | \mathbf{k} \rangle c^\dagger_{\mathbf{k}'} c_{\mathbf{k}} \tag{273}$$

$$= \frac{1}{N} \sum_{\mathbf{k}\mathbf{q}\mathbf{R}} e^{-i\mathbf{q}\cdot(\mathbf{R}+\mathbf{r}_{\mathbf{R}})} U_{\mathbf{q}} c^\dagger_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} \tag{274}$$

with $\mathbf{q} = \mathbf{k}' - \mathbf{k}$. We assume that the displacements $\mathbf{r}_{\mathbf{R}}$ from the equilibrium positions are small so that we can write

$$e^{-i\mathbf{q}\cdot\mathbf{r}_{\mathbf{R}}} = 1 - i\mathbf{q} \cdot \mathbf{r}_{\mathbf{R}}. \tag{275}$$

The first term gives the Bloch periodic potential

$$U = \frac{1}{N} \sum_{\mathbf{k}\mathbf{k}'\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} U_{\mathbf{q}} c^\dagger_{\mathbf{k}+\mathbf{q}} c_{\mathbf{k}} \tag{276}$$

$$U = \sum_{\mathbf{k}\mathbf{K}} U_{\mathbf{K}} c^\dagger_{\mathbf{k}+\mathbf{K}} c_{\mathbf{k}} \tag{277}$$

$$\tag{278}$$

The second term gives the electron-phonon interaction

$$H_{ep} = -i\frac{1}{N}\sum_{\mathbf{kqR}} e^{-i\mathbf{q}\cdot\mathbf{R}}\mathbf{q}\cdot\mathbf{r}_{\mathbf{R}}U_{\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}} = -i\frac{1}{N}\sum_{\mathbf{kqR}} e^{-i\mathbf{q}\cdot\mathbf{R}}\frac{1}{\sqrt{N}}\sum_{\mathbf{q}'} e^{i\mathbf{q}'\cdot\mathbf{R}}\mathbf{q}\cdot\mathbf{r}_{\mathbf{q}'}U_{\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}} \tag{279}$$

$$= -i\frac{1}{\sqrt{N}}\frac{1}{N}\sum_{\mathbf{kqq}'\mathbf{R}} e^{-i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{R}}\mathbf{q}\cdot\mathbf{r}_{\mathbf{q}'}U_{\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}} \tag{280}$$

$$= -i\frac{1}{\sqrt{N}}\sum_{\mathbf{kq}}\mathbf{q}\cdot\mathbf{r}_{\mathbf{q}}U_{\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}. \tag{281}$$

Expressing the displacement in creation and annihilation operators using

$$\mathbf{r}_{\mathbf{q}} = \sum_s \sqrt{\frac{\hbar}{2M\omega_{\mathbf{q}}}}(a^{\dagger}_{-\mathbf{q}s} + a_{\mathbf{q}s})\hat{\mathbf{e}}_s \tag{282}$$

gives

$$H_{ep} = -i\sum_{\mathbf{kq}s}\sqrt{\frac{\hbar}{2NM\omega_{\mathbf{q}s}}}\mathbf{q}\cdot\hat{\mathbf{e}}_s U_{\mathbf{q}}(a^{\dagger}_{-\mathbf{q}s} + a_{\mathbf{q}s})c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}. \tag{283}$$

For simplicity, we shall assume that the phonon spectrum is isotropic. This implies that phonons are either lingitudinally or transversely polarized. In that case, only the longitudinal phonon with the polarization vector parallel to the wavevector contribute. In the following, we will also neglect the effects of the periodic potential U. We are then left with the Fröhlich Hamiltonian

$$H = \sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}c^{\dagger}_{\mathbf{k}}c_{\mathbf{k}} + \sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}c^{\dagger}_{\mathbf{q}}c_{\mathbf{q}} + \sum_{\mathbf{kq}}M_{\mathbf{q}}(a^{\dagger}_{-\mathbf{q}} + a_{\mathbf{q}})c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}, \tag{284}$$

where the matrix element is given by

$$M_{\mathbf{q}} = i\sum_{\mathbf{kq}s}\sqrt{\frac{\hbar}{2NM\omega_{\mathbf{q}}}}qU_{\mathbf{q}}. \tag{285}$$

The Hamiltonian consists of two components. In one case, $a_{\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}$, the electron is scattered by the absorption of a phonon with momentum $\mathbf{q}$, in the other case, $a^{\dagger}_{-\mathbf{q}}c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}$ the electron is scattered by emission of a phonon with momentum $-\mathbf{q}$. Note that the total momentum of the creation operators equals that of the annihilation operators (in principle, they could differ by a reciprocal lattice vector $\mathbf{K}$ but we will neglect this and reduce everything to the first Brillouin zone). We now want to consider the change of the ground state energy due to the presence of electron-phonon interactions. This will modify the excitation spectra and even result in an effective attractive interaction between the electrons mediated by the phonons.

Let us study the change in total energy up to second-order perturbation theory, this gives

$$E = E_0 + \langle\Phi|H_{ep}|\Phi\rangle + \langle\Phi|H_{ep}\frac{1}{E_0 - H_0}H_{ep}|\Phi\rangle, \tag{286}$$

where $|\Phi\rangle$ is the unperturbed state characterized by the occupation numbers $n_{\mathbf{q}}$ for phonons and $n_{\mathbf{k}}$ for electrons. Since H_{ep} involves the creation or annihilation of a phonon, the first term is zero. The second term gives

$$E_2 = \langle\Phi|\sum_{\mathbf{kq}}M_{\mathbf{q}}(a^{\dagger}_{-\mathbf{q}} + a_{\mathbf{q}})c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}\frac{1}{E_0 - H_0}\sum_{\mathbf{k}'\mathbf{q}'}M_{\mathbf{q}'}(a^{\dagger}_{-\mathbf{q}'} + a_{\mathbf{q}'})c^{\dagger}_{\mathbf{k}'+\mathbf{q}'}c_{\mathbf{k}'}|\Phi\rangle. \tag{287}$$

Since we start with the state $|\Phi\rangle$ and end with the same state, the H_{ep}'s have to cancel each others excitations. This is achieved for $\mathbf{q}' = -\mathbf{q}$. The terms that remain

$$E_2 = \sum_{\mathbf{kq}}|M_{\mathbf{q}}|^2\left[\langle\Phi|a^{\dagger}_{-\mathbf{q}}c^{\dagger}_{\mathbf{k}}c_{\mathbf{k}-\mathbf{q}}\frac{1}{E_0 - H_0}a_{-\mathbf{q}}c^{\dagger}_{\mathbf{k}-\mathbf{q}}c_{\mathbf{k}}|\Phi\rangle + \langle\Phi|a_{\mathbf{q}}c^{\dagger}_{\mathbf{k}}c_{\mathbf{k}-\mathbf{q}}\frac{1}{E_0 - H_0}a^{\dagger}_{\mathbf{q}}c^{\dagger}_{\mathbf{k}-\mathbf{q}}c_{\mathbf{k}}|\Phi\rangle\right]. \tag{288}$$

FIG. 36: Schematic plot of the Kohn anomaly. The energy is given by $E = q + \alpha \ln \sqrt{(1-2q/k_F)^2 + \gamma^2}$ with $\alpha = 0.1$ and $\gamma = 0.03$. In the absence of electron-phonon interactions, the phonon energy would be a straight line $E = q$. The presence of these interactions gives rise to an anomaly around $q/k_F = 2$.

We see that the combinations of creation and annihilation operators form number operators $n_{\mathbf{k}} = c^\dagger_{\mathbf{k}} c_{\mathbf{k}}$. Note that $c_{\mathbf{k}} c^\dagger_{\mathbf{k}} = 1 - n_{\mathbf{k}}$. It is also straightforward to obtain the difference in energy between the excited state and E_0. This leads to the expression

$$E_2 = \sum_{\mathbf{kq}} |M_{\mathbf{q}}|^2 \langle n_{\mathbf{k}}(1 - n_{\mathbf{k-q}})\rangle \left[\frac{\langle n_{-\mathbf{q}}\rangle}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}} + \hbar\omega_{-\mathbf{q}}} + \frac{\langle n_{\mathbf{q}} + 1\rangle}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}} - \hbar\omega_{\mathbf{q}}} \right], \tag{289}$$

where $\langle \cdots \rangle$ gives the expectation value. Since we considered an isotropic system, we can assume that $\omega_{\mathbf{q}} = \omega_{-\mathbf{q}}$ and $\langle n_{\mathbf{q}}\rangle = \langle n_{-\mathbf{q}}\rangle$. The second term in the above equation can be split into two terms. We then obtain

$$E_2 = \sum_{\mathbf{kq}} |M_{\mathbf{q}}|^2 \langle n_{\mathbf{k}}(1 - n_{\mathbf{k-q}})\rangle \left[\frac{2(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}})\langle n_{\mathbf{q}}\rangle}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}})^2 - (\hbar\omega_{\mathbf{q}})^2} + \frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}} - \hbar\omega_{\mathbf{q}}} \right], \tag{290}$$

The total energy is given by $E_0 + E_2$. Note that the phonon part of the ground state energy can be given $\sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} \langle n_{\mathbf{q}}\rangle$. We can find the change in the phonon energy due to the electron-phonon interaction by determing the change in energy with respect to a change in the phonon occupation number $n_{\mathbf{q}}$, giving

$$\hbar\omega'_{\mathbf{q}} = \frac{\partial}{\partial \langle n_{\mathbf{q}}\rangle}(E_0 + E_2) = \hbar\omega_{\mathbf{q}} + \sum_{\mathbf{k}} |M_{\mathbf{q}}|^2 \frac{2\langle n_{\mathbf{k}}(1 - n_{\mathbf{k-q}})\rangle(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}})}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}})^2 - (\hbar\omega_{\mathbf{q}})^2} \tag{291}$$

Since phonon energies are generally small, let us have a look at this result when we neglect $\hbar\omega_{\mathbf{q}}$ in the denominator:

$$\hbar\omega'_{\mathbf{q}} = \hbar\omega_{\mathbf{q}} + \sum_{\mathbf{k}} |M_{\mathbf{q}}|^2 \frac{2\langle n_{\mathbf{k}}(1 - n_{\mathbf{k-q}})\rangle}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}}}. \tag{292}$$

We can interpret this expression as follows. A phonon will be absorbed under the creation of an electron-hole pair with energy $\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}}$. The electron-hole pair is then annihilated under the emission of a phonon. We expect the largest change in the phonon energy to occur when the energy of the electron-hole pair approaches zero. Let us suppose that $\mathbf{q}$ is in the x direction. An electron-hole pair of zero energy can be created by scattering across the Fermi surface with $q = 2k_F$. Integrating over $\mathbf{k}$ leads to a logarithmic divergence. This leads to an infinite group velocity of the phonons, known as the Kohn anomaly.

Let us try to make a very simple of the Kohn anomaly and assume a one-dimensional system with a band with a linear dispersion. Obviously, this is not very realistic, but the underlying idea is that the presence of an anomaly should not depend too much on the details of the electronic structure. The dispersion is then given by $\varepsilon_k = \alpha|k|$. We are interested in what happens if the energy of the electron-hole pair is close to zero. This occurs for scattering from $-k_F$ to k_F, i.e. for $q = 2k_F$. Let us consider scattering from negative k-values to positive k values (the other way will be equivalent). An electron at $-k$ (with $k > 0$) scatters to $q - k$. We have to be careful with the integration. When $k_F < q < 2k_F$, not all q-values give allowed transitions due to the Fermi-Dirac distribution. At $T = 0$, the maximum allowed value is $q - k_F$. The integration over momentum then becomes

$$\int_0^{q-k_F} dk \frac{1}{\alpha(q-k) - \alpha k} = \frac{1}{\alpha} \int_0^{q-k_F} dk \frac{1}{q - 2k} = \ln(q - 2(q - k_F)) - \ln q = \ln(\frac{2k_F}{q} - 1) \tag{293}$$

For $q > 2k_F$, we can always scatter from the negative k values to positive k values. The maximum k value is then k_F, since we cannot remove electrons from above the Fermi level. For $q > 2k_F$, the momentum is always sufficiently large to scatter the electrons and the upper bound is given by k_F

$$\frac{1}{\alpha} \int_0^{k_F} dk \frac{1}{q - 2k} = \ln(q - 2k_F) - \ln q = \ln(\frac{1 - 2k_F}{q}). \tag{294}$$

We can combine the two result, giving

$$\hbar\omega'_{\mathbf{q}} = \hbar\omega'_{\mathbf{q}} + \text{const} \times \ln|1 - \frac{2k_F}{q}| \tag{295}$$

where the constant defines the strength of the interaction. We clearly see the Kohn anomaly at $q = 2k_F$. Figure 36 shows a schematic picture of the Kohn anomaly. A broadening γ of the divergence has been included by using

$$\hbar\omega'_{\mathbf{q}} = \hbar\omega'_{\mathbf{q}} + \text{const} \times \ln\sqrt{(1 - \frac{2k_F}{q})^2 + \gamma^2}. \tag{296}$$

We can also do it the other way around and look at the change in electron energies due to the phonons. This can be obtained by calculating the change in energy due to a change in electron occupation of the electron state with momentum $\mathbf{k}$ in Eqn. (289). For simplicity, we assume that we are at low temperatures where the number of phonons is small, i.e. $\langle n_{\mathbf{q}}\rangle$. This gives

$$\begin{aligned}
\varepsilon'_{\mathbf{k}} &= \frac{\partial}{\partial\langle n_{\mathbf{k}}\rangle}(E_0 + E_2) && (297)\\
&= \frac{\partial}{\partial\langle n_{\mathbf{k}}\rangle}\left[\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}\langle n_{\mathbf{k}}\rangle + \sum_{\mathbf{k}\mathbf{k}'}|M_{\mathbf{k}'-\mathbf{k}}|^2\langle n_{\mathbf{k}}(1-n_{\mathbf{k}'})\rangle\frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'} - \hbar\omega_{\mathbf{q}}}\right] && (298)\\
&= \varepsilon_{\mathbf{k}} + \sum_{\mathbf{k}'}|M_{\mathbf{k}'-\mathbf{k}}|^2\left[\frac{1-\langle n_{\mathbf{k}'}\rangle}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'} - \hbar\omega_{\mathbf{q}}} - \frac{\langle n_{\mathbf{k}'}\rangle}{\varepsilon_{\mathbf{k}'} - \varepsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}}}\right], && (299)
\end{aligned}$$

where $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ and the momenta $\mathbf{k}$ and $\mathbf{k}'$ have been interchanged in the second term.

$$\varepsilon'_{\mathbf{k}} = \varepsilon_{\mathbf{k}} + \sum_{\mathbf{q}}|M_{\mathbf{q}}|^2\left[\frac{1}{\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}}} - \frac{2\hbar\omega_{\mathbf{q}}\langle n_{\mathbf{k}+\mathbf{q}}\rangle}{(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}})^2 - (\hbar\omega_{\mathbf{q}})^2}\right]. \tag{300}$$

The first term in independent of $\langle n_{\mathbf{k}+\mathbf{q}}\rangle$. We can see it as a single electron moving around in a lattice. It will create phonons while scattering temporarily to a different state $\mathbf{k}+\mathbf{q}$. It will then reabsorb the phonon. Effectively, the electron is moving around with a phonon cloud around it. This cloud will increase the effective mass of the particle. This interaction can be very strong. We only treat it up to second-order perturbation. One can imagine that the electron can emit more than one phonon at the time. The electron plus its accompanying phonon cloud is known as a polaron. The name arises from the contraction of the lattice around the negatively-charge electron leading to a polarization of the lattice.

The second term gives the change in the energy of the electron due to the presence of the other electrons. This term gives a change in the group velocity of the electron. Note that for a free electron, the group velocity is given by

$$\hbar\mathbf{v}^0_{\mathbf{k}} = \frac{\partial}{\partial\mathbf{k}}\varepsilon_{\mathbf{k}} = \frac{\partial}{\partial\mathbf{k}}\frac{\hbar^2\mathbf{k}^2}{2m} = \hbar\frac{\hbar\mathbf{k}}{m} = \hbar\frac{\mathbf{p}}{m}. \tag{301}$$

Taking the first and third term in $\varepsilon_{\mathbf{k}'}$ and differentiating with respect $\mathbf{k}$ gives

$$\begin{aligned}
\hbar\mathbf{v}_{\mathbf{k}} &= \frac{\partial\varepsilon'_{\mathbf{k}}}{\partial\mathbf{k}} = \frac{\partial\varepsilon'_{\mathbf{k}}}{\partial\varepsilon_{\mathbf{k}}}\frac{\partial\varepsilon_{\mathbf{k}}}{\partial\mathbf{k}} && (302)\\
&= \frac{\partial\varepsilon_{\mathbf{k}}}{\partial\mathbf{k}}\left[1 - \frac{\partial}{\partial\varepsilon_{\mathbf{k}}}\sum_{\mathbf{q}}|M_{\mathbf{q}}|^2\frac{2\hbar\omega_{\mathbf{q}}\langle n_{\mathbf{k}+\mathbf{q}}\rangle}{(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}})^2 - (\hbar\omega_{\mathbf{q}})^2}\right]. && (303)
\end{aligned}$$

We now argue that the major contribution in the summation comes from the derivative of fast variation of $\langle n_{\mathbf{k}+\mathbf{q}}\rangle$ around the Fermi energy E_F. We replace the summation by an integration and approximate $M_{\mathbf{q}}$ and $\omega_{\mathbf{q}}$ by their averages $\overline{M}$ and $\overline{\omega}$. For the density of states, we take the value at E_F. This gives

$$\hbar\mathbf{v}_{\mathbf{k}} \cong \hbar\mathbf{v}^0_{\mathbf{k}}\left[1 - 2\hbar\overline{\omega}\rho(E_F)|\overline{M}|^2\frac{d}{d\varepsilon_{\mathbf{k}}}\int\frac{\langle n(E)\rangle}{(\varepsilon_{\mathbf{k}} - E)^2 - (\hbar\overline{\omega})^2}dE\right]. \tag{304}$$

At low temperatures the occupation number is a step function and its derivative is therefore a δ-function at the Fermi energy

$$\frac{d\langle n(E)\rangle}{d\varepsilon_{\mathbf{k}}} = -\delta(E - E_F), \tag{305}$$

where the minus arises from the fact that $n(E)$ goes from 1 to 0.

$$\hbar \mathbf{v_k} \cong \hbar \mathbf{v_k^0} \left[1 + \frac{2\hbar\overline{\omega}\rho(E_F)|\overline{M}|^2}{(\varepsilon_\mathbf{k} - E_F)^2 - (\hbar\overline{\omega})^2} \right]. \tag{306}$$

The infinities around $\varepsilon_\mathbf{k} = E_F \pm \hbar\overline{\omega}$ are a spurious result of our averaging procedure. We are often more interested in how the group velocity around the Fermi level is affected by the interaction of the electron with the phonons. For $\varepsilon_\mathbf{k} = E_F$, we have

$$\mathbf{v_k} = \mathbf{v_k^0}(1 - \alpha), \tag{307}$$

with

$$\alpha = \frac{2\rho(E_F)|\overline{M}|^2}{\hbar\overline{\omega}}. \tag{308}$$

An alternative way to look at it is by trying to reexpress $\varepsilon_{\mathbf{k}'}$ as an effective free-electron dispersion

$$\mathbf{v_k} = \frac{\hbar\mathbf{k}}{m^*} = \mathbf{v_k^0}(1 - \alpha) = \frac{\hbar\mathbf{k}}{m}(1 - \alpha), \tag{309}$$

giving an effective mass of

$$m^* = \frac{m}{1 - \alpha}. \tag{310}$$

The electron-phonon interaction therefore gives a mass enhancement.

XXI. ATTRACTIVE POTENTIAL

We now want to see if there is an effective attractive potential between electrons. We therefore look for a term proportional to $\langle n_\mathbf{k} n_{\mathbf{k}-\mathbf{q}} \rangle$ in Eqn. (289). Originally, we had ascribed this term to the scattering of an electron under the emission of a phonon, followed by the recapturing of the phonon by the same electron. We want to reinterpret this term as the interaction between two electrons through the mediation of a phonon. We can write the term proportional to $\langle n_\mathbf{k} n_{\mathbf{k}-\mathbf{q}} \rangle$ in the limit $\langle n_\mathbf{q} \rangle \to 0$ as

$$E_c = -\sum_{\mathbf{kq}} |M_\mathbf{q}|^2 \frac{\langle n_\mathbf{k} n_{\mathbf{k}-\mathbf{q}} \rangle}{\varepsilon_\mathbf{k} - \varepsilon_{\mathbf{k}-\mathbf{q}} - \hbar\omega_\mathbf{q}} \tag{311}$$

We can rewrite this by splitting up the summation and relabeling the second summation

$$E_c = -\frac{1}{2}\sum_{\mathbf{kq}} |M_\mathbf{q}|^2 \frac{\langle n_\mathbf{k} n_{\mathbf{k}-\mathbf{q}} \rangle}{\varepsilon_\mathbf{k} - \varepsilon_{\mathbf{k}-\mathbf{q}} - \hbar\omega_\mathbf{q}} - \frac{1}{2}\sum_{\mathbf{kq}} |M_\mathbf{q}|^2 \frac{\langle n_{\mathbf{k}-\mathbf{q}} n_\mathbf{k} \rangle}{\varepsilon_{\mathbf{k}-\mathbf{q}} - \varepsilon_\mathbf{k} - \hbar\omega_{-\mathbf{q}}} \tag{312}$$

$$= \frac{1}{2}\sum_{\mathbf{kq}} |M_\mathbf{q}|^2 \frac{2\hbar\omega_\mathbf{q}}{(\varepsilon_{\mathbf{k}-\mathbf{q}} - \varepsilon_\mathbf{k})^2 - \hbar\omega_\mathbf{q}} \langle -n_\mathbf{k} n_{\mathbf{k}-\mathbf{q}} \rangle, \tag{313}$$

where we have used $\omega_{-\mathbf{q}} = \omega_\mathbf{q}$. If we define

$$V_\mathbf{q} = |M_\mathbf{q}|^2 \frac{2\hbar\omega_\mathbf{q}}{(\varepsilon_{\mathbf{k}-\mathbf{q}} - \varepsilon_\mathbf{k})^2 - \hbar\omega_\mathbf{q}}, \tag{314}$$

we obtain an effective interaction

$$V = \frac{1}{2}\sum_{\mathbf{kq}} V_\mathbf{q} \langle -n_\mathbf{k} n_{\mathbf{k}-\mathbf{q}} \rangle. \tag{315}$$

In general, we can write interaction between two particles as

$$V = \sum_{\mathbf{kk'q}} V_\mathbf{q} c^\dagger_{\mathbf{k}+\mathbf{q}} c^\dagger_{\mathbf{k'}-\mathbf{q}} c_{\mathbf{k'}} c_\mathbf{k}. \tag{316}$$

We can distinguish two contributions that are nonzero working on a Fermi sphere. We can take $\mathbf{q} = 0$.

$$V = \frac{1}{2}\sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{q}} \langle n_{\mathbf{k}} n_{\mathbf{k}'} \rangle. \tag{317}$$

This is called the Hartree or direct terms. If $V_{\mathbf{q}}$ was a Coulomb interaction this would correspond to the interaction of the electrons with each other. Another possibility is that $\mathbf{k} = \mathbf{k}' - \mathbf{q}$

$$V = \frac{1}{2}\sum_{\mathbf{k}'\mathbf{q}} V_{\mathbf{q}} \langle c^\dagger_{\mathbf{k}'} c^\dagger_{\mathbf{k}'-\mathbf{q}} c_{\mathbf{k}'} c_{\mathbf{k}'-\mathbf{q}} \rangle = -\frac{1}{2}\sum_{\mathbf{k}\mathbf{q}} V_{\mathbf{q}} \langle c^\dagger_{\mathbf{k}} c_{\mathbf{k}} c^\dagger_{\mathbf{k}-\mathbf{q}} c_{\mathbf{k}-\mathbf{q}} \rangle = \frac{1}{2}\sum_{\mathbf{k}\mathbf{q}} V_{\mathbf{q}} \langle -n_{\mathbf{k}} n_{\mathbf{k}-\mathbf{q}} \rangle, \tag{318}$$

where the prime has been dropped on the right-hand side. Although usually the electron energies are significantly larger than the phonon energies, it is always possible to find values for which $|\varepsilon_{\mathbf{k}-\mathbf{q}} - \varepsilon_{\mathbf{k}}| < \hbar\omega_{\mathbf{q}}$. This means that the matrix element is negative. Although a negative matrix element in momentum space does not always guarantee a negative interaction in real space, it does offer the possibility of an attractive interaction.

We can also obtain the attractive interaction by performing a canonical transformation on the Fröhlich Hamiltonian.

Intermezzo:canonical transformation.– We want to derive the effective interaction with a canonical transformation. Let us first review what a canonical transformation was. Let us consider a displaced harmonic oscillator

$$H = H_0 + H_{e-p} = \hbar\omega a^\dagger a + M(a^\dagger + a), \tag{319}$$

where we call the second term H_{e-p} to draw the parallel with the electron-phonon interaction. Note that this Hamiltonian has similarities with the one we are considering. We can diagonalize this by taking displaced operators

$$A = a + \lambda \quad \text{and} \quad A^\dagger = a^\dagger + \lambda. \tag{320}$$

We can then write

$$\hbar\omega A^\dagger A = \hbar\omega a^\dagger + \hbar\omega\lambda(a^\dagger + a) + \hbar\omega\lambda^2. \tag{321}$$

This means we can write our Hamiltonian as

$$H = \hbar\omega A^\dagger A - \Delta, \tag{322}$$

using $M = \hbar\omega\lambda$ or $\lambda = M/\hbar\omega$ this gives $\Delta = \hbar\omega\lambda^2 = M^2/\hbar\omega$ for the shift in energy. In order to treat a more complicated Hamiltonian, we want to take a more systematic approach using a canonical transformation. We are looking for a transformation of the form

$$H' = e^{-S} H e^{S}, \tag{323}$$

that will eliminate H_{e-p} to lowest order. Expanding the exponentials gives

$$H' = (1 - S + \frac{1}{2}S^2 - \cdots)H(1 + S + \frac{1}{2}S^2 + \cdots) \tag{324}$$

$$= H_0 + H_{e-p} + [H_0, S] + [H_{e-p}, S] + \frac{1}{2}[[H_0, S], S] + \cdots. \tag{325}$$

We neglect the higher-order terms and choose S such that the commutator with H_0 cancels H_{e-p}. If we achieve that, we end up with

$$H' = H_0 + [H_{e-p}, S].\cdots. \tag{326}$$

Let us try S or the form using

$$S = \lambda(a - a^\dagger). \tag{327}$$

We can now make a unitary transformation of $a^\dagger a$,

$$[a^\dagger a, S] = \lambda[a^\dagger a, a] - \lambda[a^\dagger a, a] \tag{328}$$

$$= \lambda(a^\dagger aa - aa^\dagger a) - \lambda(a^\dagger aa^\dagger - a^\dagger a^\dagger a) \tag{329}$$

$$= \lambda[a^\dagger, a]a - \lambda a^\dagger[a, a^\dagger] \tag{330}$$

$$= -\lambda(a + a^\dagger) \tag{331}$$

The idea for solving the electron-phonon interaction is very similar, except now we have $\mathbf{k}$ dependence and M is no longer a simple constant, but contains $c^\dagger c$ operators. However, in the end we want to look at the final change in electron energy, which is proportional to M^2 which would then become a $c^\dagger c^\dagger cc$ term, which is an effective electron-electron interaction. We write

$$H = H_0 + H_{e-p}. \tag{332}$$

Now since

$$H_0 = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}} c_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} a^\dagger_{\mathbf{q}} a_{\mathbf{q}} \tag{333}$$

and

$$H' = \sum_{\mathbf{kq}} M_{\mathbf{q}} (a^\dagger_{-\mathbf{q}} + a_{\mathbf{q}}) c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}} \tag{334}$$

we try

$$S = \sum_{\mathbf{kq}} M_{\mathbf{q}} (A a^\dagger_{-\mathbf{q}} + B a_{\mathbf{q}}) c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}}. \tag{335}$$

In order to obtain

$$H_{e-p} + [H_0, S] = 0, \tag{336}$$

we need

$$A = -\frac{1}{\varepsilon_{\mathbf{k-q}} - \varepsilon_{\mathbf{k}} + \hbar\omega_{-\mathbf{q}}} \quad \text{and} \quad B = -\frac{1}{\varepsilon_{\mathbf{k-q}} - \varepsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}}}. \tag{337}$$

This can be seen by working the relation on the ground state $|E_0\rangle$. Let us consider the term with A, which gives

$$\begin{aligned}
(H_0 S - S H_0)|E_0\rangle &= \sum_{\mathbf{kq}} M_{\mathbf{q}} A (H_0 a^\dagger_{-\mathbf{q}} c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}} - a^\dagger_{-\mathbf{q}} c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}} H_0)|E_0\rangle & (338)\\
&= \sum_{\mathbf{kq}} M_{\mathbf{q}} A (E_0 + \varepsilon_{\mathbf{k-q}} - \varepsilon_{\mathbf{k}} + \hbar\omega_{-\mathbf{q}} - E_0) a^\dagger_{-\mathbf{q}} c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}}|E_0\rangle & (339)\\
&= -\sum_{\mathbf{kq}} M_{\mathbf{q}} a^\dagger_{-\mathbf{q}} c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}}|E_0\rangle, & (340)
\end{aligned}$$

where in the last step we have used the value of A. Combined with the term with B, this will cancel H_{e-p}.

The transformed Hamiltonian then becomes

$$H' = H_0 - \frac{1}{2}\left[\sum_{\mathbf{kq}} M_{\mathbf{q}} (a^\dagger_{-\mathbf{q}} + a_{\mathbf{q}}) c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}}, \sum_{\mathbf{kq}} M_{\mathbf{q}} \left(\frac{a^\dagger_{-\mathbf{q}}}{\varepsilon_{\mathbf{k-q}} - \varepsilon_{\mathbf{k}} + \hbar\omega_{-\mathbf{q}}} + \frac{a_{\mathbf{q}}}{\varepsilon_{\mathbf{k-q}} - \varepsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}}} \right) c^\dagger_{\mathbf{k+q}} c_{\mathbf{k}} \right]. \tag{341}$$

Of the many terms in the Hamiltonian we pay special attention to those that arise from commuting the phonon operators. This gives the effective Hamiltonian

$$H' = H_0 + \sum_{\mathbf{kq}} |M_{\mathbf{q}}|^2 \frac{\hbar\omega_{\mathbf{q}}}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}}) - (\hbar\omega_{\mathbf{q}})^2} c^\dagger_{\mathbf{k-q}} c^\dagger_{\mathbf{k}} c_{\mathbf{k-q}} c_{\mathbf{k}}. \tag{342}$$

XXII. SUPERCONDUCTIVITY AND THE BCS HAMILTONIAN

Although the possibility of an attractive interaction between electrons is exciting, that it leads to such a surprising phenomena as superconductivity is really startling. At most temperatures, conventional superconductors (i.e., not high-temperature superconductors such as the cuprates) behave pretty much like normal metals. At the transition temperature T_c, the materials undergoes a phase transition which the spectacular effect that the resistivity goes to zero.

In addition, there is a discontinuity in the specific heat. Below T_c, it has a dependence $e^{-\Delta/k_BT}$, thereby providing an indication of an energy gap Δ in the excitation spectra. One also observes that magnetic fields are expelled from the superconductor. This is known as the Meissner effect and can be used to levitate the superconductor.

Since the discovery of superconductivity in 1911 by Heike Kamerlingh Onnes, physicists have been looking for an origin of the effect. Convicing evidence that the electron-phonon interaction is involved came from the discovery of the isotope effect, where it was found that the critical temperature depended on the mass of the nuclei. Our starting point is a Hamiltonian that includes the attractive interaction described in the preceding section

$$H = H_0 + \sum_{\mathbf{kk'q}\sigma\sigma'} W_{\mathbf{kq}} c^\dagger_{\mathbf{k-q},\sigma} c^\dagger_{\mathbf{k}\sigma'} c_{\mathbf{k-q},\sigma'} c_{\mathbf{k}\sigma}, \tag{343}$$

where H_0 describes the Hamiltonian in the absence of electron-phonon interactions, $\sigma, \sigma' = \pm\frac{1}{2} = \uparrow, \downarrow$ is the spin. The matrix element is given by

$$W_{\mathbf{kq}} = |M_{\mathbf{q}}|^2 \frac{\hbar\omega_{\mathbf{q}}}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k-q}}) - (\hbar\omega_{\mathbf{q}})^2}. \tag{344}$$

We will not solve this problem according to the methods of Bardeen, Cooper, and Schrieffer who used a variational technique. We follow the method of Bogoliubov. Bogoliubov's assumption was that the condenstate should have zero momentum. This implies that the electrons that couple with each other have opposite momentum, directly giving $\mathbf{q} = 2\mathbf{k}$. We shall also assume that $\sigma' = -\sigma$. It can be shown (which we will not do) that the ground state for opposite spins (singlet pairing) is in fact lower in energy than the ground state for parallel spins (triplet pairing). This leads to the effective Hamiltonian

$$H_{\text{BCS}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} - \sum_{\mathbf{kk'}} V_{\mathbf{kk'}} c^\dagger_{\mathbf{k'}\uparrow} c^\dagger_{\mathbf{-k'}\downarrow} c_{\mathbf{-k}\downarrow} c_{\mathbf{k}\uparrow}, \tag{345}$$

Where we have taken $V_{\mathbf{kk'}} = -2W_{\mathbf{k},k'-k}$, i.e. the interaction is attractive when $V_{\mathbf{k}}$ is positive. The factor 2 comes from the summation over σ.

We will now look for effective operators that help diagonalize the Hamiltonian. The operators suggested by Bogoliubov are

$$\gamma_{\mathbf{k}\uparrow} = u_{\mathbf{k}} c_{\mathbf{k}\uparrow} - v_{\mathbf{k}} c^\dagger_{\mathbf{-k}\downarrow} \quad \text{and} \quad \gamma_{\mathbf{-k}\downarrow} = u_{\mathbf{k}} c_{\mathbf{-k}\downarrow} + v_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow}, \tag{346}$$

with conjugates

$$\gamma^\dagger_{\mathbf{k}\uparrow} = u_{\mathbf{k}} c^\dagger_{\mathbf{k}\uparrow} - v_{\mathbf{k}} c_{\mathbf{-k}\downarrow} \quad \text{and} \quad \gamma^\dagger_{\mathbf{-k}\downarrow} = u_{\mathbf{k}} c^\dagger_{\mathbf{-k}\downarrow} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}. \tag{347}$$

The constants $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are real and positive and satisfy

$$u^2_{\mathbf{k}} + v^2_{\mathbf{k}} = 1. \tag{348}$$

With this condition, the operators satisfy the commutation relations

$$\{\gamma_{\mathbf{k}\uparrow}, \gamma_{\mathbf{k'}\uparrow}\} = \{\gamma_{\mathbf{k}\uparrow}, \gamma_{\mathbf{-k'}\downarrow}\} = \{\gamma_{\mathbf{k}\uparrow}, \gamma^\dagger_{\mathbf{-k'}\downarrow}\} = 0 \tag{349}$$

$$\{\gamma^\dagger_{\mathbf{k}\uparrow}, \gamma_{\mathbf{k'}\uparrow}\} = \{\gamma_{\mathbf{-k}\downarrow}, \gamma^\dagger_{\mathbf{-k'}\downarrow}\} = \delta_{\mathbf{k},k'}. \tag{350}$$

Using the Bogoliubov transformation does not allow us to diagonalize the Hamiltonian entirely. It will contain two-particle term (including four operators). However, we hope that an appropiate choice of $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ will remove the dominant terms.

We can rewrite H_{BCS}, using the inverse operators

$$c_{\mathbf{k}\uparrow} = u_{\mathbf{k}} \gamma_{\mathbf{k}\uparrow} + v_{\mathbf{k}} \gamma^\dagger_{\mathbf{-k}\downarrow} \quad \text{and} \quad c_{\mathbf{-k}\downarrow} = u_{\mathbf{k}} \gamma_{\mathbf{-k}\downarrow} - v_{\mathbf{k}} \gamma^\dagger_{\mathbf{k}\uparrow} \tag{351}$$

$$c^\dagger_{\mathbf{k}\uparrow} = u_{\mathbf{k}} \gamma^\dagger_{\mathbf{k}\uparrow} + v_{\mathbf{k}} \gamma_{\mathbf{-k}\downarrow} \quad \text{and} \quad c^\dagger_{\mathbf{-k}\downarrow} = u_{\mathbf{k}} \gamma^\dagger_{\mathbf{-k}\downarrow} - v_{\mathbf{k}} \gamma_{\mathbf{k}\uparrow} \tag{352}$$

Let is first rewrite the kinetic part of the Hamiltonian. Substituting the expressions for c and $c^\dagger$ gives

$$H_0 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c^\dagger_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} [c^\dagger_{\mathbf{k}\uparrow} c_{\mathbf{k}\uparrow} + c^\dagger_{\mathbf{k}\downarrow} c_{\mathbf{k}\downarrow}] \tag{353}$$

$$= \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} [u^2_{\mathbf{k}} \gamma^\dagger_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}\uparrow} + v^2_{\mathbf{k}} \gamma_{\mathbf{-k}\downarrow} \gamma^\dagger_{\mathbf{-k}\downarrow} + u_{\mathbf{k}} v_{\mathbf{k}} (\gamma^\dagger_{\mathbf{k}\uparrow} \gamma^\dagger_{\mathbf{-k}\downarrow} + \gamma_{\mathbf{-k}\downarrow} \gamma_{\mathbf{k}\uparrow}) \tag{354}$$

$$+ v^2_{\mathbf{k}} \gamma_{\mathbf{k}\uparrow} \gamma^\dagger_{\mathbf{k}\uparrow} + u^2_{\mathbf{k}} \gamma^\dagger_{\mathbf{-k}\downarrow} \gamma_{\mathbf{-k}\downarrow} - u_{\mathbf{k}} v_{\mathbf{k}} (\gamma^\dagger_{\mathbf{-k}\downarrow} \gamma^\dagger_{\mathbf{k}\uparrow} + \gamma_{\mathbf{k}} \gamma_{\mathbf{-k}})]. \tag{355}$$

H_0 can be simplified by introducing te number operators

$$m_{\mathbf{k}\uparrow} = \gamma^\dagger_{\mathbf{k}\uparrow}\gamma_{\mathbf{k}\uparrow}; \qquad m_{-\mathbf{k}\downarrow} = \gamma^\dagger_{-\mathbf{k}\downarrow}\gamma_{-\mathbf{k}\downarrow}, \tag{356}$$

and making use of the commutation relationships of the γ's. We then obtain

$$H_0 \;=\; \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}[2v^2_{\mathbf{k}} + (u^2_{\mathbf{k}} - v^2_{\mathbf{k}})(m_{\mathbf{k}\uparrow} + m_{-\mathbf{k}\downarrow}) + 2u_{\mathbf{k}}v_{\mathbf{k}}(\gamma^\dagger_{\mathbf{k}\uparrow}\gamma^\dagger_{-\mathbf{k}\downarrow} + \gamma_{-\mathbf{k}\downarrow}\gamma_{\mathbf{k}\uparrow}). \tag{357}$$

There are three different types of terms here: a constant, a term containing the number operators m, and a term containing creation and annihilation of pairs of quasi particles.

The interaction part of the Hamiltonian can now be written as

$$H_V \;=\; -\sum_{\mathbf{k}} V_{\mathbf{k}\mathbf{k}'}(u_{\mathbf{k}'}\gamma^\dagger_{\mathbf{k}'\uparrow} + v_{\mathbf{k}'}\gamma_{-\mathbf{k}'\downarrow})(u_{\mathbf{k}'}\gamma^\dagger_{-\mathbf{k}'\downarrow} - v_{\mathbf{k}'}\gamma_{\mathbf{k}'\uparrow})(u_{\mathbf{k}}\gamma_{-\mathbf{k}\downarrow} - v_{\mathbf{k}}\gamma^\dagger_{\mathbf{k}\uparrow})(u_{\mathbf{k}}\gamma_{\mathbf{k}\uparrow} + v_{\mathbf{k}}\gamma^\dagger_{-\mathbf{k}\downarrow}) \tag{358}$$

$$= \; -\sum_{\mathbf{k}} V_{\mathbf{k}} \,[u_{\mathbf{k}'}v_{\mathbf{k}'}u_{\mathbf{k}}v_{\mathbf{k}}(1 - m_{\mathbf{k}'\uparrow} - m_{-\mathbf{k}'\downarrow})(1 - m_{\mathbf{k}\uparrow} - m_{-\mathbf{k}\downarrow}) \tag{359}$$

$$+u_{\mathbf{k}'}v_{\mathbf{k}'}(u^2_{\mathbf{k}} - v^2_{\mathbf{k}})(1 - m_{-\mathbf{k}'\downarrow} - m_{\mathbf{k}'\uparrow})(\gamma^\dagger_{\mathbf{k}\uparrow}\gamma^\dagger_{-\mathbf{k}\downarrow} + \gamma_{-\mathbf{k}\downarrow}\gamma_{\mathbf{k}\uparrow})\Big] + \text{higher order terms.} \tag{360}$$

We now want to eliminate all the off-diagonal terms to obtain a Hamiltonian of independent fermions γ. The first assumption is that there are the occupations $m_{\mathbf{k}\uparrow}$ and $m_{-\mathbf{k}\downarrow}$ are zero in the ground state. We can later verify this assumption. The off-diagonal terms that remain are

$$\sum_{\mathbf{k}} 2\varepsilon_{\mathbf{k}}u_{\mathbf{k}}v_{\mathbf{k}}(\gamma^\dagger_{\mathbf{k}\uparrow}\gamma^\dagger_{-\mathbf{k}\downarrow} + \gamma_{-\mathbf{k}\downarrow}\gamma_{\mathbf{k}\uparrow}) + \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}u_{\mathbf{k}'}v_{\mathbf{k}'}(u^2_{\mathbf{k}} - v^2_{\mathbf{k}})(\gamma^\dagger_{\mathbf{k}\uparrow}\gamma^\dagger_{-\mathbf{k}\downarrow} + \gamma_{-\mathbf{k}\downarrow}\gamma_{\mathbf{k}\uparrow}) + \text{higher order terms.} \tag{361}$$

If we neglect the higher-order contributions, we are left with

$$2\varepsilon_{\mathbf{k}}u_{\mathbf{k}}v_{\mathbf{k}} + (u^2_{\mathbf{k}} - v^2_{\mathbf{k}})\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}u_{\mathbf{k}'}v_{\mathbf{k}'} = 0. \tag{362}$$

However, $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ are not independent due to the condition $u^2_{\mathbf{k}} + v^2_{\mathbf{k}} = 1$, and we can express them in a single variable $x_{\mathbf{k}}$,

$$u_{\mathbf{k}} = \sqrt{\frac{1}{2} - x_{\mathbf{k}}} \quad \text{and} \quad v_{\mathbf{k}} = \sqrt{\frac{1}{2} + x_{\mathbf{k}}}. \tag{363}$$

This transforms the equation into

$$2\varepsilon_{\mathbf{k}}\sqrt{\frac{1}{4} - x^2_{\mathbf{k}}} + 2x_{\mathbf{k}}\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}\sqrt{\frac{1}{4} - x^2_{\mathbf{k}'}} = 0. \tag{364}$$

If we define a new quantity

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}\sqrt{\frac{1}{4} - x^2_{\mathbf{k}'}}, \tag{365}$$

then we obtain

$$2\varepsilon_{\mathbf{k}}\sqrt{\frac{1}{4} - x^2_{\mathbf{k}}} + 2x_{\mathbf{k}}\Delta_{\mathbf{k}} = 0 \quad \Rightarrow \quad \varepsilon^2_{\mathbf{k}}(\frac{1}{4} - x^2_{\mathbf{k}}) = x^2_{\mathbf{k}}\Delta^2_{\mathbf{k}} \tag{366}$$

$$\Rightarrow \quad x^2_{\mathbf{k}}(\Delta^2_{\mathbf{k}} + \varepsilon^2_{\mathbf{k}}) = \frac{1}{4}\varepsilon^2_{\mathbf{k}} \tag{367}$$

or

$$x_{\mathbf{k}} = \frac{\varepsilon_{\mathbf{k}}}{2\sqrt{\Delta^2_{\mathbf{k}} + \varepsilon^2_{\mathbf{k}}}} \tag{368}$$

Substituting $x_{\mathbf{k}}$ in the expression for $\Delta_{\mathbf{k}}$, leads to the following integral equation

$$\Delta_{\mathbf{k}} = \sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \frac{\Delta_{\mathbf{k}}}{\sqrt{\varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}}}, \tag{369}$$

if $V_{\mathbf{k}\mathbf{k}'}$ is known, we can use this to solve for $\Delta_{\mathbf{k}}$. Let us make a simple assumption for $V_{\mathbf{k}\mathbf{k}'}$. We know that the matrix element is given by

$$V_{\mathbf{k}\mathbf{k}'} = -2|M_{\mathbf{k}'-\mathbf{k}}|^2 \frac{\hbar\omega_{\mathbf{k}'-\mathbf{k}}}{(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) - (\hbar\omega_{\mathbf{k}'-\mathbf{k}})^2}. \tag{370}$$

We want $V_{\mathbf{k}\mathbf{k}'}$ to be positive for an attractive interaction. This is the region that $|\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}| < \hbar\omega_{\mathbf{k}'-\mathbf{k}}$. In general, phonon frequency have an energy significantly smaller the Fermi energy. E_F is generally of the order of a few electron volts, whereas phonon frequencies are in the region of several tenths of meV. Let us denote the maximum phonon frequency ω_D, known as the Debye frequency. Let us for mathematical simplicity (and also for lack of information of a better $\mathbf{k}$ dependence) assume

$$V_{\mathbf{k}\mathbf{k}'} = \begin{cases} V & \text{if } |\varepsilon_{\mathbf{k}}| < \hbar\omega_D \\ 0 & \text{otherwise} \end{cases} \tag{371}$$

Replacing the sum over momentum by an integral over energy, we obtain

$$\Delta = \frac{1}{2}\int_{-\infty}^{\infty} \rho(E) \frac{\Delta}{\sqrt{E^2 + \Delta^2}} V(E) = \frac{1}{2} V\rho(E_F) \int_{-\hbar\omega_D}^{\hbar\omega_D} \frac{\Delta}{\sqrt{E^2 + \Delta^2}} dE, \tag{372}$$

where we have assumed that the density of states does not vary too much in a region $\hbar\omega_D$ around the Fermi surface. This equation has the solution

$$\Delta = \frac{\hbar\omega_D}{\sinh[1/V\rho(E_F)]}. \tag{373}$$

An estimate of the magnitude of $V\rho(E_F)$ can be obtained by noting that

$$V \cong \frac{|M_{\mathbf{q}}|^2}{\hbar\omega_D}. \tag{374}$$

Earlier we had seen that

$$|M_{\mathbf{q}}|^2 \cong \frac{\hbar k_F}{MN\omega_D} |U_{\mathbf{k}}|^2 \cong \frac{m}{M} \frac{E_F}{N\hbar\omega_D} |U_{\mathbf{k}}|^2. \tag{375}$$

For a constant density of states, we can roughly estimate $\rho(E_F) = N/E_F$. This leaves us with

$$|M_{\mathbf{q}}|^2 \cong \frac{m}{M} \frac{1}{\rho(E_F)\hbar\omega_D} |U_{\mathbf{k}}|^2, \tag{376}$$

and hence

$$V\rho(E_F) \cong \frac{m}{M} \left(\frac{U_{\mathbf{k}}}{\hbar\omega_D}\right)^2. \tag{377}$$

The value of $\hbar\omega_D$ is of the order of 10^{-2} eV, whereas the screened Coulomb potential can be several eV. The mass ratio m/M is about 10^{-5}. This makes $V\rho(E_F)$ roughly equal to 0.1. We can therefore write

$$\Delta = 2\hbar\omega_D e^{-1/V\rho(E_F)}. \tag{378}$$

This rough estimate shows that the Δ is a small quantity, about 1% of the Debye energy and hence corresponding to thermal energies of about 1 K.

Note that the total number of electrons is given by

$$N = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} \tag{379}$$

$$= \sum_{\mathbf{k}} [2v_{\mathbf{k}}^2 + (u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2)(m_{\mathbf{k}\uparrow} + m_{-\mathbf{k}\downarrow}) + 2u_{\mathbf{k}}v_{\mathbf{k}}(\gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{-\mathbf{k}\downarrow}^\dagger + \gamma_{-\mathbf{k}\downarrow}\gamma_{\mathbf{k}\uparrow})] \tag{380}$$

which reduces to

$$\langle N\rangle = \sum_{\mathbf{k}} 2v_{\mathbf{k}}^2. \tag{381}$$

In the absence of interactions this would be

$$\langle N\rangle = \sum_{\mathbf{k}} 2, \tag{382}$$

where the factor 2 comes from the spin. The presence of Δ will cause a disturbance around the Fermi level given by

$$v_{\mathbf{k}}^2 = \frac{1}{2} - \frac{\varepsilon_{\mathbf{k}}}{\sqrt{\varepsilon_{\mathbf{k}}^2 + \Delta_{\mathbf{k}}^2}}, \tag{383}$$

which basically causes a smoothing of the electron density around E_F, of the order of Δ.

XXIII. BCS GROUND STATE WAVEFUNCTION AND ENERGY GAP

First, we would like to see how the ground state energy is changed by the presence of an attractive electron-phonon coupling. By performing a Bogliubov transformation, we have removed the off-diagonal terms. In addition, we have assumed that $m_{\mathbf{k}\uparrow} = m_{-\mathbf{k}\downarrow} = 0$. We can then write the ground state energies as

$$\begin{aligned} E_S &= \sum_{\mathbf{k}} 2\varepsilon_{\mathbf{k}} v_{\mathbf{k}}^2 - \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}'} u_{\mathbf{k}} v_{\mathbf{k}} && (384)\\ &= \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}}(1+2x_{\mathbf{k}}) - \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} \sqrt{(\frac{1}{4} - x_{\mathbf{k}'}^2)(\frac{1}{4} - x_{\mathbf{k}}^2)}. && (385)\end{aligned}$$

In the normal state, we have $x_{\mathbf{k}}^2 = \frac{1}{4}$. We want to find the difference between the energy in the superconducting state and the energy in the normal state, known as the condensation energy

$$\begin{aligned} E_c &= E_S - E_N = \sum_{k<k_f} \varepsilon_{\mathbf{k}}(2x_{\mathbf{k}} - 1) + \sum_{k>k_f} \varepsilon_{\mathbf{k}}(2x_{\mathbf{k}} + 1) - \sum_{\mathbf{k}} \sqrt{\frac{1}{4} - x_{\mathbf{k}}^2}\Delta && (386)\\ &= 2\rho(E_F) \int_0^{\hbar\omega_D} \left[E - \frac{2E^2 + \Delta^2}{2\sqrt{E^2+\Delta^2}}\right] dE && (387)\\ &= D(E_F)\left[(\hbar\omega_D)^2 - \hbar\omega_D\sqrt{(\hbar\omega_D)^2 + \Delta^2}\right] && (388)\\ &= (\hbar\omega_D)^2 \rho(E_F)\left[1 - \coth\left(\frac{1}{V\rho(E_F)}\right)\right]. && (389)\end{aligned}$$

In the weak coupling regime, this becomes

$$E_c \cong -2(\hbar\omega_D)^2 \rho(E_F) e^{-2/V\rho(E_F)} = -\frac{1}{2}\rho(E_F)\Delta^2. \tag{390}$$

This condensation energy is very small, only of the order of 10^{-7} eV per electron, equivalent to about a millidegree Kelvin. Obviously, these are all the electrons and only the electrons in the region $E_F - \Delta$ to $E_F + \Delta$ are acutally affected by the attractive interaction, i.e. only a fraction Δ/E_F of the whole number. Note that we cannot expand Δ in terms of the interaction V, since it appears as $1/V$ and has a singularity as $V \to 0$. Therefore, superconductivity cannot be understood in terms of perturbation theory.

In our derivation of the ground state, we had assumed that $m_{\mathbf{k}\uparrow}$ and $m_{-\mathbf{k}\downarrow}$ are zero for all $\mathbf{k}$. This means that there are no quasiparticles in the ground state and

$$\gamma_{\mathbf{k}\uparrow}|0\rangle = \gamma_{-\mathbf{k}\downarrow}|0\rangle = 0 \tag{391}$$

Since the γ's are fermions, we have $\gamma_{\mathbf{k}\uparrow}\gamma_{\mathbf{k}\uparrow} = 0$ and $\gamma_{-\mathbf{k}\downarrow}\gamma_{-\mathbf{k}\downarrow} = 0$, we can satisfy the above criterium by creating a ground state by working with the γ's on the vacuum

$$\begin{aligned} (\prod_{\mathbf{k}} \gamma_{\mathbf{k}\uparrow}\gamma_{-\mathbf{k}\downarrow})|0\rangle &= [\prod_{\mathbf{k}} (u_{\mathbf{k}} c_{\mathbf{k}\uparrow} - v_{\mathbf{k}} c_{-\mathbf{k}\downarrow}^\dagger)(u_{\mathbf{k}} c_{-\mathbf{k}\downarrow} + v_{\mathbf{k}} c_{\mathbf{k}\uparrow}^\dagger)]|0\rangle && (392)\\ &= [\prod_{\mathbf{k}} (u_{\mathbf{k}} v_{\mathbf{k}} + v_{\mathbf{k}}^2 c_{\mathbf{k}\uparrow}^\dagger c_{-\mathbf{k}\downarrow}^\dagger)]|0\rangle. && (393)\end{aligned}$$

We see that this is not normalized. We can do this by dividing by $v_{\mathbf{k}}$,

$$|\Psi_0\rangle \;=\; [\prod_{\mathbf{k}}(u_{\mathbf{k}} + v_{\mathbf{k}} c^{\dagger}_{\mathbf{k}\uparrow} c^{\dagger}_{-\mathbf{k}\downarrow})]|0\rangle. \tag{394}$$

We see that this ground state does not conserve the total number of particles. However, we need to be sure that the average number of particles is still equal to N.

The quasi-particle excitation of the system are created by the operators $\gamma^{\dagger}_{\mathbf{k}\uparrow}$ and $\gamma^{\dagger}_{-\mathbf{k}\downarrow}$. We can look again at the Hamiltonian and look at the terms with $m_{\mathbf{k}\uparrow}$ and $m_{-\mathbf{k}\downarrow}$. This gives

$$H_{\rm BCS} = E_S + \sum_{\mathbf{k}}(m_{\mathbf{k}\uparrow} + m_{-\mathbf{k}\downarrow})[(u^2_{\mathbf{k}} - v^2_{\mathbf{k}})\varepsilon_{\mathbf{k}} + 2u_{\mathbf{k}}v_{\mathbf{k}}\sum_{\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'}u_{\mathbf{k}'}v_{\mathbf{k}'}] + \text{higher order terms}, \tag{395}$$

which becomes

$$H_{\rm BCS} = E_S + \sum_{\mathbf{k}}\sqrt{\varepsilon^2_{\mathbf{k}} + \Delta^2}(m_{\mathbf{k}\uparrow} + m_{-\mathbf{k}\downarrow}) + \cdots \tag{396}$$

We see that the energy to make an elementary excitation is

$$E_{\mathbf{k}} = \sqrt{\varepsilon^2_{\mathbf{k}} + \Delta^2}. \tag{397}$$

Note that this energy is always larger than Δ. This is the opening of a superconducting gap.