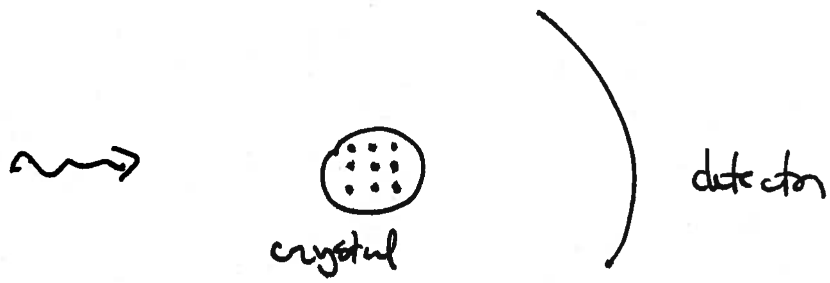
June 5

Quantum Mechanics in Periodic Structures

Throughout this course, we have discussed scattering from a single scattering center. In these last two lectures, I would like to discuss a little about the generalization of these ideas to systems with a periodic array of scatterers. Most solids, from rocks to metals, have a periodic arrangement of atoms on the microscopic scale. So this is an important subject about which much has been written. I cannot discuss this subject comprehensively, but I would like to introduce some of its main concepts.

To begin, I will discuss the scattering of Schrödinger particles from a periodic array of atoms



The spacing of atoms in a crystal is about 1 Å, so we will get the most information if we use a probe of wavelength $\lambda \sim 1$ Å. This probe might be an electron, an X-ray photon, or a neutron. X-rays scattering, first studied by Bragg, is the classic technique. Electrons are strongly absorbed in solids but are useful for analyzing the detailed structure of surfaces. Neutron scattering is sensitive to spin alignment and so is especially useful in studies of magnetism.

For a first, simple example, consider scattering from a line of N atoms periodically arranged,

$$\vec{x}_m = m\vec{a}$$

For scattering from one atom at $\vec{x} = \vec{x}_0$, the scattering wavefunction is

$$\varphi(\vec{x}) = e^{i\vec{k}\cdot\vec{x}} + \frac{e^{ik|\vec{x}-\vec{x}_0|}}{|\vec{x}-\vec{x}_0|} e^{i\vec{k}\cdot\vec{x}_0} f(\vec{q})$$

where $\vec{q}$ is the momentum transfer. The scattering amplitude from an array of atoms is then

$$\varphi(\vec{x}) = e^{i\vec{k}\cdot\vec{x}} + \sum_{m=0}^{N-1} \frac{e^{ik|\vec{x}-\vec{x}_m|}}{|\vec{x}-\vec{x}_m|} e^{i\vec{k}\cdot\vec{x}_m} f(\vec{q}_m)$$

If the detection point $\vec{x}$ is very far outside the sample, we can approximate

$$|\vec{x}-\vec{x}_m| \cong r - \hat{r}\cdot\vec{x}_m + \cdots$$

$$\vec{q}_m = k\,(\widehat{\vec{x}-\vec{x}_m} - \hat{z}) \cong k\,(\hat{r} - \hat{z})$$

Then this expression becomes

$$\varphi(\vec{x}) = e^{i\vec{k}\cdot\vec{x}} + \sum_{m=0}^{N-1} \frac{e^{ikr}}{r} e^{-ik\hat{r}\cdot m\vec{a}} e^{ik\hat{z}\cdot m\vec{a}} f(\vec{q})$$

$$= e^{i\vec{k}\cdot\vec{x}} + \frac{e^{ikr}}{r} f(q) \cdot \sum_{m=0}^{N-1} e^{-i\vec{q}\cdot\vec{a}\,m}$$

The sum that appears in this expression is

$$F(\vec{q}) = \sum_{m=0}^{N-1} \left(e^{-i\vec{q}\cdot\vec{a}}\right)^m = \frac{1 - e^{-i\vec{q}\cdot\vec{a}N}}{1 - e^{-i\vec{q}\cdot\vec{a}}} \approx \frac{\sin N\frac{\vec{q}\cdot\vec{a}}{2}}{\sin\frac{\vec{q}\cdot\vec{a}}{2}}$$

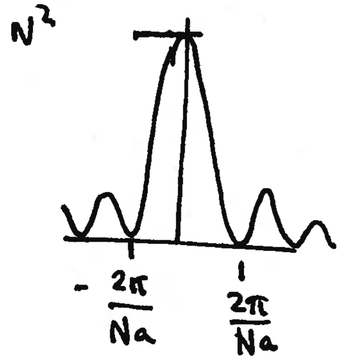
This is a function with an enormous peak at $\vec{q} = 0$

$$F(\vec{q}=0) = N$$

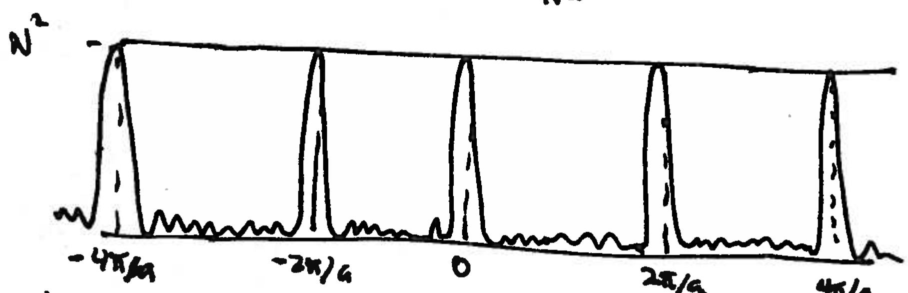
and much smaller peaks at the subsidiary maxima of the sine function in the numerator. However, when we reach

$$\vec{q} = \frac{2\pi}{a}\hat{a}$$

there is another enormous peak. The form of $|F(\vec{q})|^2$ is



near $\vec{q} = 0$, and



on a larger scale of $\vec{q}$. At the major peaks, all N atoms contribute *coherently* to the scattering amplitude. The integral of $|F(\vec{q})|^2$ over one major period is

$$\int_{-\pi/a}^{\pi/a} dq \left| \sum_{m=0}^{N-1} e^{-iqam} \right|^2 = N \cdot \frac{2\pi}{a}$$

since there are N terms equal to 1 and all other terms integrate to 0. Then, as $N \to \infty$,

$$|F(q)|^2 \to N \sum_{n=-\infty}^{\infty} \frac{2\pi}{a} \delta\left(q - n\frac{2\pi}{a}\right)$$

This calculation generalizes immediately to a 3-dimensional lattice of atoms. Consider a lattice with elementary vectors

$$\vec{e}_1 \quad \vec{e}_2 \quad \vec{e}_3$$

so that a general point of the array is

$$\vec{x}_m = m_1\vec{e}_1 + m_2\vec{e}_2 + m_3\vec{e}_3 \qquad\qquad m_i \text{ integers}$$

The points $\{\vec{x}_m\}$ form a lattice that I will call Λ. Then the wavefunction representing scattering from this array is

$$\varphi(\vec{x}) = e^{i\vec{k}\cdot\vec{x}} + \frac{e^{ikr}}{r} f(\vec{q}) \cdot F(\vec{q})$$

with

$$F(\vec{q}) = \sum_{\vec{x}\in\Lambda} e^{-i\vec{q}\cdot\vec{x}}$$

This sum is a function with enormous peaks, $F(\vec{q}) = N$, at values of $\vec{q}$ satisfying

$$\vec{q}\cdot\vec{x} = 2\pi \cdot \text{integer} \quad \text{for all } \vec{x}\in\Lambda$$

These values of $\vec{q}$ also form a lattice, called the *reciprocal lattice* Λ^*. Let $\vec{\kappa}_1$, $\vec{\kappa}_2$, $\vec{\kappa}_3$ be three vectors such that

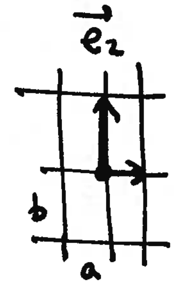
$$\vec{\kappa}_i \cdot \vec{e}_j = 2\pi\delta_{ij}$$

Then the reciprocal lattice is

$$\Lambda^* = \{ n_i \vec{K}_i \} \qquad n_i \text{ integers}$$

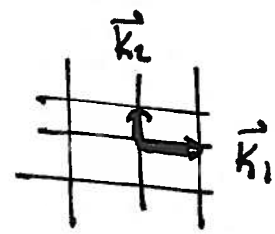
Some examples of 2-dimensional lattices illustrate the form of the reciprocal lattice. For a rectangular lattice

$$\vec{e}_1 = a\,\hat{1} \qquad e_2 = b\,\hat{2}$$



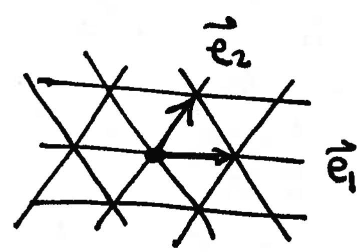
the elementary vectors of the reciprocal lattice are

$$\vec{K}_1 = \frac{2\pi}{a}\,\hat{1} \qquad \vec{K}_2 = \frac{2\pi}{b}\,\hat{2}$$



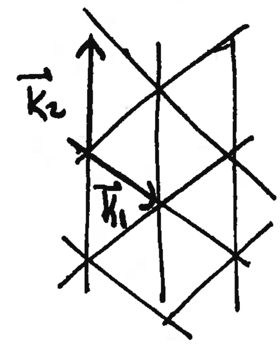
For a triangular lattice

$$\vec{e}_1 = a\,\hat{1} \qquad \vec{e}_2 = a\left(\tfrac{1}{2}\,\hat{1} + \tfrac{\sqrt{3}}{2}\,\hat{2}\right)$$



the elementary vectors of the reciprocal lattice are

$$\vec{K}_1 = \frac{4\pi}{\sqrt{3}a}\left(\frac{\sqrt{3}}{2}\hat{1} - \frac{1}{2}\hat{2}\right) \quad \vec{K}_2 = \frac{4\pi}{\sqrt{3}a}\hat{2}$$



In 2 dimensions, we can have square or quadrilateral and triangular or hexagonal lattices only. In 3 dimensions, there are 14 possible lattice structures. These are nicely presented, for example, in Ashcroft and Mermin, *Solid State Physics.* That is also an excellent reference for the study of electrons wavefunctions in solids, which we will take up in a moment. For the rest of these lectures, I will generally use only the simplest examples of cubic lattices.

If v is the volume of the unit cell in Λ,

$$v = \det(e_i^a)$$

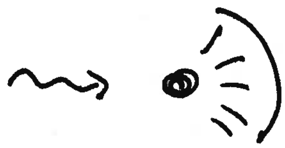
the volume of the unit cell in Λ^* is

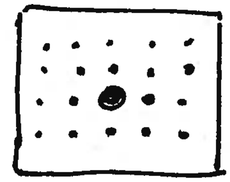
$$v_* = \frac{(2\pi)^3}{v}$$

Then the squared sum $|F(\vec{q})|^2$ has the limit for large N

$$|F(\vec{q})|^2 \to N \sum_{\vec{k} \in \Lambda^*} v_* \, \delta^{(d)}(\vec{q} - \vec{k})$$

In a scattering experiment, then, the scattering probability as a function of the scattering angles will have sharp peaks at the values of $\vec{q}$ that are reciprocal lattice vectors. These are called *Bragg peaks.*





By measuring the positions of the peaks, we can determine the reciprocal lattice Λ^* and, from this, the atomic lattice Λ. Each peak has a strength proportional to

$$|f(\vec{q})|^2$$

where $f(\vec{q})$ is the form factor of the atom or molecule from which the lattice is built. By measuring the strengths of the peaks for a crystal of an organic compounds, using these to determine the form factor $f(\vec{q})$, and then inverting the Fourier transform, it is possible to work out the structure of an organic molecule, even one as large as a protein or DNA.

The reciprocal lattice has another, quantum mechanical, derivation. In the first quarter of your quantum mechanics course, you learned that, if the Hamiltonian is translation invariant, momentum is conserved. I will remind you of the derivation: In quantum mechanics, translations are implemented by unitary operators, of the form

$$U(\vec{a}) = e^{i\vec{P}\cdot\vec{a}}$$

where $\vec{P}$ is a Hermitian operator. If

$$[U(\vec{a}), H] = 0$$

for all $\vec{a}$, then this operator $\vec{P}$ satisfies

$$[\vec{P}, H] = 0$$

The fundamental definition of $\vec{P}$ is that it is the Hermitian operator that generates translations.

A crystal lattice is not translation invariant. However, it is invariant under discrete translations

$$[U(\vec{a}), H] = 0 \quad \text{for} \quad \vec{a} \in \Lambda$$

In particular

$$[U(\vec{e}_i), H] = [e^{i\vec{P}\cdot\vec{e}_i}, H] = 0$$

Thus, it is possible to diagonalize these unitary operators simultaneously with the Hamiltonian. We can then choose a basis of energy eigenstates such that, for each state $|\alpha\rangle$,

$$e^{i\vec{P}\cdot\vec{e}_i}|\alpha\rangle = e^{i\alpha_i}|\alpha\rangle$$

We can think of $|\alpha\rangle$ as a state with conserved momentum

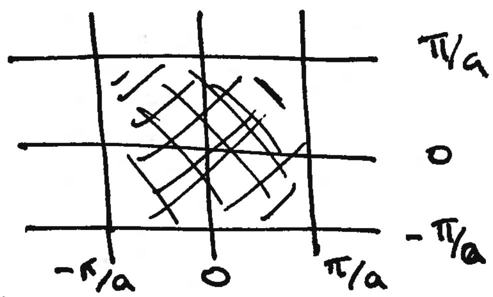
$$\vec{P} = \sum_i \alpha_i \vec{K}_i$$

However, notice that changing $\vec{p}$ by a reciprocal lattice vector

$$p \to p + \sum_i n_i \vec{K}_i$$

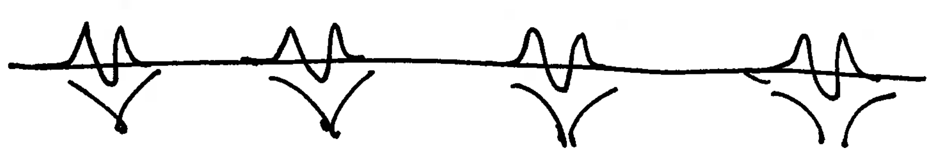
has no effect on the actual eigenvalues $e^{i\alpha_i}$. A way to think about this is that the lattice conserves momentum *except that* momentum can be violated by a reciprocal lattice vector.

The conserved momenta $\vec{p}$ can be represented conveniently as points in the *unit cell* of the reciprocal lattice. This region is called the *Brillouin zone.* For a square lattice of spacing a, the Brillouin zone is



All of the points in momentum space are connected to the points in the Brillouin zone by shifts by reciprocal lattice vectors, which represent allowed momentum non-conservations. The reduced momenta $\vec{p}$ are called *lattice momenta.*

I would now like to explore the implications of these ideas for electrons in a solid. Let's first compute the electron energy spectrum in a very simple model, called the *tight-binding model.* In this model, we have localized electron orbitals on the individual atoms of the crystal, and we add coupling of these orbitals to one another. For simplicity, I will start with a periodic array of atoms in 1 dimension



Let the state in which the electron is on atom k, at position ka, be $|k\rangle$. Let all of these states have energy $\mathcal{E}$. Now add a term to the Hamiltonian that allows the electron to hop between neighboring atoms

$$\langle k+1|\Delta H|k\rangle = \langle k|\Delta H|k+1\rangle = -\Delta$$

Then if we write

$$|\psi\rangle = \sum_k a_k |k\rangle$$

the time-independent Schrödinger equation is

$$E\left(\sum_k a_k |k\rangle\right) = \sum_k a_k \left(\mathcal{E}|k\rangle - \Delta|k-1\rangle - \Delta|k+1\rangle\right)$$

or

$$E a_k = \mathcal{E} a_k - \Delta(a_{k+1} + a_{k-1})$$

A solution to this equation is

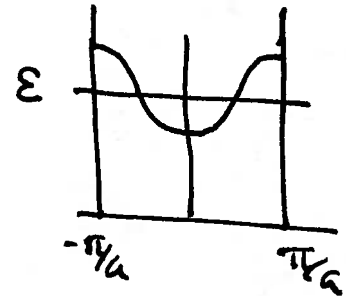
$$a_k = e^{ip\cdot ka}$$

where

$$E = \mathcal{E} - \Delta\left(e^{ipa} + e^{-ipa}\right)$$

that is,

$$E(p) = \mathcal{E} - 2\Delta \cos(pa)$$



Near $p = 0$ this has the form

$$E(p) \cong (\mathcal{E} - 2\Delta) + \Delta a^2 p^2$$

so for small p this is a familiar nonrelativistic energy-momentum relation with effective electron mass

$$m = \frac{1}{2\Delta a^2}$$

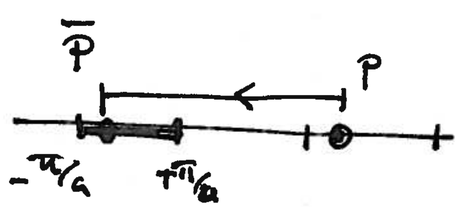
Notice that this mass becomes large as $\Delta \to 0$.

The values of p lying in the Brillouin zone

$$-\frac{\pi}{a} < p < \frac{\pi}{a}$$

all describe independent states. A value of p outside the Brillouin zone gives a state that is *identical* to a state in the Brillouin zone, at

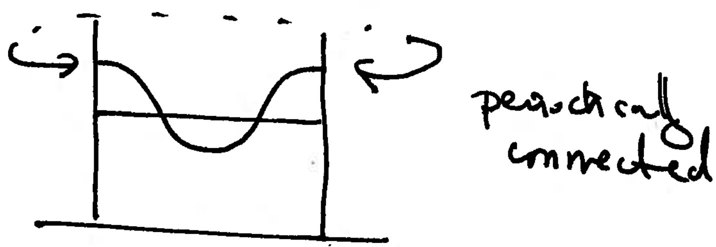
$$\bar{p} = p - m\frac{2\pi}{a}$$



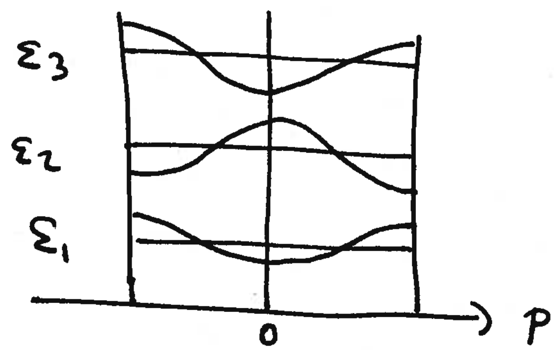
for some integer m. So, the solutions to the tight-binding problem are labeled by lattice momentum. This constraint implies that the energy function $E(p)$ must be periodic in p.

$$E(p + \frac{2\pi}{a}) = E(p)$$

The expression that we have found is also analytic at the zone boundaries.

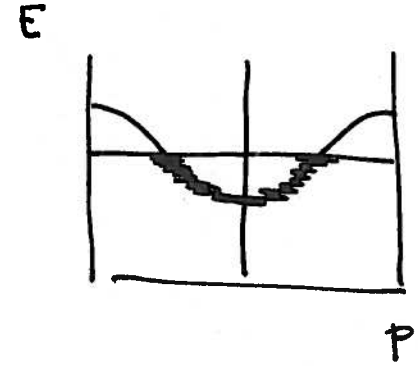


If we add further tight-binding levels, we might find an energy level diagram that looks like this:



Each set of levels is called an *energy band.* If the bands are separated, the intervening energy regions are called *band gaps.*

A simple system to think about is a crystal made of alkali atoms (Li, Na, K, etc.). In these systems, the tight-binding approximation is not unreasonable. The tight-binding states are the highest occupied S states. These form an energy band in the way that I have indicated. However, each atom contributes only 1 electron to the band, while the Pauli exclusion principle allows the band to hold 2 electrons per p state, one of each spin. If we fill states from the lowest energy in the band, the band will be end up only half full



With a tiny expenditure of energy, we can move electrons from the highest filled states to the lowest empty states. These electrons have nonzero momentum, and so they move freely and can transport electric charge. This system is a *metal*. In the limit where the lattice is perfectly periodic, a moving electron experiences no forces that could slow it down; then we have perfect conductivity. Before the invention of quantum mechanics, physicists were puzzled by the existence of metals. Why didn't the electrons moving in solids scatter off the atoms that were obviously in their way? The answer is that, in a perfect crystal, an electron cannot change its momentum, except to a value related by a reciprocal lattice vector.

In general, electrons in a metal fill all available states up to a level, called the *Fermi energy*, at which we run out of electrons. It is instructive to make a simple estimate of the Fermi energy. Let us assume 1 electron per atom and assign it a free-particle dispersion relation $E = p^2/2m$. If the system is restricted to a large box of size L, the number of states up to energy E_F is

$$\sum_n = 2 \cdot \frac{L^3}{(2\pi)^3} \int_{|p|<p_F} d^3p = 2L^3 \frac{1}{(2\pi)^3} \left(\frac{4\pi}{3} p_F^3 \right)$$

where p_F is the corresponding momentum

$$E_F = \frac{p_F^2}{2m}$$

and I have accounted 2 electron spin states per momentum state. The density of electrons is then

$$n = \frac{1}{3\pi^2}\frac{p_F^3}{\hbar^3}$$

Setting this equal to

$$n \sim \frac{1}{(1\,\text{Å})^3} \sim \frac{1}{(2a_0)^3}$$

we find

$$p_F \cong \frac{(3\pi^2)^{1/3}}{2a_0}\hbar$$

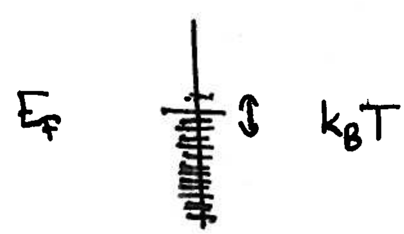
Then

$$E_F \cong \frac{(3\pi^2)^{2/3}\hbar^2}{8ma_0^2} \sim \frac{(3\pi^2)^{2/3}}{4} R_y \sim 30\,\text{eV}$$

This is a large energy compared to the typical energy of a thermal fluctuation at room temperature

$$k_B T \sim \frac{1}{40}\,\text{eV}$$

Then the filling of states ends quite abruptly at the Fermi energy, with a transition region of only parts in 10^{-3}.



In general, if the Fermi energy in a solid is such that we have a partially filled band, that solid will be a metal with good conductivity. In a real metal, there will be some finite resistance induced by the scattering of electrons from lattice vibrations, from other out-of-place electrons, and from lattice imperfections.