Computational Nanoscience
NSE C242 & Phys C203
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Lecture Eighteen and One Half:

A little more, and lots of repetition, on solids.

Date: Timeless

Jeffrey C. Grossman

Elif Ertekin

Solids

A number of approaches are used for studying solid systems.

We'll discuss a couple of these here, for example, the band theory approach vs. the free-electron model.

Band Theory
- Atomic orbitals are combined to give the equivalent of molecular orbitals.
- Based on the assumption that the effect of orbital overlap is to modulate but not change completely the initial atomic levels.
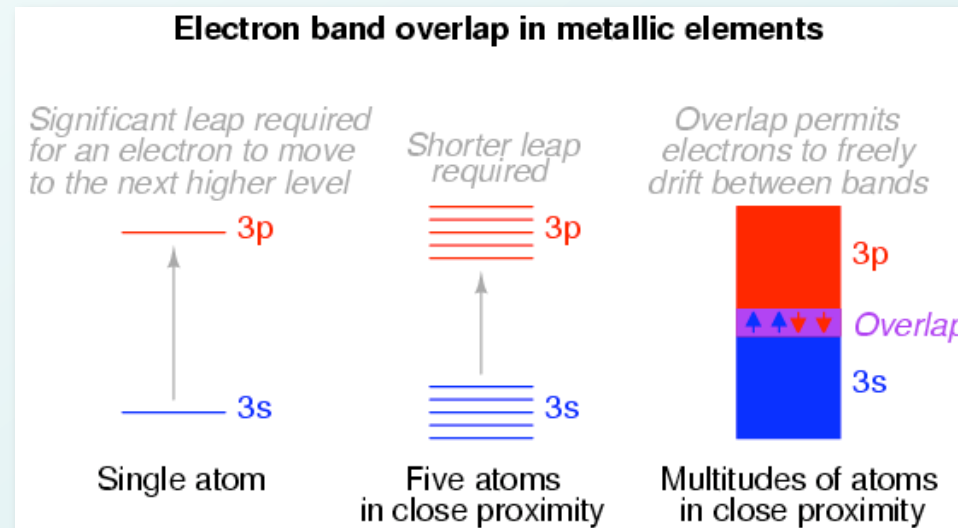- Good approach for insulators and transition metals

Nearly Free-Electron Theory
- Electrons are free particles whose motion is modulated by the presence of a lattice
- Good for metals where there is large overlap among valence orbitals

Band Theory

Band theory begins from an atomic orbital picture.

If we start from a single atom and then add more and more, the energy levels merge to give what is essentially a continuous band of energy levels.

Electron band overlap in metallic elements

Significant leap required for an electron to move to the next higher level — 3p — 3s — Single atom

Shorter leap required — 3p — 3s — Five atoms in close proximity

Overlap permits electrons to freely drift between bands — 3p — *Overlap* — 3s — Multitudes of atoms in close proximity

http://www.allaboutcircuits.com/vol_3/chpt_2/3.html

An even simpler way to get a metal is to start with atom species that only have 1 valence electron, say Na. Then the band is by default half-filled and the electrons are very mobile (easy to excite, etc).

Metal, Semiconductor, Insulator

The energy gap E_g between the conduction band and the valence band (LUMO and HOMO in a molecule) determines whether the system is a metal, semiconductor, or insulator.

In metals, E_g is zero, and a significant amount of electrons are thermally excited into empty levels.

In semiconductors, E_g is small, typically on the order of $k_B T$, so that excitation between bands can take place at room temperature.

In insulators, E_g is large so exciting an electron from the valence to conduction band requires considerable energy.

http://www.chemistry.adelaide.edu.au/external/soc-rel/content/bands.htm
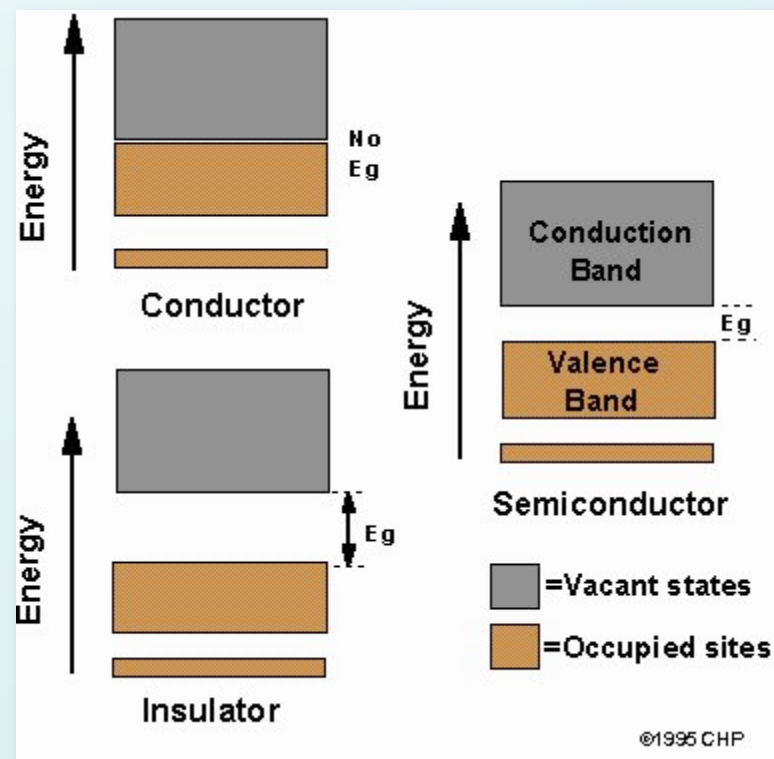
Periodicity

The periodicity of the lattice in a solid means that the values of a function (e.g., density) will be identical at equivalent points on the lattice.

The wavefunction, on the other hand, is periodic but only when multiplied by a phase factor.

This is known as Bloch's theorem. For a 1-D periodic system with a lattice constant of a, it reads:

$$\varphi^k(x + a) = e^{ika}\varphi^k(x)$$

The label k for the wavefunction can be considered an index.

There are as many values of k as there are atoms in the lattice.

By the way, what are we talking about?

Let's take a step back.

Lattices

The first thing one must do for a solid system is to define the unit cell.

This is nothing more than our usual periodic boundary conditions. However, thus far we have stuck with a simple cubic unit cell.

Now that we're discussing solids, we need to have a little more freedom in how we define it.

The simplest way is to define the unit cell as a parallelepiped that is characterized by three vectors **a**, **b**, **c**, and the angles between them.

There are 14 different types of basic unit cells, called *Bravais* lattices.

The lattice itself can have a particular symmetry (i.e., cubic), and the atoms within the cell can have some symmetry as well.

The combination of symmetry elements in the crystal is known as the space group. (There are 230 different space groups).

Bravais

The most common Bravais lattices are the cubic ones (simple, body-centered, and face-centered) plus the hexagonal close-packed arrangement.

These are the most common simply because so many crystalline materials in nature fall into one of these kinds of lattices.

Why are these lattices named after Auguste Bravais (1811-1863)?

Cubic   BCC   FCC

Tetragonal

Orthorhombic systems

Rhombohedral systems

Monoclinic   Triclinic
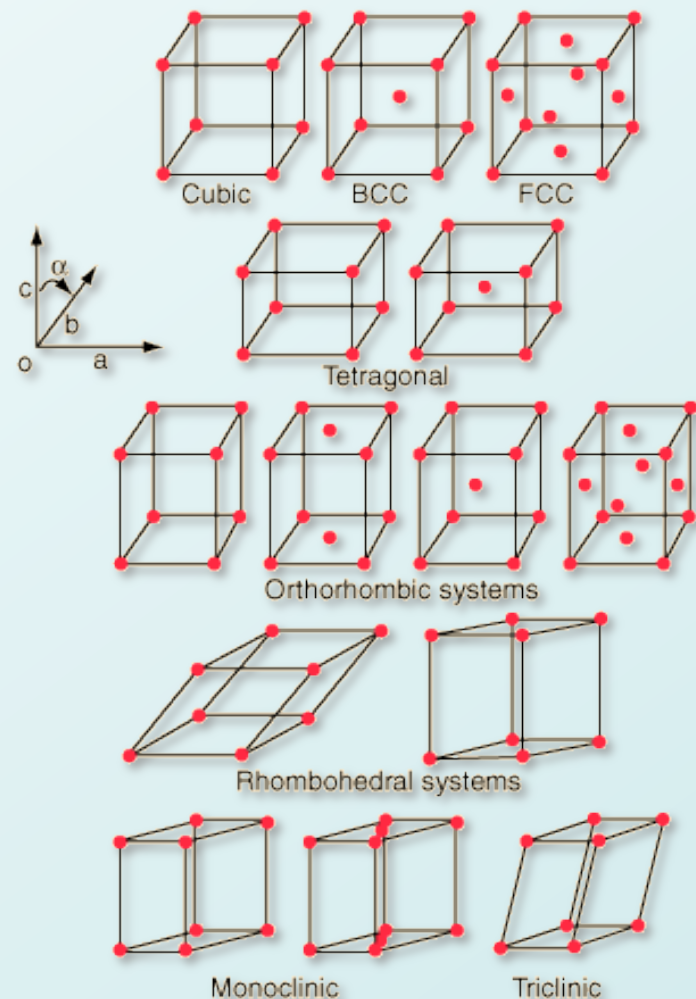
Reciprocal Lattice

The reciprocal lattice is defined by a set of vectors **a***, **b***, and **c*** such that **a*** is perpendicular to **b** and **c** of the Bravais lattice, and the product **a* x a** is 1.

In particular, $\mathbf{a}^* = \dfrac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$

And **b*** and **c*** are defined in a similar manner.

Note that the denominator in each case is equal to the volume of the unit cell.

Also, note the units.

The units being 1/length gives rise to the term "reciprocal lattice" or "reciprocal space".

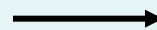These are the vectors used in x-ray crystallography.

The reciprocal lattice vectors, often called **G**, define a unit cell in reciprocal space known as the primitive cell or the "Wigner-Seitz" cell or the "1st Brillouin zone".

Brillouin

Leon Billouin (1854-1948) - another French dude - studied the close packing of structures in reciprocal space.
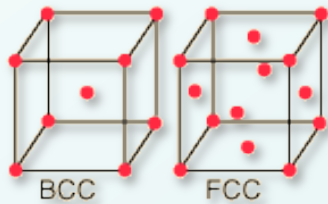
$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}$$
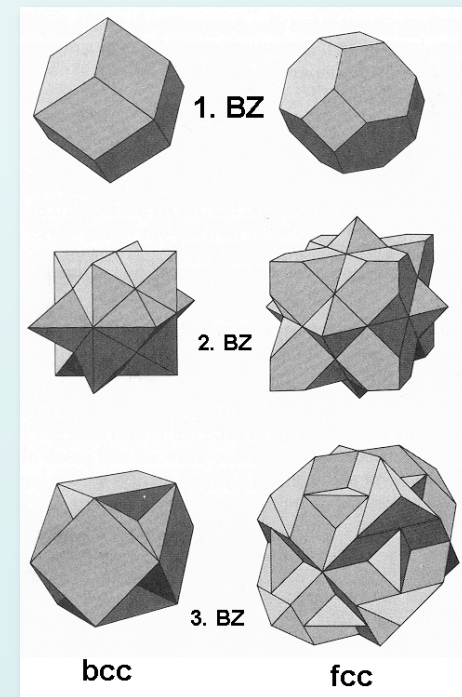
Bragg

If a wave impinges on a crystal - regardless of whether it is an **X**-ray, an electron, or neutron "wave" - its reflection must obey the Bragg condition.

This means that the wave will be reflected at a particular set of lattice "planes" characterized by its reciprocal lattice vector *G only* if the **Bragg condition** is met. (Derived by Sir W.H. Bragg and his son Sir W.L. Bragg in 1913).

Let the wave vector of the incoming wave be *k*, the wave vector of the reflected wave is *k′*.

The Bragg condition correlates the three vectors involved - *k*, *k′*, and *g* - in the *simplest possible form*: *k* - *k′* = *g*

If the Bragg condition is not met, then the incoming wave just moves through the crystal and emerges on the other side.

Both father and son Bragg won the Nobel prize in 1915 for their condition.
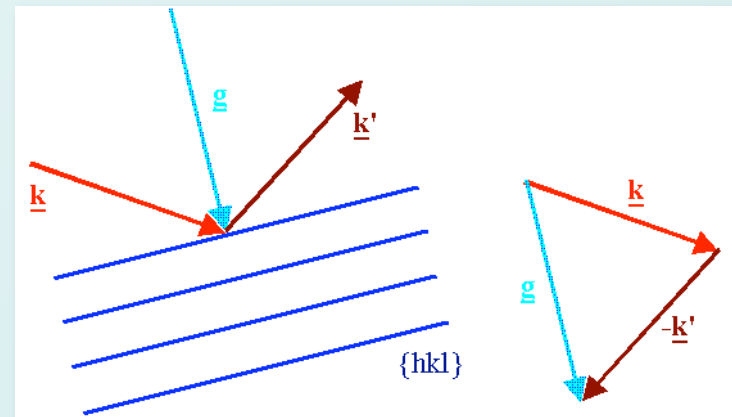
Reciprocal Lattice Vectors

Reciprocal lattice vectors have some special properties that are of particular value for solid-state electronic structure calculations.

Remember that we usually write the reciprocal lattice vector as:

$$\mathbf{G} = 2\pi n\mathbf{a}^* + 2\pi m\mathbf{c}^* + 2\pi o\mathbf{c}^*$$

We added the 2π simply for convenience, and the *n*, *m*, *o*, are integers.

Now consider the behavior of the function exp(*i***G·r**):

$$\exp(i\mathbf{G}\cdot\mathbf{r}) = \exp\left[i(2\pi n\mathbf{a}^* + 2\pi m\mathbf{c}^* + 2\pi o\mathbf{c}^*)\cdot(\alpha\mathbf{a} + \beta\mathbf{b} + \gamma\mathbf{c})\right]$$

$$= \exp\left[i(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)\right]$$

$$= \cos(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma) + i\sin(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)$$

Reciprocal Lattice Vectors

$$\exp(i\mathbf{G} \cdot \mathbf{r}) = \cos(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma) + i\sin(2\pi n\alpha + 2\pi m\beta + 2\pi o\gamma)$$

As **r** is varied, the coefficients of the lattice vectors (α, β, γ) change between 0 and 1 and the value of the function exp(*i***G·r**) changes too.

However, since *n, m,* and *o* are integral, the function exp(*i***G·r**) will always vary with the periodicity of the real-space lattice.

A couple of interesting observations of this function:

1) If we were to write a function as a Fourier series of terms from exp(*i***G·r**) the resulting series will be periodic on the real lattice.

2) These are called planewaves.

3) Such exponential functions represent wavefunctions for a free particle.

Periodicity

Ok, now where were we?

Yes, Bloch's theorem.

For a 1-D periodic system with a lattice constant of a, it reads:

$$\varphi^k(x + a) = e^{ika}\varphi^k(x)$$

Any overall wavefunction we come up with for our solid should meet the Bloch requirement.

Suppose we have a certain type of orbital in our lattice, labelled χ_n where the nth orbital is located at position x=na.

Then a linear combination of these orbitals that also satisfies Bloch's theorem would be:

$$\varphi^k = \sum_n e^{ikna}\chi_n$$

Periodicity and Bloch's Theorem

$$\varphi^k = \sum_n e^{ikna} \chi_n$$

At k=0, we would have:

$$\varphi^{k=0} = \sum_n \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + L$$

At k=π/a, all the sine terms (imaginary ones) would be zero, and we'd have cosine terms that can be expressed as $(-1)^n$:

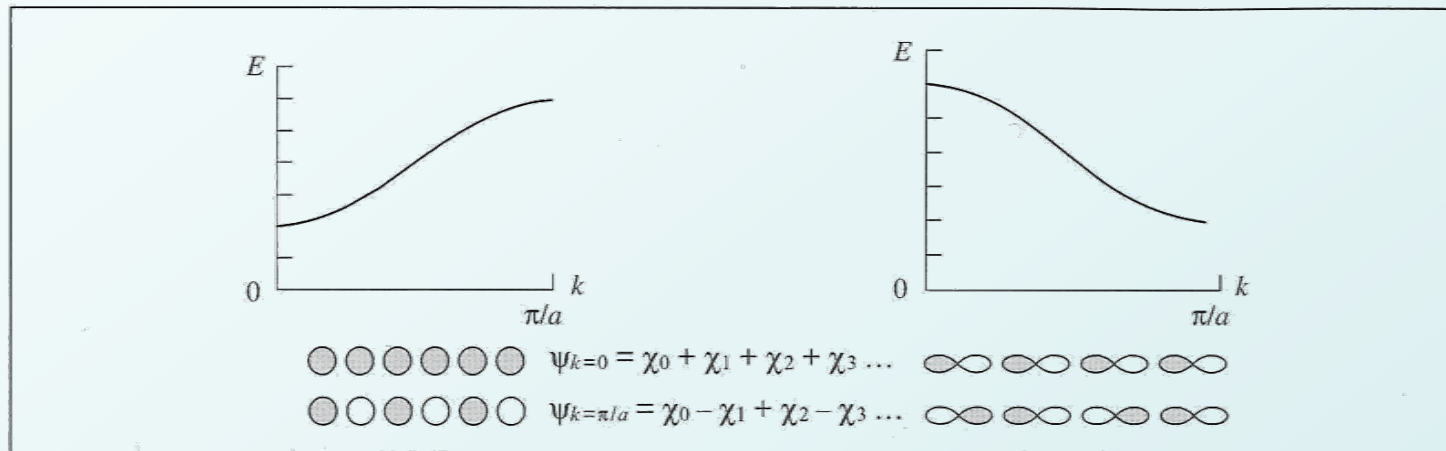$$\varphi^{k=\pi/a} = \sum_n (-1)^n \chi_n = \chi_0 - \chi_1 + \chi_2 - \chi_3 + L$$

These limits - k= 0 and k=π/a - correspond to the lowest and highest-energy wavefunctions.

The energy varies in a cosine-like manner in between.

Band Structure

The graph of energy versus k is called the band structure.

This variation in energy depends on the type of orbital that was used to construct the wavefunction.

For a 1-D lattice, as in this example, the bandwidth (difference in energy between the highest and lowest levels in the band) is determined by the distance between the atoms.

Band Structure
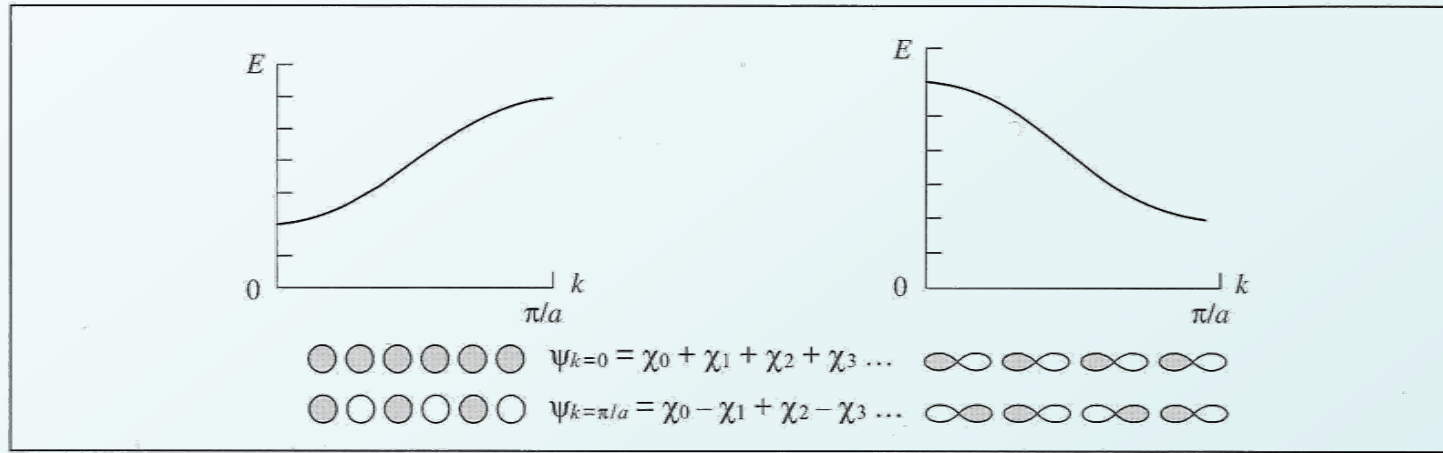
As we increase the number of dimensions, the band structure becomes more and more complex.

Note that for more than 1 dimension, **k** becomes a vector, known as the wavevector (having components k_x, k_y, for example in 2-D).

In calculations of solids, we restrict the values of k to one cell in the reciprocal space - usually in the 1st Brillouin zone.

Band Structure

Then, energy is usually plotted as a function of **k** along certain lines of symmetry within the first Brillouin zone.

For example, here is a band structure for a 2-D square lattice of hydrogen atoms.
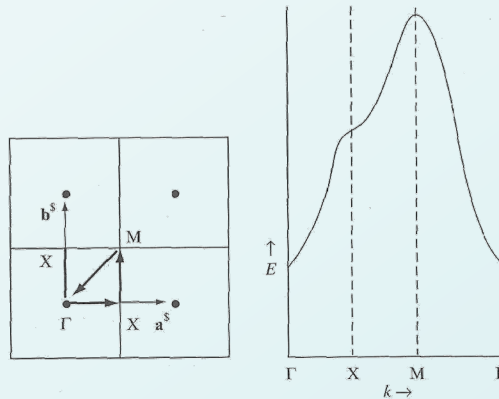
In this case, we took a "tour" of reciprocal space by varying **k** from (0,0) to (π /a, 0) to (π/a, π/a) and then back to (0,0).

Along the way, the energy changes and that is what is plotted in a band structure. Greek symbols are used to show certain high-symmetry points of **k**.

Band Structure

In 3-D the Brillouin zones are more complicated, but the idea is the same.

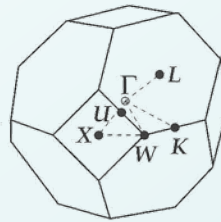For example, here is the band structure for silicon in the diamond structure.
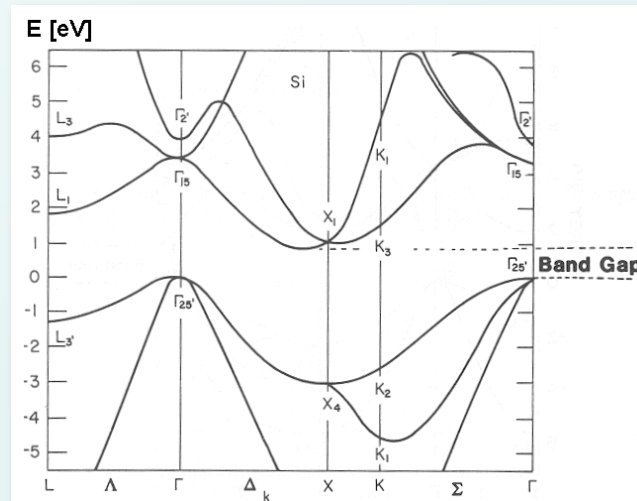
Some interesting things to note:
- There is a lot of information in these kinds of plots.
- The band gap can be either direct or indirect.

Nearly Free-electron Approximation
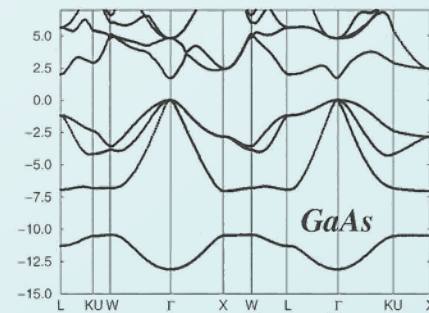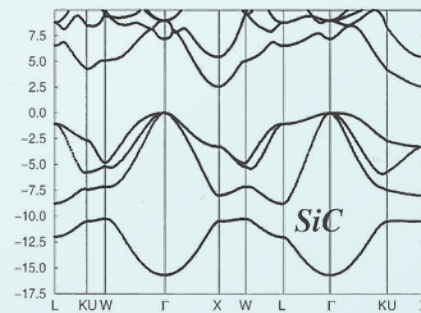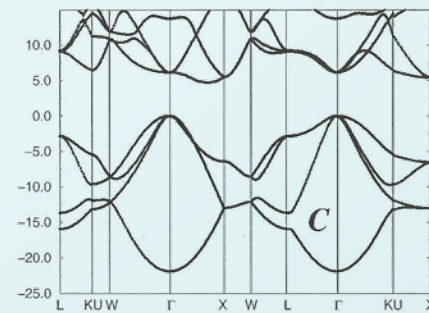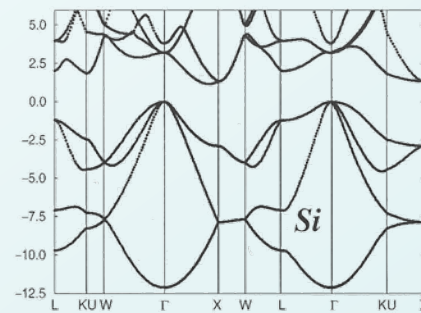
Here are some more band structures*

$X = (1,0,0)$
$L = (0.5, 0.5, 0.5)$
$K = (0.75, 0.75, 0)$
$W = (1, 0.5, 0)$
$U = (1, 0.25, 0.25)$

*Atomic and Electronic Structure of Solids, E. Kaxiras, Cambridge University Press (2003).

Nearly Free-electron Approximation

For some systems, it is more useful to consider the valence electrons as free particles whose motion is modulated by the presence of the lattice.

In this case, we start from the Schrodinger equation for a free particle in 1-D infitely large box:

$$\frac{d^2}{dx^2}\psi = -\left(\frac{2mE}{h^2}\right)\psi$$

Solutions to this equation look like:

$$\psi = C\exp(ikx)$$

$$E = (h^2 k^2)/2m$$

And energy is related to momentum, so one could write:

$$\psi = C\exp(\pm ipx/h)$$

Note that the parameter k has units of reciprocal length.

Nearly Free-electron Approximation

When we consider a periodic system as opposed to an infinite box, what changes?

The wavefunction must now satisfy Bloch's theorem.

Remember the wavevector **k** from Bloch's theorem? It plays the same role here, with one important difference.

For a free particle the wave vector is directly related to the momentum, **k=p**/(hbar).

This not the case for a "Bloch particle" due to the presence of the external potential (i.e., the nuclei).

However, it is convenient to consider (hbar)**k** as analogous to the momentum and it is often referred to as the crystal momentum.

Nearly Free-electron Approximation

Remember that the wave vector **k** in Bloch's theorem can be considered as a point in reciprocal space defined by the reciprocal lattice vectors.

A wavefunction is usually written in the following form:

$$\psi^k(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u^k(\mathbf{r})$$

Where u(r) is a function that is periodic on the lattice.

Also remember that we can construct a periodic function as a Fourier series expansion of plane waves:

$$u^k(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}}^k \exp(i\mathbf{G} \cdot \mathbf{r})$$

In a simple example, **G**=one of the reciprocal lattice vectors, say **a**.

Then, the exponent corresponds to a wave traveling perpendicular to the real-space axes of **b** and **c** with a wavelength that just fits in the unit cell.

Nearly Free-electron Approximation

One can also introduce an external potential (i.e., the crystal lattice):

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$$

When this form of potential is incorporated into the Schrodinger equation, one can derive the following equation*

$$\left(\frac{h^2}{2m} |\mathbf{k} + \mathbf{G}|^2 - E \right) c_{\mathbf{G}}^{k} + \sum_{\mathbf{G}'} U_{\mathbf{G}' + \mathbf{G}} c_{\mathbf{G}'}^{k} = 0$$

In the free-particle limit, setting all Fourier coefficients of U to zero, we recover the wavefunction and energies of a free particle.

Each equation for a given value of **k** can be written for a different **G** which gives rise to a solution - labeled with a band index *n*.

There are as many values of *n* as there are reciprocal lattice vectors **G**.

* See, e.g., Ashcroft and Mermin

Nearly Free-electron Approximation

The band structure of a solid is then simply an understanding of the variation in both *n* and **k**.
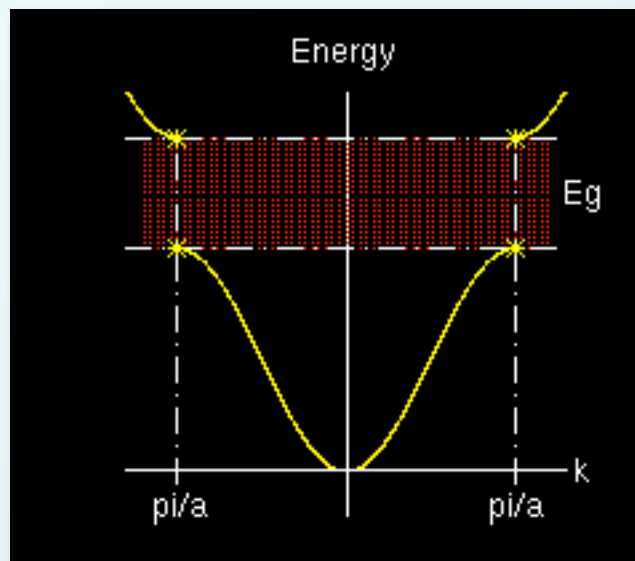
To derive the energy diagram, we start with a reciprocal lattice vector **G**, and vary k over the first Brillouin zone.

Nearly Free-electron Approximation

For a free particle in 1-D, the energy varies as a function of k, as we have described:
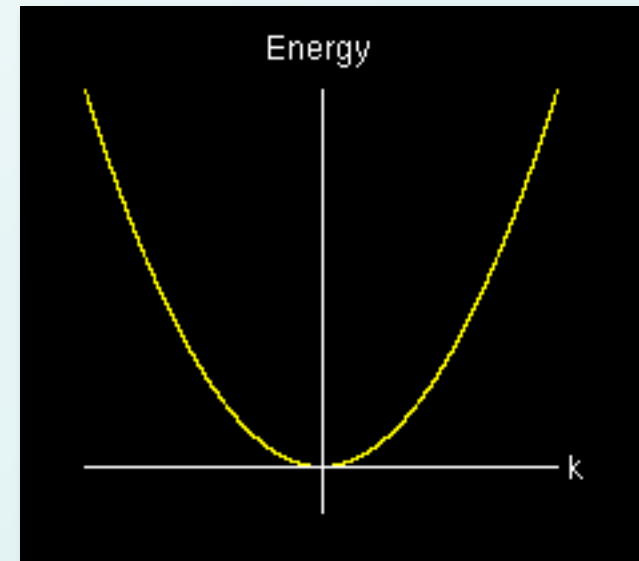
And yet, as soon as we "turn on" the potential of the crystal lattice, gaps open up:

Gavi, why is this the case?

Nearly Free-electron Approximation

Yes, it is indeed because, even in simple 1-D lattice there is a degeneracy due to different reciprocal lattice vectors at k=0 and k=π/a.

But, Gavi, why does the potential perturb these energy levels in such a way to lift the degeneracy and create a gap?

That's right! The Bragg reflection.
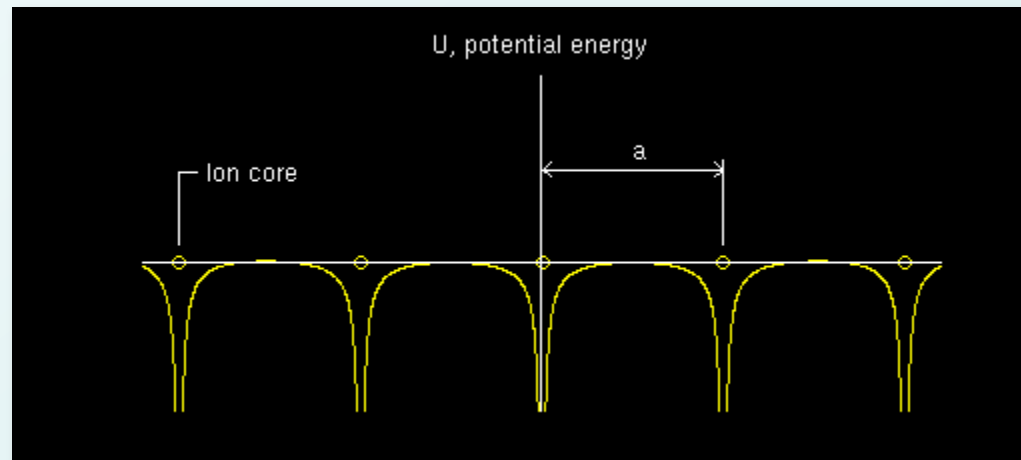
The Bragg condition for this system states that wavelike solutions to the Schrodinger equation do not exist for k=0 and k=π/a.

Nearly Free-electron Approximation

The energy gap is associated with the fact that at the Brillouin zone boundaries, a wave in the crystal is a standing wave.

And now the degeneracy comes into play, since we have two possible standing waves:
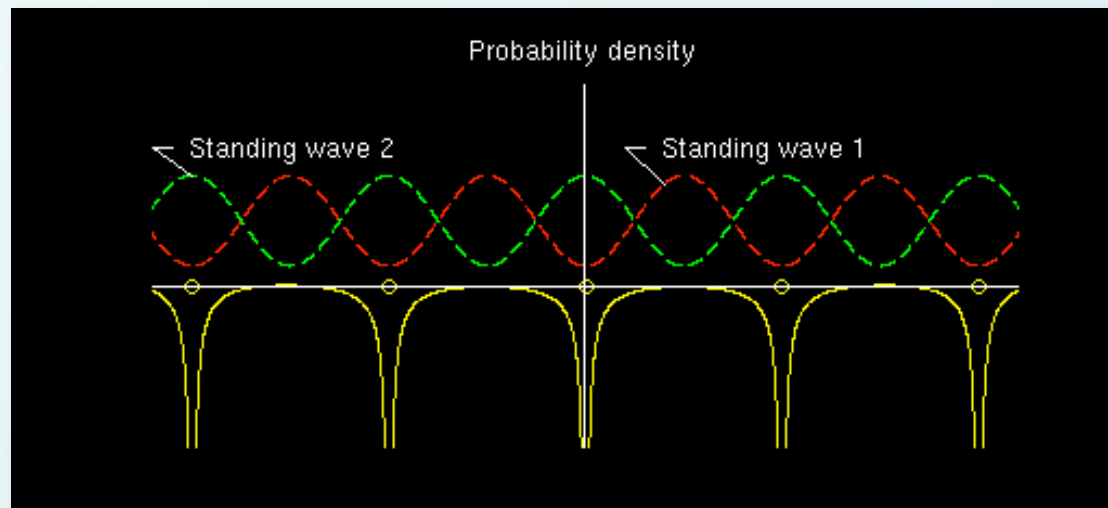
One standing wave piles electrons on the ions and the other in between. These have different energies, which creates the gap.

Nearly Free-electron Approximation

Now the Schrodinger equation is solved in the presence of the lattice, and we obtain the band structure.

There are different ways to view the same information, for example in the extended or reduced zone scheme: