Computational Nanoscience

NSE C242 & Phys C203
Spring, 2008

Lecture 19:

Solids: Band Structure, Density of States, & In-Class Simulation

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Updates

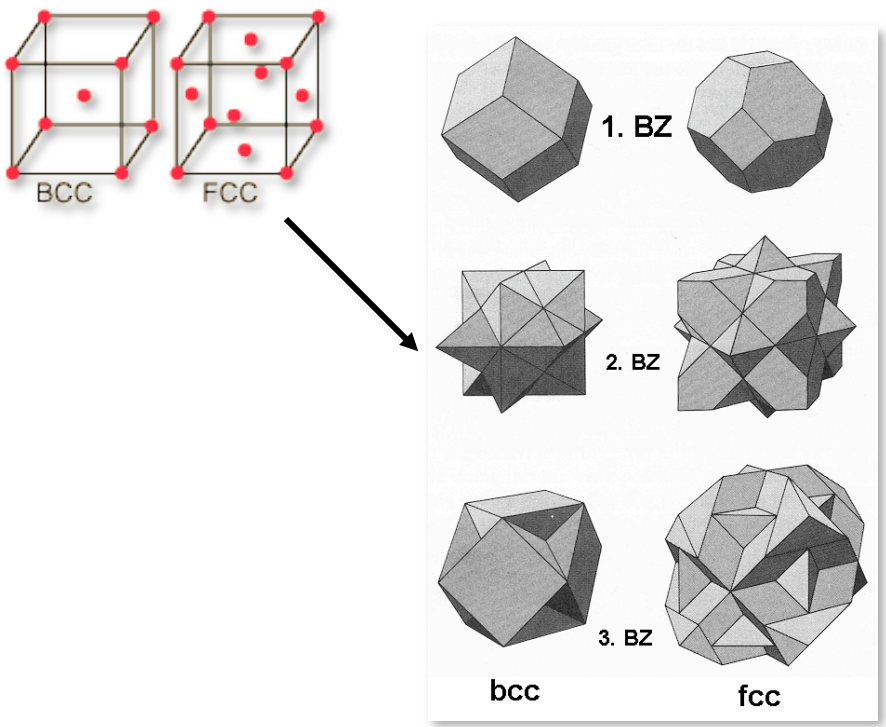
Homework Assignment: Hartree-Fock and DFT on molecules via GAMESS and SIESTA. Due: April 10th

Class Projects: Abstract/Proposal for your class project is due on April 10th. (one or two paragraphs)

From last time: Brillouin Zone, Bloch Theorem

Associated with each real space lattice {R}, there exists a reciprocal lattice {G}.

The Wigner-Seitz cell of the reciprocal lattice is the first Brillouin zone.



According to Bloch's theorem, on a periodic lattice, the wavefunction must satisfy.

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

Bloch's theorem is satisfied by a linear combination of planewaves, in which we write:

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

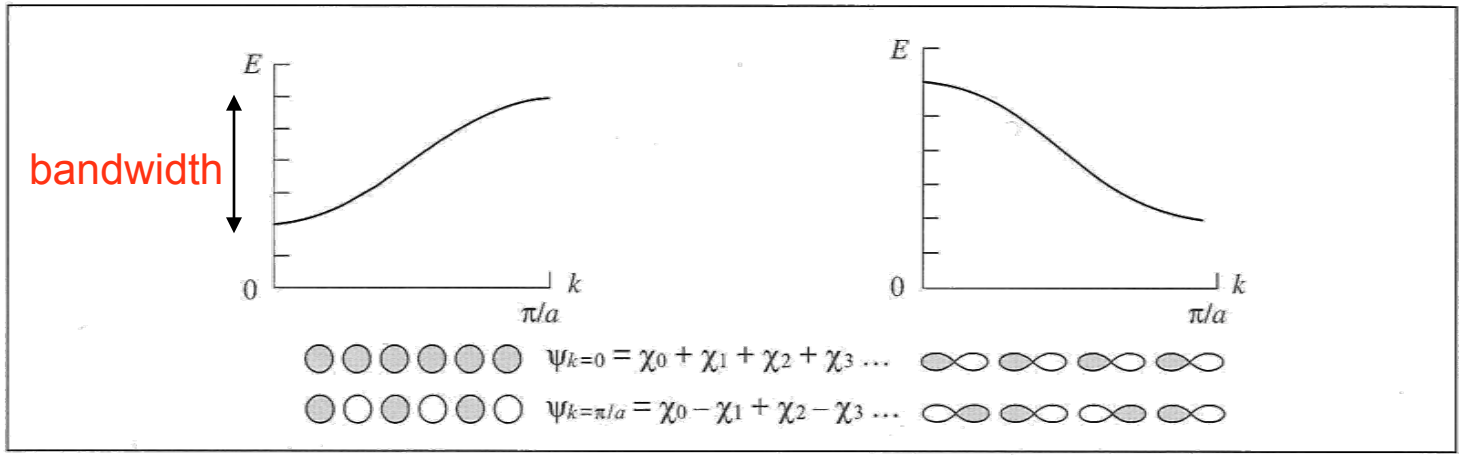
$$\varphi^{k=0} = \sum_n \chi_n = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \mathrm{L}$$

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

"k" can be thought of as an index for all the states. All values of k yielding distinct states lie within the first BZ.

Band Structure

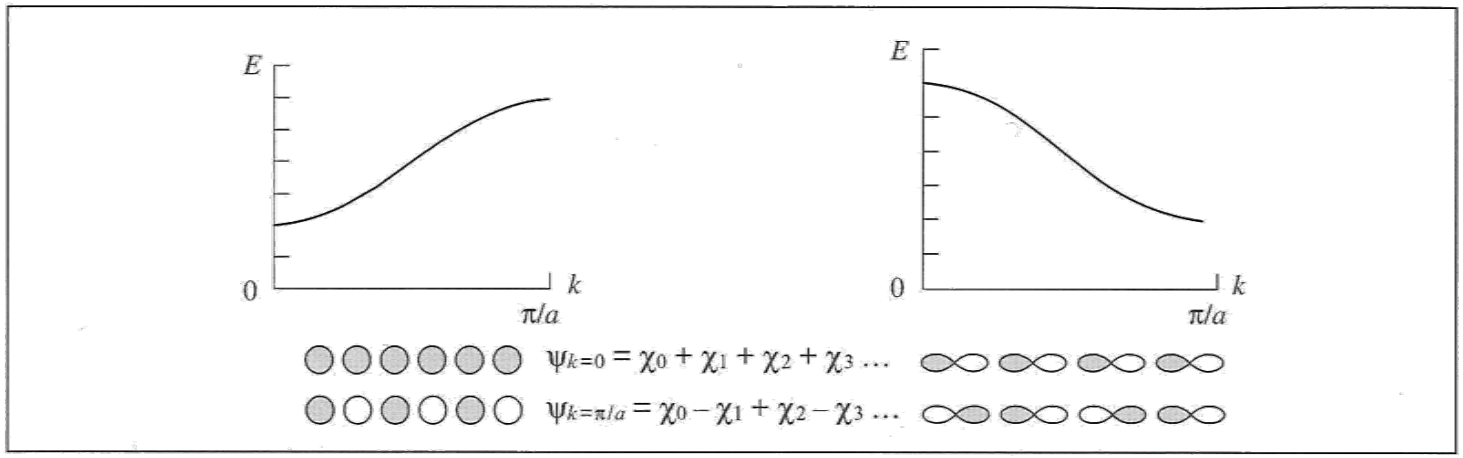
The graph of energy versus k is called the band structure.



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



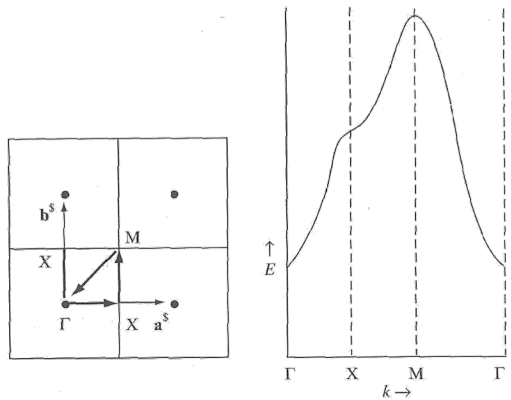
As we increase the number of dimensions, the band structure becomes more and more complex.

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).

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.



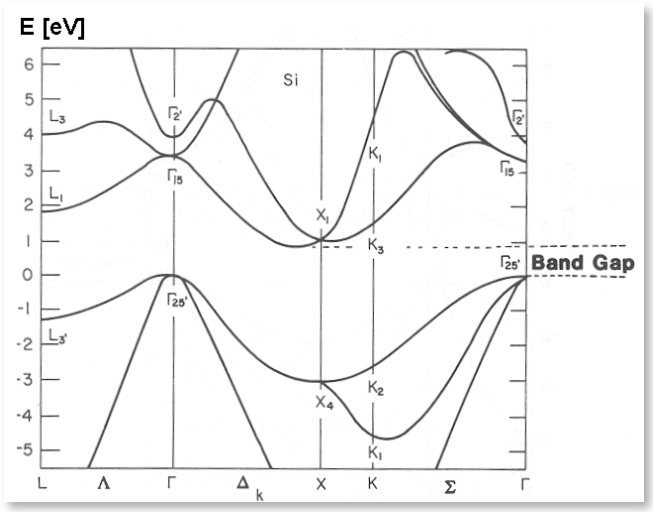
In this case, we took a "tour" of reciprocal space by varying **k** from (0,0) to (π /a, 0) to (π/a, π/a) and then back to (0,0).

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.

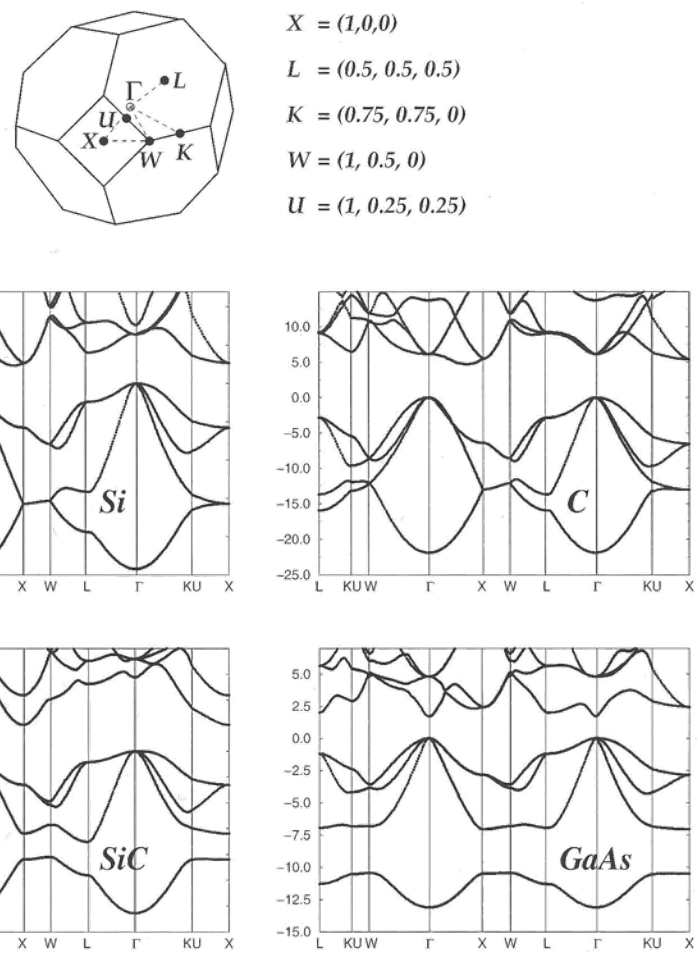


Some interesting things to note:

- There is a lot of information in these kinds of plots.
- The band gap can be either direct or indirect.

Bandstructure for Common Semiconductors

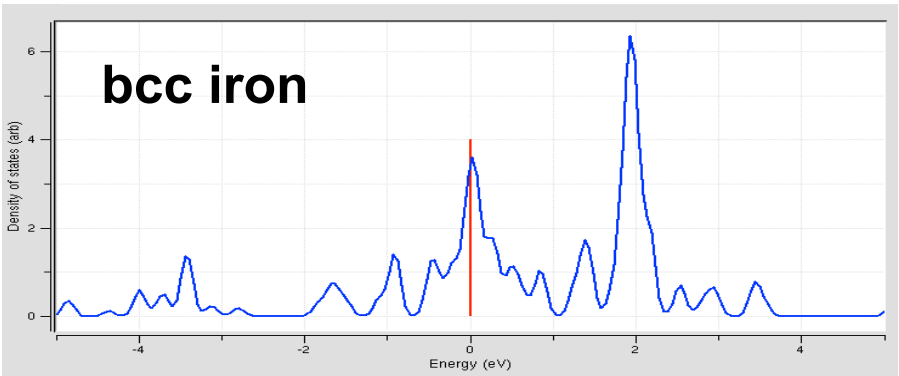
Here are some more band structures*

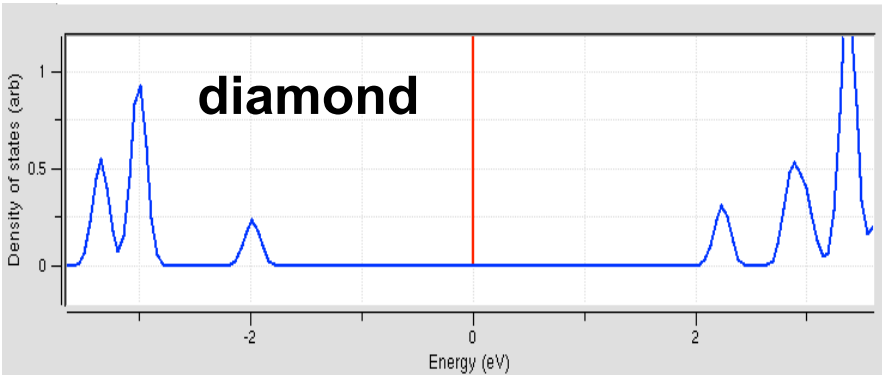


*Atomic and Electronic Structure of Solids, E. Kaxiras, Cambridge University Press (2003).

Density of States

- The “density of states” is a measure of the number of states in a given energy interval that are available to be occupied.
- The density of states can be computed from the band structure.
- Here are some examples for metals and semi-conductors:





In-Class Simulation: Task 1

Structure Optimization for Semi-conductors

- Optimize the bulk silicon (diamond structure) within both LDA and GGA, choosing two basis sets for each.
- How many k-points are needed for convergence for these runs?
- Now, choose a basis set and an xc functional. Make a plot of cohesive energy vs. lattice constant for both bulk Si and bulk C in diamond structure. (You will need to vary the lattice constant now.)
- Use these plots to compute the bulk modulus for these two materials. Compare your result to experiment.

In-Class Simulation: Task 2

Structure Optimization for Rocksalt

- Now, choose NaCl and optimize the structure using a basis and xc functional of your choice.
- Shift one of the atoms in the unit cell from it's equilibrium position, and optimize again. Look at the plots showing the energy at each atomic iteration.
- Does the energy converge properly (and the atom move back to the right position) over the course of the run?

In-Class Simulation: Task 3

Structure Optimization for Metals

- Pick a basis and optimize the fcc and bcc iron structures in both LDA and GGA.
- For metals, how many k-points are needed for convergence compared to semiconductors?
- Does LDA or GGA get the ground state right?

In-Class Simulation: Task 4

Band Structure and Density of States

- Find the band structure and the density of states for C, Si, Ge, GaAs.
- Compare the band gap to experiment.
- Which are direct/indirect?

- Choose bcc iron, but make the lattice constant large enough so that the atoms do not interact. Plot the density of states and identify the peaks.
- Now, start slowly shrinking the lattice constant step by step. Observe how the density of state changes as the atoms get closer together. What happens to the peaks? Which electrons are responsible for bonding?