MATRL 218/CHEM 277: Class 9 — More on electronic structure

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- In traditional solid state physics treatments (Kittel), we are taught that band gaps arise due to translational periodicity, that there is Bragg reflection of free electrons at the edges of the Brillouin zone and this open up gaps. In 1D, the free electron wavefunction is:

  $$\psi_k(x) = \exp(ik \cdot x)$$

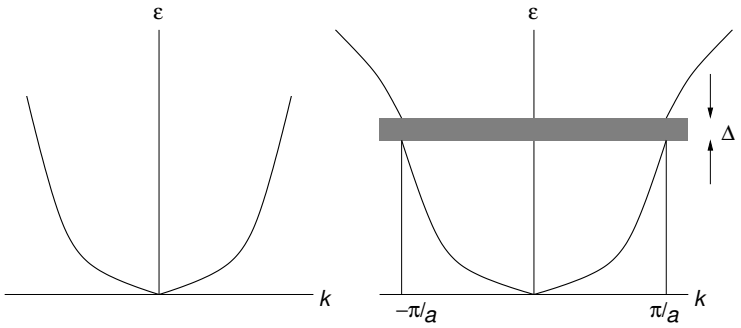
  These are plane wave solutions to the free electron Schrödinger equation. The energy and momentum are given by:

  $$\epsilon_k = \frac{\hbar^2}{2m}k^2; \;\; p = \hbar k$$

  Instead of a free electron in 1D, consider a 1D lattice with lattice constant a. The Bragg condition for diffraction by waves of wavevector k is $(k + G)^2 = k^2$ where G is the reciprocal lattice vector, and $G = 2\pi n/a$ for the 1D lattice where n is some integer. Therefore, the Bragg condition solves to

  $$k = \pm\frac{1}{2}G = \pm n\pi/a$$

  The first reflections and therefore, the first energy gaps occur at $k = \pm\pi/a$.



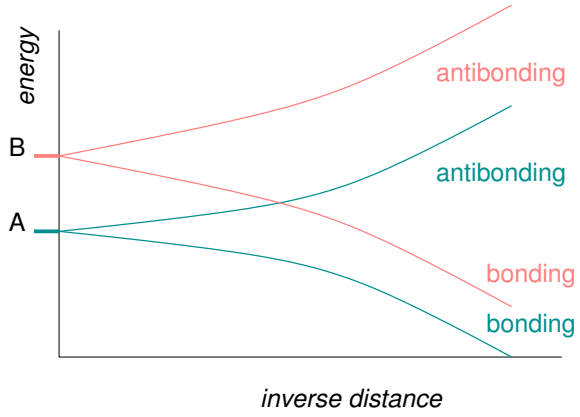
  On the left is a sketch of the free electron wave function and on the right is a sketch of the effect of imposing a lattice on the free electron wave function with lattice parameter a.[1] At the k points $k = \pm\pi/a$, an energy gap Δ opens up.

  The second allowed band starts after the first one gives up. The second band is in the *second* Brillouin zone.

- Such a description is limited in its applicability. What about a defect, a surface or an amorphous material that would not have translational periodicity, and therefore would not have Bragg reflection of electrons ? We know that such materials do have band gaps (window glass !) The solution is to look at real-space pictures and return to tight-binding models.

- For the real space description, consider two energy levels, on two different orbitals A and B. When the orbitals are far apart, the energy levels are at the atomic limit. When they approach, bonding and antibonding combinations form, splitting the two levels. The bonding energy level is the bottom of that particular DOS, and the antibonding level, the top.

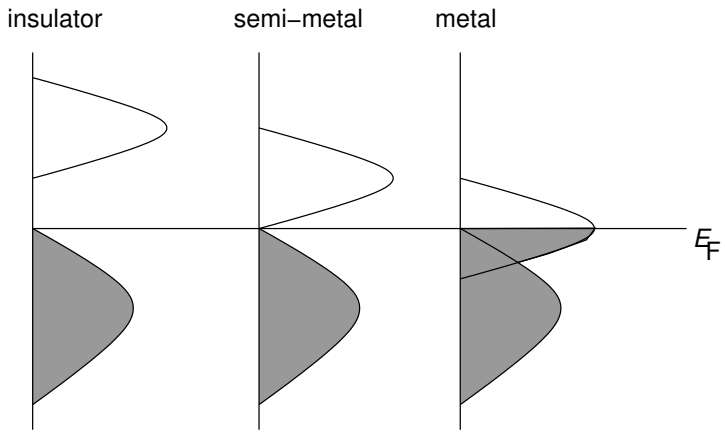
[1] This is referred to as the nearly free electron model. Note its resemblance to the kinds of dispersion relations we derived for s orbital bands.



Notice how the levels broaden. Somewhere in-between, there is some dispersion of the individual states, but there is still a gap. When the atoms approach very close, the gap vanishes.

Such a picture is physically quite realistic. Many semiconductors (which have a gap) become metallic on being subject to hydrostatic pressure.

- When states in a crystal are filled up, the rules are the same as what is required for filling up atomic orbital states. Start with the lowest energies, and pay heed to Pauli's exclusion principle. The exclusion principle says that no band can have more than two electrons.

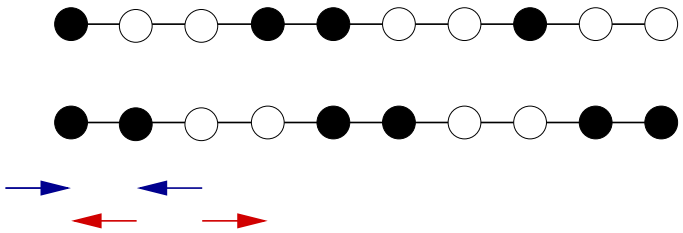


Electrons in filled bands do not carry a current because they cannot move without violating Pauli's exclusion principle. If they do move, their motion must be compensated by the motion of a hole in the same direction, or of an electron in the opposite direction.

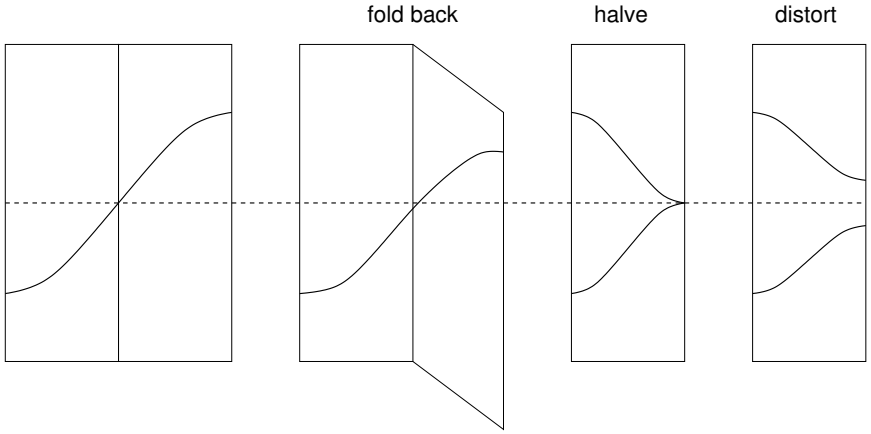
- The Peierls distortion:

  1D Lattices with 1/2-filled (and indeed, $1/n$ filled bands) susceptible to distort in a special way that permits opening of a gap at the Fermi energy. This is called the Peierls distortion. Polyacetylene is a typical 1D system that undergoes such a distortion, as first suggested by Salem and Longuet-Higgins.

  The simple, tight-binding picture of such a gap opening up can be obtained by considering crystal orbitals formed from a 1D lattice of s orbitals. At the center of the band, the number of bonds equals the number of antibonds. Two kinds of crystal orbitals can be envisioned, which are degenerate in energy:

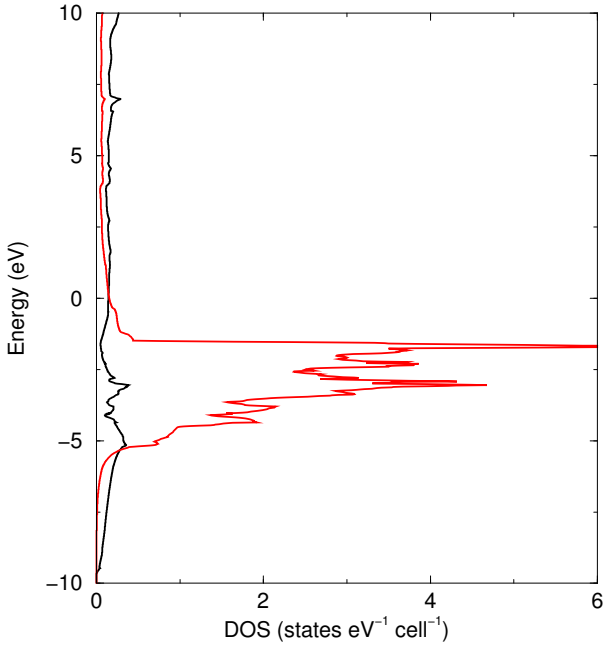


If the lattice is alternately contracted and expanded as shown using the blue and red arrows, the cell parameter becomes $2a$ instead of a. This means that the X point is now at $k = \pi/2a$. The doubling of the cell in real space corresponds to halving in k space. Also the bands are no longer disperse. The scheme below is the opening of a gap as a result:

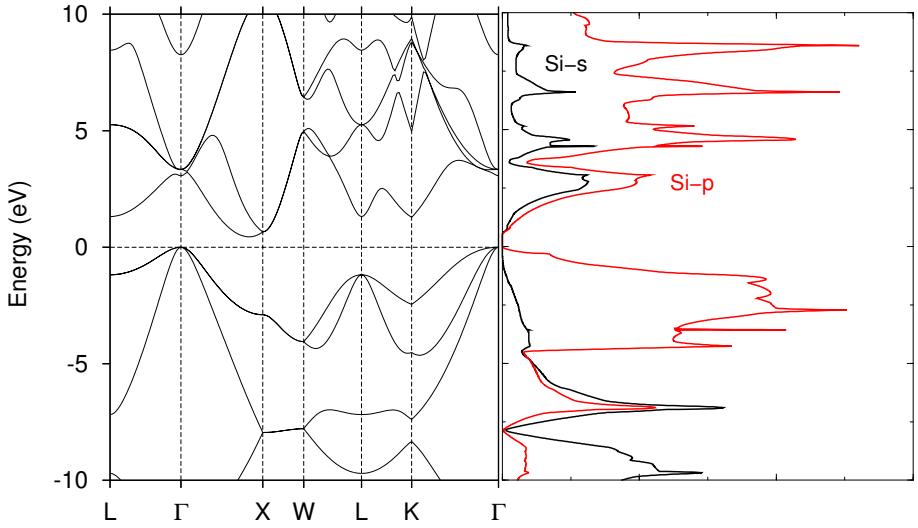


The dotted line is the Fermi energy. The Peierls distortion is an example of symmetry-breaking lifting a degeneracy. The Jahn-Teller distortion in d orbital solids is another such example.

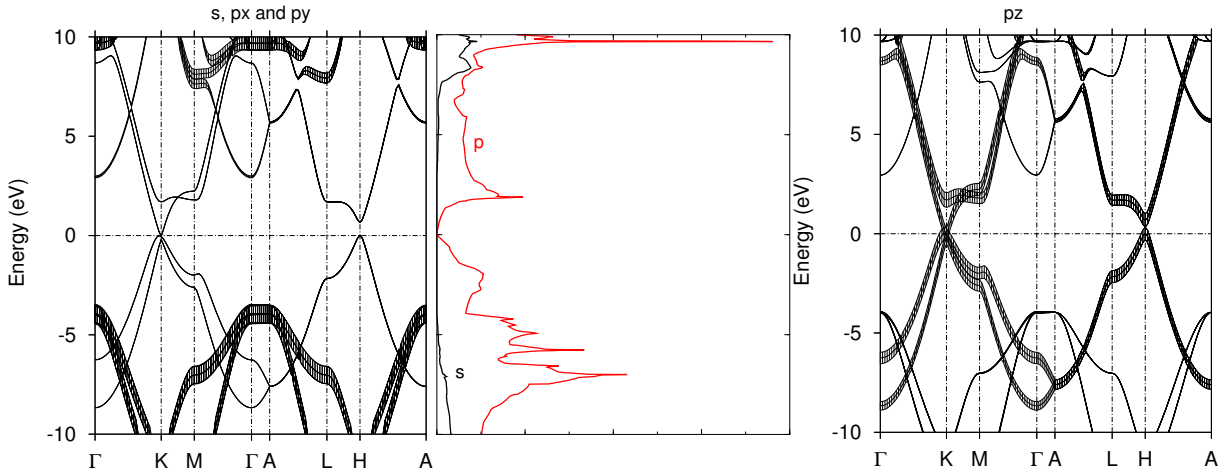
- Some examples of "real" electronic structures: Cu metal:



- Si:



- C (graphite):



- Screening in metals.

  In a good metal, the density of electrons is very high – of the order of 10^{22} cm^{-3}. These electrons should *repel* strongly. We recollect that hard spheres crystallize, and that repulsive interactions are sufficient for this. It is therefore surprising that electrons *do not* crystallize in metals. If they did crystallize, they would stop moving and the metal would no longer conduct.

  The answer to this is that paradoxically, when the concentration of electrons is high, the electrons form a sea of negative charge that actually prevent one electron from seeing another. The formula for such *screening* in a crystal is the so-called Thomas-Fermi formula for the screened Coulomb potential (Kittel):[2]

$$\varphi(r) = \frac{q}{r}\exp(-k_s r)$$

  where q is the charge and r is the distance. The wavevector k_s defines the screening length $1/k_s$. k_s is a function of the DOS at the Fermi energy:

$$k_s^2 = 4\pi e^2 D(E_{\mathrm{F}})$$

[2]Note the similarity with the repulsive part of the DLVO potential for colloids.

where e is the charge on an electron. When the density of states at the Fermi energy $D(E_{\mathrm{F}})$ is large (as in a metal), k_s is large and the screening length is small. A small screening length means that electrons have to come very close before they start seeing each others' potential.

- Breakdown of Band theory: Mott insulators:

  Sometimes, we find that systems which should be metallic from considerations of the electron count are in reality, insulating. In such systems, the screening is not effective and electrons start repelling one another. In the simplest model, as atoms move away from one another, the bands become narrow and this weakens screening.

  Examples where such phenomena are observed are dilute solutions of metals in liquid ammonia, the oxide NiO, lightly doped semiconductors *etc.*