

Chem 630, Fall 2006
Problem Set #1
Due in class Friday, Sept. 29

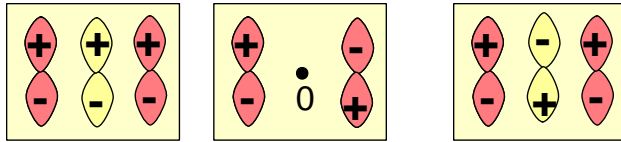
- 1) Diamond has a lattice constant of 3.5668 Angstroms.
- Calculate the number of atoms per unit area created by fracturing along at (111) crystal plane. Only include atoms that have one or more bonds “cut” in the process of forming the surface. You must show all your work to get credit. Express your results in atoms/cm².
 - How many bonds are cut per cm²? (Take the number of atoms/cm² and multiply by the number of bonds/atom that are cut in forming the surface).
 - How many atoms/cm² are exposed at the diamond (100) surface.
 - How many bonds per unit area are cut in forming the (100) surface?
 - Based on the above, which crystal face of diamond is the one most like to be formed by cleaving ?
- 2) Explain why GaAs cleaves along the (110) crystal face, while silicon cleaves along the (111) crystal face.
- 3) In deriving the expressions for atoms-on-a-ring, we made two fundamental assumptions. “a” is the lattice constant, N is the number of atoms in the ring, and “n” is any integer.
- One assumption was that $|\Psi(x + na)|^2 = |\Psi(x)|^2$ where x is any arbitrary position, a is the lattice constant, and n is any integer. What is the physical significance of this statement?
 - A second assumption was $\Psi(x + Na) = \Psi(x)$. What is the physical significance of this statement ?
- 4) Consider a hypothetical compound with a three-atom basis which all three atoms are **nearly** identical. (So, this is the limit of small perturbation from the perfect atoms-in-a-line). This could, for example, be something like FeS₂, in the formFe-S-S-Fe-S-S-Fe-S-S..... in which all the atoms are arranged in a (long) line and in which we assume that the Fe and S atoms are all very similar.



It would also represent a set of alternating single and double bonds in which we had two single bonds and one double bonds arranged as below:



We will pretend we have the FeS₂ problem. Assume that the bond distances are all the same, so that the Fe-S and the S-S distance are both equal to $a_{\text{undistorted}} = 2.0$ Angstroms. This forms a unit cell containing three atoms, or a three-atom basis. As discussed in lecture, this should lead to three bands within the first Brillouin Zone. In the reduced band scheme, these bands can be made up from the three combinations of atomic orbitals shown below, where within each little sub-unit, the Fe atom is in the middle and the S atoms are at the left and right. The three sub-units that can be formed are:



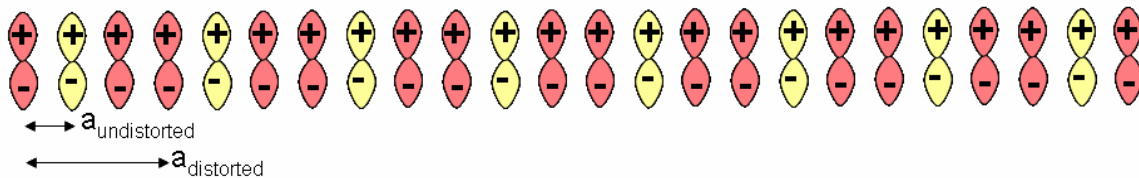
In the second (middle) sub-unit, the “basis” AO in the center has zero density on the center (Fe) atom. In this particular case, each S atom has zero interaction with the central Fe atom, and there is a node exactly in the center of the three-atom sub-unit.

a) Now consider what happens when we form a long line of atoms. Using the three sub-units shown above, explicitly draw what the molecular orbital looks like at $k=0$ and at the Brillouin zone boundary (reduced-zone scheme) for each of the three bands. Remember that you do this by taking the repeating unit, and multiplying it by a sinusoidal function whose wavelength (number of waves/unit length) increases from 0 to some higher number that defines the Brillouin Zone boundary. Remember that in this case you are assuming that the lattice constant is $a_{\text{distorted}} = 3 * a_{\text{undistorted}} = 6.0$ Angstroms. So, you should draw *six* different molecular orbitals.

b) If you assume that the energy changes continuously within each band, you can estimate what the band structure looks like simply by counting the number of nodes in the orbitals. This is easy to do the $k=0$ and at the Brillouin zone boundary. For each of the six MO's you found in part (a), count how many nodes you have per unit cell. Now, just assume that the energy is proportional to the number of nodes, and sketch qualitatively what the band structure should look like for all three bands. Be sure to explicitly label the axes, and to indicate the value k at the Brillouin zone boundary

c) If each atom contributed one electron in its p-orbital, draw where the highest occupied molecular orbital would be on the band diagram. In this case, would it be subject to a Peierls distortion? Explain why or why not.

5) Now look at this same problem in the extended-zone scheme. Again, assume that all bond lengths are almost equal, $a_{\text{undistorted}} = 2.0$ Angstroms



a) Draw the band structure in the “extended-zone” scheme, in which you assume that the periodicity of the unit cell is just $a_{\text{undistorted}}$.

b) Now, show how you can fold the band structure into a smaller Brillouin zone appropriate for a unit cell with a lattice constant of $a_{\text{distorted}} = 3 * a_{\text{undistorted}}$. Be sure to explain exactly what you are doing.

c) Compare your result with that from problem 4.