MS 131, Problem Set #5

revised 11/07/05
due 11/09/05

1. Show that the Bloch function $\psi(r) = u(r)*\exp(ikr)$ leads to a periodic electron density, so long as $u(r)$ is periodic.

2. Consider a one-dimensional solid comprised of A with a uniform interatomic spacing of a.

   (a) Use the LCAO method to show that energy has a cosine dependence on k. Start with the total wave function defined as a linear combination of atomic orbitals. Assume second nearest neighbor and higher interactions are negligible. You need not worry about proper normalization.

   (b) Plot $E(k)$ to the edge of the first Brillioun zone, for both s and p_z orbitals treated in this way.

3. For the 1s orbitals of the atoms of problem 2, draw out $\psi_k(r)$ for $k = 0$, $\frac{1}{4}(2\pi/a)$, $\frac{1}{2}(2\pi/a)$, $\frac{3}{4}(2\pi/a)$, $1(2\pi/a)$ and $2(2\pi/a)$. Superimpose $\cos(kr_n)$ [the real part of $\exp(ikr_n)$] over the plot of $\psi_k(r)$ and clearly indicate the wave length. In addition, carefully compare the plots for $k = 0$ and $k = 2(2\pi/a)$.

4. Consider a one-dimensional solid comprised of A and B atoms, where the atoms alternate and are equally spaced. The lattice constant (distance between A atoms) is a (so the distance between A and B atoms is $\frac{1}{2}\ a$). Let B be somewhat more electronegative than A, and let the relevant local atomic orbitals on the A and B atoms be the s and p_z orbitals, respectively. The total wave function for this situation is a linear combination of the Bloch sum for the χ^A and the Bloch sum for the χ^B:

$$\psi_k^1(r) = a_k \sum_{n=1}^{N} e^{ikr_n} \chi_n^A(r) + b_k \sum_{n=1}^{N} e^{ikr_n} \chi_n^A(r)$$

$$\psi_k^2(r) = b_k \sum_{n=1}^{N} e^{ikr_n} \chi_n^A(r) - a_k \sum_{n=1}^{N} e^{ikr_n} \chi_n^A(r)$$

   where r_n describes the location of the n^{th} A atom for χ^A and of the n^{th} B atom for χ^B, and a_k and b_k describe the bond mixing between A and B orbitals.

   (a) Plot schematically the orbitals and their signs for $k = 0$. Rationalize why $a_0 = 0$ and $b_0 = 1$ (for $k = 0$). What are the relative energies of the two branches of the wave function? These two wave functions can be considered non-bonding LCAOs. Explain

   (b) Plot schematically the orbitals and their signs for $k = \pi/a$. What are the relative energies of the two branches of the wave function? One wave function can be considered bonding and the other antibonding. Explain.

   (c) Plot schematically the band diagram, that is, energy as a function of k, for the two branches of the wave function.