Problem set 7

This problem deals with the effects of orbital symmetry and size in a tight-binding band structure. The idea is to model the band structure of a transition metal with valence s and d bands. Recall that these bands may come from orbitals of different principle quantum numbers, and therefore have of very different atomic radii. For example, Cu has 4s and much smaller 3d orbitals in the valence band. Thus, take two valence orbitals on each lattice site in a *two-dimensional* square lattice (of lattice constant $a = 1$). One of these orbitals should be a d-orbital, and one an s-orbital. For simplicity, approximate

$$\psi_d = \psi_{d0} e^{-r/a_d}(x^2 - y^2) \qquad \psi_s = \psi_{s0} e^{-r/a_s} \tag{1}$$

where $r = \sqrt{x^2 + y^2}$ and let $a_s = 1.5$ and $a_d = 0.9$ in units of a.

Calculate ψ_{d0} and ψ_{s0} to normalize the wave functions, then taking the perturbation v as a sum of screened coulomb potentials ($v_0 a/(r + 0.001)Exp[-r/a]$–the small number is added to the denominator to cut off the divergence) on the four nearest neighbors, calculate the overlap orbitals called B in class (there is no need to calculate those called A, since they simply renormalize the orbital energies, and are therefore unimportant in this less-than-realistic model). You should have a B_{dd}, a B_{ss} and a B_{sd}. Set the renormalized orbital energies to zero, and in terms of these B's, find an analytic solution for the dispersion $E(\mathbf{k})$ (don't forget that the sign of the overlap integrals will depend upon the orientation of the orbitals; you should find two bands). Plot both bands along the high symmetry directions $(-\pi, -\pi) \to (\pi, \pi)$ and $(-\pi, 0) \to (\pi, 0)$, and estimate the widths of these bands. Why is there a gap for one of these directions and not the other? From the eigenfunctions that correspond to the eigenvalues, you can estimate the consistency of the bands (i.e. the extent of s and d character), what is the fraction of d-character of the highest an lowest energy states?

Hints. I did the entire calculation using NIntegrate without usingthe symmetry of the system to improve convergence. This greatly slowed the calculation. If you want, several of the integrals can be calculated analytically, and the symmetry of the orbitals can be used to speed the numerical quadratures. The different band structure seen in the two plots has to do with the symmetry of the system. You will also need to make several approimations resulting from the exponential nature of the wavefunctions and potentials. More hints will be added to this assignment as I talk with you about it.