

**6.730 PHYSICS FOR SOLID STATE APPLICATIONS**  
**Department of Electrical Engineering and Computer Science**  
**Massachusetts Institute of Technology**  
**“REAL” SEMICONDUCTOR PROJECT**

**Part III: Electronic Band Structure (DUE IN CLASS, FRIDAY, 16 APRIL 2004)**

In this part of the project, you will be developing an LCAO picture for the valence and conduction bands of your semiconductor. As in the phonon part of the project, you will first develop a general form for the solution. You will then apply that form to your material, compare your calculated results with results reported in the literature, and use your results to evaluate physically interesting material properties.

**A. Background Questions** - Before developing the Hamiltonian matrix, answer the following general questions about the LCAO method:

1. For our LCAO model we construct our trial wave function typically using only the outermost (highest principal quantum number) orbitals (atomic wave functions). In other words, in a system with  $b$  atoms in the basis and  $n$  outermost orbitals per atom, the total number of orbitals in the LCAO wave function is  $nb$ . How many atomic orbitals will you have for your material? Why?
2. Conceivably one could also construct the LCAO wave function out of core orbitals as well as valence orbitals. If you did so, how many atomic wave functions would you have to use for your material? How large would your Hamiltonian matrix be in this case? How do you expect your results would differ from those you would get with just valence orbitals? What if we used higher (totally unoccupied) orbitals, too? How many orbitals per atom would we have to use to get an “exact” band structure? Why?

**B. Construction of Hamiltonian Matrix**

1. What are the atomic configurations of the two atoms in your material? Which orbitals do you expect to play a significant role in bonding?
2. Draw all the atoms in the basis and all their nearest neighbors with appropriate orbitals on each atom. Label the orbitals according to their lattice vector, basis vector, orbital type, and the type atom they are associated with (cation or anion). For example, the s orbital on the cation at lattice vector  $\mathbf{R}$ , basis vector  $\boldsymbol{\tau}$  would be labeled  $|\phi_{sc}(\mathbf{R}+\boldsymbol{\tau})\rangle$
3. Show that one can approximate all the nearest neighbor interactions with one of the following (to within a sign). Pictorial arguments (with accompanying explanation) are acceptable.

$$E_{ss} = \langle \phi_{sc}(\mathbf{0}) | H | \phi_{sa}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle$$

$$E_{sp} = \langle \phi_{sc}(\mathbf{0}) | H | \phi_{pxa}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle$$

$$E_{xx} = \langle \phi_{pxc}(\mathbf{0}) | H | \phi_{pxa}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle$$

$$E_{xy} = \langle \phi_{pxc}(\mathbf{0}) | H | \phi_{pya}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle$$

Is this approximation reasonable? Comment on the validity of

$$\langle \phi_{sc}(\mathbf{0}) | H | \phi_{pxa}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle = \langle \phi_{sa}(\mathbf{0}) | H | \phi_{pxc}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle$$

Given this approximation, can we write

$$\langle \phi_{sc}(\mathbf{0}) | H | \phi_{sc}(\mathbf{0}) \rangle = \langle \phi_{sa}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) | H | \phi_{sa}(\mathbf{a}/4, \mathbf{a}/4, \mathbf{a}/4) \rangle ?$$

Calculate values for  $E_{ss}$ ,  $E_{sp}$ ,  $E_{xx}$ , and  $E_{xy}$  in terms of  $V_{ss\sigma}$ ,  $V_{sp\sigma}$ , etc.

4. Write your trial wave function as a linear combination of these extended orbitals. Be explicit about your choice of phase factors.
5. Find the Hamiltonian matrix for the nearest neighbor approximation. Your answer should contain only  $E_{ss}$ ,  $E_{sp}$ ,  $E_{xx}$ ,  $E_{xy}$ , the s and p energies of the anion and cation ( $E_{sa}$ ,  $E_{sc}$ ,  $E_{pa}$ , and  $E_{pc}$ ) and phase factors. NOTE: You will be able to find this matrix in the literature. However, several of the sources (including Harrison, 1980 and Slater and Koster, 1954) have minor errors in their matrices or matrix elements, so check your answer carefully.

### C. Band Calculations

1. Look up a “real” energy band diagram for your material. Include a copy in your report.
2. Write a matlab program to plot the free-electron band structure for your material along the same directions as used in the energy band you found in the literature [Note: neglecting factors of  $\pi/a$ , the symmetry points are  $\Gamma = (0,0,0)$ ;  $X = (1,0,0)$ ;  $L = (1/2, 1/2, 1/2)$ ;  $K = (3/4, 3/4, 0)$ ; and  $W = (1, 1/2, 0)$ ]. Indicate the degeneracies of the different bands. Where is the Fermi level located? How does the free electron band structure compare to the real band structure?
3. Algebraically diagonalize the Hamiltonian matrix at the  $\Gamma$  point. What are the different energies and eigenvectors, and what do they correspond to physically? Using Harrison’s Solid State Table (attached) find numerical values for  $E_{sa}$ ,  $E_{sc}$ ,  $E_{pa}$ ,  $E_{pc}$ ,  $E_{ss}$ ,  $E_{sp}$ ,  $E_{xx}$ , and  $E_{xy}$ . Compare your calculated energies at the  $\Gamma$  point with values from the literature.
4. Write a matlab program to plot the LCAO energy bands along the same directions as above, along with the approximate location of the Fermi level. How do your results compare (qualitatively) with the band structure you found in the literature? If you wish, optimize the matrix elements for your material.
5. Where are the valence band maximum and the conduction band minimum located? What is the energy gap? Is your material direct or indirect?

### D. Effective Masses, Constant Energy Surfaces, Density of States

1. Plot constant energy contours near the valence and conduction band edges for “appropriate” planes. For example, if your minimum is at  $\mathbf{k}_{\min}$  along  $\Gamma$ -X, you should probably plot an energy contour for the  $k_x$ - $k_y$  plane, and for the plane parallel to  $k_y$ - $k_z$  that contains  $\mathbf{k}_{\min}$ . For a minimum along  $\Gamma$ -L, the plane containing the  $\Gamma$ -L direction and the plane perpendicular to that direction would make sense.
2. Solve for the energy at a number of k points near the valence and conduction band edges. Fit these points using a quadratic polynomial (be sure to think about your results from D1 when you do this). Use your results to find the effective masses for both the valence bands and the conduction band. How do your results compare with results from the literature? How would you improve your results?
3. Plot the total density of states (histogram method, include all bands) versus energy. Use your calculated effective masses to determine an approximate expression for the density of states near the valence and conduction band edges. How does this calculation compare with the total density of states?
4. Using your total density of states, calculate the electronic specific heat of your material as a function of temperature. Compare this with your calculations for the phonons, and comment.
5. Use the band structure you found in the literature to discuss the characteristics of your material. What electronic/optical applications would your material be good/bad for? Why?