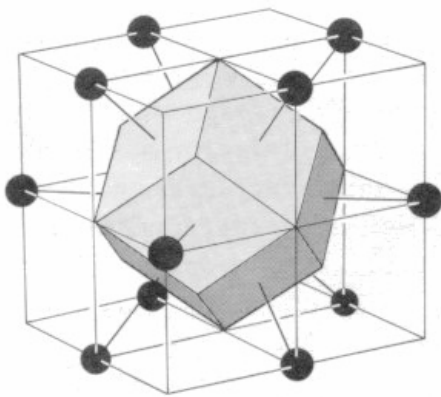


1. We discussed the H_2^+ ion extensively in class, when we allowed only a 1s orbital on each atom. Now let each atom have two orbitals, a 1s and a 2s, and denote the orbitals by $|1,1s\rangle, |1,2s\rangle, |2,1s\rangle, |2,2s\rangle$ for atom #1 and #2 respectively. Assume all orbitals are orthogonal to all others. Further, the onsite energy for the 1s orbitals is E_{1s} , the onsite energy for the 2s orbitals is E_{2s} , the hopping integral for the 1s orbitals is $\langle 2,1s | \hat{H} | 1,1s \rangle = \beta_{1s}$, the hopping integral for the 2s orbitals is $\langle 2,2s | \hat{H} | 1,2s \rangle = \beta_{2s}$. There is no hopping integral between the 1s and 2s states on the same atom, nor on different atoms.
 - (a) Construct the Hamiltonian matrix in the 4-orbital basis.
 - (b) What are the energy eigenvalues and eigenstates?
(you should be able to see the result almost by inspection and argue based on what you know about the 1 orbital per atom problem).
 - (c) Now let's go a bit further and imagine a linear chain of N identical atoms, each atom with two orbitals, 1s and 2s. The same assumptions as above apply, and when there is coupling, it is between nearest neighbor atoms only. Based on your knowledge of the dispersion relation for the linear chain with one orbital per atom and nearest neighbor coupling, draw the E vs. k band structure diagram for this system, for the first Brillouin zone. (It is not essential to use Mathematica or similar for the plot, but it is a good idea – it helps you build up programs that you can use for visualization. Choose sensible parameters, label axes etc.)
2. In 3 dimensions, molecular orbitals are identified by a k index with 3 components, $\vec{k} = (k_x, k_y, k_z)$. The allowed states are evenly distributed in each of the 3 indices (just like the 1D and 2D examples). Further, suppose there is a simple parabolic dispersion relation $E(k) = \frac{\hbar^2 k^2}{2m^*}$ that depends only on the magnitude of $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$. Find the density of states $D(E)$. Then include the fact that the electron has spin in the simplest possible way.
3. This problem is based on Sutton, problem #19.



- (a) Find the general dispersion relation for a 3-dimensional solid of identical atoms arranged in a face-centered-cubic (FCC) lattice. An FCC arrangement is shown at left with the Wigner Seitz unit cell shown (there is also an atom at the center). Make sure you agree – it's not the usual way an FCC is drawn, but it does make the nearest neighbors clear. Assume a 1s orbital on each atom and nearest-neighbor interactions with hopping matrix element β . Start with the dispersion relation we derived in class (Eq. 4.10 in Sutton) and with no loss of generality, put the \vec{R}' vector at the origin.

$$E(k) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \langle \vec{R}' | \hat{H} | \vec{R} \rangle$$

- (b) Look up the reciprocal lattice of the FCC structure and find some of the labels conventionally used for special k -points. Draw the dispersion relation between Γ and at least two other high-symmetry k -points.
- (c) Which k -vector gives the minimum energy? Which k -vector(s) give the maximum energy?
- (d) In the limit of small k (where k is the magnitude of the k -vector), show that the dispersion relation is parabolic. Use the work from problem 1 to write down the density of states.
4. This is a qualitative problem that guides you to think about the dispersion relation for a linear chain of alternating atoms -A-B-A-B-A-. The starting point is the familiar linear crystal with identical atoms, each with a $1s$ atomic orbital at every site, separated by a distance a .
(... -A-A-A-A-A- ...)
- (a) (i) Write down and sketch the dispersion relation for the (... -A-A-A-A-A- ...) system within the first Brillouin zone, defining all values at the extreme points.
- (ii) Write down and sketch the nature of the molecular wave function at the zone center (Γ -point) and at the zone edge (X-point).
- (b) Consider the *identical* system, but now think of the unit cell as a diatomic molecule, so that unit cells are separated by a distance $2a$. The goal is to show that the same information is contained in this “new” dispersion relation.
- (i) What is the new value of k at the Brillouin zone boundary?
- (ii) First focus on the one of the new unit cells, say atom 1 and 2, which is a diatomic molecule (A-A). What are the states of the unit cell in terms of the atomic orbitals?
- (ii) Now think about the wave function for this chain of diatomic molecules. Sketch the nature of the molecular wave function(s) at the zone center and show that these are identical to the 2 MOs sketched in (a).
- (iv) Sketch the two MOs corresponding to the value of k at the new zone edge, and show that they are the same.
- (v) Sketch the dispersion relation – is all the information in the first Brillouin zone as it should be?
- (c) Finally, change the identity of one of the atoms in the unit cell, so that one can distinguish between the two atoms in the cell (A-B). Notice that you are now forced to consider the “diatomic molecule” as the unit cell.
- (i) Sketch (qualitatively) the dispersion relation and discuss the wave functions at the zone edge.
5. A “mini project” that everyone must do before you start your individual class computational project is to use Open MX to calculate the band structure and density of states of Si. To do this, you will need to set up your space on the servers in Weniger 412 so that you can run the OpenMX software (see PH 575 web page under “OpenMX” for instructions in the tutorial file). After you’ve done that, you should be able to access the system remotely. You will make use of the information about Si that you found in Hwk 1. We will have some class time to work on this, but it is important to make progress out of class, too.
Report on the progress you have made on installing and running OpenMX with Si as a test system.

6. *Nothing to turn in. Make sure you have gone through the tutorials on the listed on the class web page under "online resources". They are fun and don't take much time.*

- Basic tutorial on [unit cells, lattices, symmetry](#) - Cambridge University DoITPoMS.
- YouTube video (6 min) about [conventional unit cells for cubic crystals](#).
- Basic tutorial on [Brillouin zone construction for 2-D square & hexagonal lattice](#) - Cambridge University DoITPoMS.