Handout on Tight-binding Calculation for Band Structures

1. Bloch’s theorem

The ions of a solid are assumed to be in a perfect arrangement, and they introduce a periodic potential, infinitely large in size. We would start from the ‘one electron approximation’ for convenience. For many solids, the existence of the core electrons can be ‘ignored’ because of screening. The problem is now to calculate the wavefunction of one electron as a function of energy. Using the Schrödinger equation to describe the lattice system, we have:

\[ H\psi(r) = (-\frac{\hbar^2}{2m}\nabla^2 + V(r)) = \epsilon\psi(r), \quad (1) \]

with the fact that the potential term \( V(x) \) is a periodic function of the lattice. Note here that with a constant potential we simply go back to the free electron case.

A word on Bloch’s theorem. Bloch’s theorem can be stated in the following form: The eigenstates \( \psi \) of the one-electron Hamiltonian (equation (1)) can be represented in the form of a plane wave times a function periodic in the Bravais lattice of the solid. That is:

\[ \psi_{nk}(r) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{nk}(r), \quad (2) \]

where \( u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r}) \) for all \( \mathbf{R} \) of the Bravais lattice. (That is, \( u_{nk} \) is a periodic function of the lattice.)

From Bloch’s theorem, we get this following result:

\[ \psi_{nk}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{nk}(\mathbf{r}). \]

That is, when the physical location in real space is shifted by \( \mathbf{R} \), only the phase of the wavefunction will be changed.

For a proof of Bloch’s theorem, see, e.g.,:

(1) C. Kittel: Introduction to Solid State Physics;
(2) Ashcroft and Mermin: Solid State Physics.

2. Using atomic wavefunction to construct a set of basis for actual wavefunction of electrons in a solid (LCAO)

Define \( \phi_n(\mathbf{r} - \mathbf{r}_j) \) as the atomic wavefunctions at the lattice point \( \mathbf{r}_j \), and \( n \) labels the atomic orbitals at a particular lattice point (but over every atom in the basis) that participate in bonding. For example, in the case of silicon, there are two atoms per basis. The conventional ”unit cell” is not the ”basis,” and it has four times the volume of a basis. And, \( n \) would be 3s, or 3p_x, or 3p_y, or 3p_z for the ”cation”, and another four for the “anion.” The wavefunctions of the inner core electrons are hardly perturbed.

We first construct a function \( \psi_{nk} \) from the Linear Combinations of the Atomic Orbitals (called “LCAO” in Chemistry when explaining chemical bonds of molecules, and “Tight-
Binding” in Solid State Physics):

\[ \psi_{nk}(r) = \sum_j c_{kj} \phi_n(r - r_j), \]  

(3)

where the summation of \( j \) is over all atomic (all lattices and all bases) sites. The atomic orbitals form a complete basis (because they are eigenstates of a Hermitian operator), and they can be used to build any functions of space. \( \psi_{nk} \) will be of a Bloch functional form, if:

\[ c_{kj} = \frac{1}{\sqrt{N}} e^{i \mathbf{k} \cdot \mathbf{r}_j}, \]  

(4)

where the normalization factor \( N \) is the number of the particular atomic orbital \( n \) at site \( j \). (For Si, Ge, and GaAs, e.g., \( N = 8 - sp^3 \) hybrid bonds for each atom in the two-atom-basis.) We can test this statement by plugging Eq. (4) into Eq. (3) and we find:

\[ \psi_{nk}(r) = \frac{1}{\sqrt{N}} \sum_j e^{i \mathbf{k} \cdot \mathbf{r}_j} \phi_n(r - r_j). \]  

(5)

Is this also a Bloch function? (Yes.) We can certainly test it by applying the translational operation. Now, add the translational vector \( \mathbf{R} \):

\[ \psi_{nk}(r + \mathbf{R}) = \frac{1}{\sqrt{N}} \sum_j e^{i (r_j + \mathbf{R}) \cdot \mathbf{k}} \phi_n(r + \mathbf{R} - r_j). \]  

(6)

Taking that \( e^{i (r_j + \mathbf{R}) \cdot \mathbf{k}} = e^{i r_j \cdot \mathbf{k}} e^{i \mathbf{R} \cdot \mathbf{k}} \) and that \( \phi_n(r + \mathbf{R} - r_j) = \phi_n(r - r_j) \), the constructed LCAO function is:

\[ \psi_{nk}(r + \mathbf{R}) = e^{i (\mathbf{k} \cdot \mathbf{R})} \psi_{nk}(r). \]  

(7)

So, we have shown that the constructed wavefunction is also a Bloch function. Therefore, the linear combination of a Bloch function should also be a Bloch function.

Now, what we will do is to construct the actual wavefunction of electrons in a 3D lattice as a linear combination of the \( \psi \)'s. We take the \( \psi \)'s as basis, and try to find the coefficients to get the wavefunctions. So, the problem to solve can be represented as:

\[ H \Psi_{bk}(r) = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) = \epsilon \Psi_{bk}(r), \]  

where \( \Psi_{bk}(r) = \sum_n \chi_{bn}(\mathbf{k}) \psi_{nk}(r), \)  

(8)

and \( b \) is the energy band index, \( n \) labels the atomic orbitals, \( \mathbf{k} \) the wavevector, and \( \chi_{bn}(\mathbf{k}) \) are the coefficients that we want to solve. (The meaning of the labels should become clear at the end.)
3. Tight-binding calculation

Using matrix presentation, we want to solve the eigenenergies and eigenstates by ‘diagonalize’ the matrix. That is, we just want to “block diagonalize” the matrix. Using \( \psi \) (see equation 5) as a basis, an element for a specific \( k \) is of this form:

\[
< 1 \sqrt{N} \sum_m e^{i\mathbf{k} \cdot \mathbf{r}_m} \phi_n (\mathbf{r} - \mathbf{r}_m) | H | \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{r}_j} \phi_n (\mathbf{r} - \mathbf{r}_j) > .
\]

The sum over \( m \) and \( j \) are initially over all the lattice points.

The above equation can be expressed in the matrix form:

\[
\begin{pmatrix}
\vdots & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & |n \times n| & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & |n \times n| & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & |n \times n| & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & |n \times n| & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & |n \times n| & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & |n \times n| & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & |n \times n| & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \ddots
\end{pmatrix},
\]

(10)

where each \( n \times n \) matrix is for a particular wavevector \( \mathbf{k} \), and \( n \) is the number of atomic orbitals that we want to consider. This size of this matrix is basically of the order of \( 10^{22} \) times \( n \) in one dimension — there are as many different \( \mathbf{k} \)s as the number of lattice points.

Using the first order perturbation theory, we can calculate the elements of an individual \( n \) by \( n \) matrix:

\[
< \mathbf{k} | H | \mathbf{k} >= \frac{1}{N} \sum_m \sum_j e^{-i\mathbf{k} \cdot \mathbf{r}_m} e^{i\mathbf{k} \cdot \mathbf{r}_j} \int dV \phi^*_n (\mathbf{r} - \mathbf{r}_m) H \phi_n (\mathbf{r} - \mathbf{r}_j) .
\]

(11)

Define \( \rho_j = \mathbf{r}_j - \mathbf{r}_m \), and using the fact that there is translational invariance in a Bravais lattice, the sum over \( m \) atoms is done \( N \) times, and therefore the sum over \( m \) can cancel the prefactor \( N \):

\[
< \mathbf{k} | H | \mathbf{k} >= \sum_j e^{i\mathbf{k} \cdot \rho_j} \int dV \phi^*_n (\mathbf{r} - \mathbf{r}_m) H \phi_n (\mathbf{r} - \mathbf{r}_j) = \sum_j e^{i\mathbf{k} \cdot \rho_j} \int dV \phi^*_n (\mathbf{r}) H \phi_n (\mathbf{r} - \rho_j) .
\]

(12)

So, what comes down to is to sum up the contribution of all atoms in the solid, relative to a particular atom at a particular lattice point.

In a solid, there are many orbitals to sum over. So, our calculation scheme is only useful when we can limit ourselves to deal with a small number of orbitals (small \( n \)) and a small
number of atoms, so that the computation problem can be handled by a computer. Nearest neighbor approximation can greatly help reduce the number of atoms. The tight-binding approximation will only be accurate if the overlaps between wavefunctions on one atom and the potential of nearby atoms is small enough (but not entirely zero) that only nearly degenerate levels are ‘mixed’ together. It works well for valence electrons, i.e., those electrons contribute to binding the atoms together. The computed coupling strength will often need to be changed slightly, so that the calculated results can be close to what measured. Such fitting procedure generates empirical coupling constants.

4. The ONE-BAND tight-binding calculation as an example

If we consider only one s state, e.g., then,

$$< k | H | k > = \sum_j e^{-ik \cdot \rho_j} \phi_s^*(r)H\phi_s(r - \rho_j) .$$

(13)

Define $\int dV \phi_s^*(r)H\phi_s(r) = \alpha$, and $\int dV \phi_s^*(r)H\phi_s(r - \rho_j) = \gamma$ (assuming that the nearest neighbors are indeed equally distant and the s-like symmetry makes things simple), we have:

$$< k | H | k > = -\alpha - \gamma \sum_j e^{-ik \cdot \rho_j} = \epsilon_k .$$

(14)

The overlap energy $\gamma$ depends on the interatomic spacing $\rho$, and can be pretty accurately calculated, and the energy $\alpha$ is the original ground state energy of this s state in the atom.

The number of nearest neighbors depends on the lattice. Taking the Simple Cubic lattice for an example, the nearest atoms would be at $\rho = (\pm a, 0, 0); (0, \pm a, 0); and(0, 0, \pm a)$.

And, the eiganenergy is: $\epsilon_k = -\alpha - 2\gamma(cosk_xa + cosk_ya + cosk_za)$ . The energy band is 12$\gamma$ wide, indicating that the stronger the coupling between neighboring atoms, the broader the band is. This trend is exactly what we expect from perturbation theory.

Question: Based on the s-band model, calculate the dispersion relation for a b.c.c. lattice. Use Taylor expansion to derive the dependence of energy on $k$ up to the third order ($k^3$).

Question: Calculate the dispersion relation for an f.c.c. lattice.

5. Tight-binding band structure using 8 and 10 bands

To better describe the band structure of the valence band for Si, Ge (of Diamond structure), and GaAs (of Zincblende structure), the number of orbitals to be considered would be at least 8, since there are two atoms (two Si atoms, or two Ge atoms, or Ga and As, respectively) per lattice point. And, the nature of the bonding electron is really in a hybrid $sp^3$ orbital. Using the terminology in atomic orbitals, there are the $s$, $p_x$, $p_y$, and $p_z$ orbitals at the ‘cation’ site and $s$, $p_x$, $p_y$, and $p_z$ orbitals at the ‘anion’ site.) Here, the convention is to use the term ‘cation’ and ‘anion’ to distinguish these two atoms in the basis of both the diamond structure and the Zincblende structure. The value of the matrix elements ($n$ by $n$, or, 8 by 8) can be carefully calculated by, e.g., tracing what the ‘coupling’ strength between the $s$ orbital and
the $p_x$ orbital is. In theory, there are 64 such elements to calculate, but, due to symmetry properties, many are complex conjugates and some are zero.

When all the matrix elements are obtained, we diagonalize it, and obtain the eigenstates and eigenenergies. (First order perturbation theory for degenerate states.) The eigenenergies would be the energies of the electronics states for this particular $k$. The number of eigenenergies is exactly the same as the number of orbitals. Some are still degenerate as a result of symmetry in the lattice.

By using the calculation scheme outlined above, the full 8-band structure in three-dimensional $k$-space can be calculated. The final band structure (like the one shown in Fig. 14 in Kittel, page 199) is a plot of the calculated eigenenergies versus $k$. The selection of the wavevector $k$ is within the Brillouin Zone, when the ‘reduced zone scheme’ is used.

The basic idea of the tight-binding approximation is to deal with the valence electrons. Therefore, the model does not accurately describe the dispersion relation for conduction band electrons. For a more accurate description, we can add an two additional bands, called excited states, one for the cation, and one for the anion. Such approach is called 10-band approximation. Since we then have more fitting parameters, the results are often satisfactory enough in explaining experimental results involving the conduction band.