3. Electronic Structure

When we talk about semiconductors, we invariably come across the concept of electronic structure in one form or another. The reason for this ubiquity is the fact that all of the unique properties of semiconductors stem from their unique electronic structure (sometimes called band structure). By this term we mean the relationship between a wavevector \( \mathbf{k} \) at a particular state in the crystal and its energy, and this is written as \( E(\mathbf{k}) \), where \( \mathbf{k} \) is the same as the \( \mathbf{k} \) in \( \psi_k(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} \psi_k(\mathbf{r}) \) in the Bloch wave we already discussed how the periodicity of the crystal and its potential \( V(\mathbf{r}) \) results in these Bloch waves and how they represent all of the available solutions of the Schrödinger equation in the semiconductor crystal.

We have not specified these solutions further, nor have we specified the crystal potential, other than to...
state that they are both periodic and both can be expanded into a sum of Fourier coefficients:

\[ V(\vec{r}) = \sum_{\vec{k}} V_{\vec{k}} e^{i \vec{k} \cdot \vec{r}} \]

and

\[ \psi_{\vec{k}}(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} \sum_{\vec{h}} A_{\vec{h} \vec{k}} e^{i \vec{h} \cdot \vec{r}} \]

Let us first work with the 2nd equation for the wave function and introduce it into the time-independent Schrödinger equation to try to look for a solution:

\[ H \psi_{\vec{k}}(\vec{r}) = E(\vec{k}) \psi_{\vec{k}}(\vec{r}) \]

\[ \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_{\vec{k}}(\vec{r}) = E(\vec{k}) \psi_{\vec{k}}(\vec{r}) \]

Now plug in the expansion for \( \psi_{\vec{k}} \):

\[ \begin{align*}
-\frac{\hbar^2}{2m} \nabla^2 \left[ \sum_{\vec{h}} A_{\vec{h} \vec{k}} e^{i \vec{h} \cdot \vec{r}} \right] + V(\vec{r}) \sum_{\vec{h}} A_{\vec{h} \vec{k}} e^{i \vec{h} \cdot \vec{r}} &= E(\vec{k}) \sum_{\vec{h}} A_{\vec{h} \vec{k}} e^{i \vec{h} \cdot \vec{r}} \\
&= E(\vec{k}) \sum_{\vec{h}} A_{\vec{h} \vec{k}} e^{i \vec{h} \cdot \vec{r}}
\end{align*} \]
First let us apply the Laplacian to the exponential term:

\[ \nabla^2 e^{-i(G_h \cdot \mathbf{r} + k \cdot \mathbf{r})} = -\left| G_h + k \right|^2 \]

to get the following:

\[
\frac{-i}{2m} \sum_h \left| k + G_h \right|^2 A^*_h e^{i(k + G_h) \cdot \mathbf{r}} - i(k + G_h) \cdot \mathbf{r} \sum_h A^*_h e^{i(k + G_h) \cdot \mathbf{r}} + V(\mathbf{r}) \sum_h A^*_h e^{i(k + G_h) \cdot \mathbf{r}} = E(k) \sum_h \nabla^2 e^{i(k + G_h) \cdot \mathbf{r}} \]

Next we pull the standard trick: multiply by a complex exponential \( \exp[-i(k + G_h) \cdot \mathbf{r}] \) so that we annihillate the \( h \) terms and leave only the terms where \( k = h \). Of course we need to integrate over the crystal volume \( \text{Vol} \). The RHS term will be:

\[
E(k) \int_{\text{Vol}} e^{-i(k + G_h) \cdot \mathbf{r}} \sum_h A^*_h e^{i(k + G_h) \cdot \mathbf{r}} \, d\mathbf{r} = E(k) \sum_h A^*_h \int_{\text{Vol}} e^{i(G_h - G_k) \cdot \mathbf{r}} \, d\mathbf{r} = E(k) \sum_h A^*_h E_{k_h} \]
\[ = E(\vec{k}) \, A_{G_e}^3 \]

The first term on the LHS will be

\[
\frac{\hbar^2}{2m} \int_{\text{vol.}} e^{-i(\vec{k} + \vec{G}_e) \cdot \vec{r}} \sum_n \frac{1}{\hbar} (\vec{k} + \vec{G}_e)^2 |A_{G_n}\rangle \langle A_{G_n}| \, d\vec{r}
\]

\[ = \hbar^2 \sum_n \frac{1}{\hbar} (\vec{k} + \vec{G}_e)^2 |A_{G_n}\rangle \langle A_{G_n}| \int_{\text{vol.}} e^{-i(\vec{k} + \vec{G}_e) \cdot \vec{r}} \, d\vec{r}
\]

\[ = \frac{\hbar^2}{2m} \sum_n |\vec{k} + \vec{G}_e|^2 |A_{G_n}\rangle \langle A_{G_n}| \, \delta_{\epsilon, \epsilon_n} = \frac{\hbar^2}{2m} (\vec{k} + \vec{G}_e)^2 |A_{G_e}\rangle
\]

Both LHS and RHS terms end up being a single coefficient with \( A_{G_e}^3 \) not so lucky with the middle term:

\[ \int_{\text{vol.}} e^{V(\vec{r})} \sum_n \frac{1}{\hbar} (\vec{k} + \vec{G}_e)^2 |A_{G_n}\rangle \langle A_{G_n}| \, d\vec{r}
\]

\[ = \sum_n |A_{G_n}\rangle \int_{\text{vol.}} e^{V(\vec{r})} e^{-i(\vec{k} + \vec{G}_e) \cdot \vec{r}} \, d\vec{r}
\]

Now we need to introduce some new notation in order to handle this term more elegantly. This notation will allow us to convert
our integrals over \( \tilde{r} \) into coefficients of a matrix so that our entire problem now becomes a matrix (linear algebra problem). Let us label each state \( \tilde{k} \) by replacing

\[\psi_k(\tilde{r}) = \frac{e^{-i k \tilde{r}}}{\sqrt{\text{vol}}} = |\tilde{k}\rangle \leftarrow \text{this is called a "ket"}
\]

and

\[\psi^*_k(\tilde{r}) = \frac{e^{i k \tilde{r}}}{\sqrt{\text{vol}}} = \langle \tilde{k} | \leftarrow \text{called a "bra"}
\]

Together, "bra" and "ket" make a bra-ket like this with a special meaning:

\[\langle \tilde{k} | \tilde{l} \rangle = \int \frac{\psi^*_k(\tilde{r}) \psi_l(\tilde{r}) \text{d}\tilde{r}}{\text{vol}}
\]

Now we see that \( \langle \tilde{k} | \tilde{k} \rangle = 1 \)

and \( \langle \tilde{k} | \tilde{l} \rangle = 0 \) or \( \langle \tilde{k} | \tilde{l} \rangle = \delta_{k,l} \)

We can stick other things inside the bra-ket such as potentials:

\[\langle \tilde{k} | V(\tilde{r}) | \tilde{k} \rangle = \int \psi^*_k(\tilde{r}) V(\tilde{r}) \psi_k(\tilde{r}) \text{d}\tilde{r}
\]

We also called this quantity the matrix element \( M_{k\tilde{k}} \) and we shall soon
see why. We can also write

\[ M_{k\ell} = \langle \ell' | V | k \rangle = \int \frac{d^3v}{(2\pi)^3} \psi_{\ell'}^{\ast}(v) \psi_{k}(v) \, dv \]

\[ = \frac{1}{(2\pi)^3} \int \frac{d^3v}{v \ell} e^{-i k \cdot v} \frac{k'}{V(v)} e^{i k' \cdot v} \, dv \]

and also:

\[ \int \frac{d^3v}{v \ell} e^{-i (k + G) \cdot v} \frac{v}{V(v)} e^{i (k + G') \cdot v} \, dv \]

\[ = \int \frac{d^3v}{v \ell} e^{-i G \cdot v} \frac{G}{V(v)} e^{i G' \cdot v} \, dv = \langle G_e | V | G_{\ell} \rangle \]

This we can call the matrix element

\[ M_{G_{\ell}G_e} = \langle G_e | V | G_{\ell} \rangle. \]

More generally we can also put any wavefunction into bra's & kets like this \( |\phi_n \rangle \) so we can write

\[ \psi = \sum_{n} C_{n} |\phi_n \rangle \text{ or } H |\psi \rangle = E |\psi \rangle \]

and \( H |\phi_n \rangle = E_{n} |\phi_n \rangle \). This notation makes the Schrödinger equation look
like an eigenvalue problem from linear algebra with the matrix \( H \) and eigenvectors \( |E_n \rangle \) eigenvalues \( E_n \) and all the rules that come from linear algebra.

Let us work the simplest example now and that is the case when \( V(\tau) = 0 \) so that \( \frac{\hbar^2}{2m} k^2 = \langle \phi_n | V | \phi_n \rangle = 0 \) is zero and we are left with the equation

\[
\frac{\hbar^2}{2m} \left[ k^2 + G^2 e^2 \right] A_{qe}^2 = E(k) A_{qe}^2
\]

which is trivially solved by

\[
E(k) = \frac{\hbar^2}{2m} \left( k^2 + G e^2 \right)^{\frac{1}{2}}
\]

This is called the empty lattice approximation because we do have a lattice (from the reciprocal lattice vectors \( \vec{G} \)) but it does not have a potential \( V(\tau) \). The solution looks like the free electron solution, but now it is modified by the reciprocal lattice vectors \( \vec{G} \). In fact we have as many solutions
as there are lattice vectors, including the $\mathbf{g}_k = (0, 0, 0) \cdot \frac{2\pi}{a}$ at the origin.

For $\mathbf{G}_k = (0, 0, 0)$ the solution will indeed be that of the free electron,

$$E(k) = \frac{\hbar^2 k^2}{2m}$$

while for other non-zero $\mathbf{g}_k$ the solution will be a parabola centered at $k = \mathbf{G}_k$.

We can plot this for a 1D lattice with lattice spacing $a$ where $R_k = Na$ and $G_k = \frac{2\pi}{a}$.

The 1st Brillouin zone will be between $-\pi/a$ and $\pi/a$ and it will look like we simply "folded" the original free electron bands into the 1st BZ by reflecting them back around the $k = \pm \pi/a$ points. The $E(k)$ is indeed periodic with $2\pi/a$. 

\[ k = \frac{\pi}{a}, \quad k = \frac{\pi}{a}, \quad k = \frac{3\pi}{a}, \quad k = \frac{4\pi}{a} \]
Next step would be to assume
\( V(\vec{r}) = E_0 \) some constant.
Then \( M_{G, \vec{G}} = E_0 \) So the entire
problem is now
\[
\frac{\hbar^2}{2m} \left| \vec{k} + \vec{G}_e \right|^2 A_{\vec{G}_e}^0 + E_0 A_{\vec{G}_e}^0 = E(\vec{k}) A_{\vec{G}_e}^0
\]
or
\[
E(\vec{k}) = \frac{\hbar^2}{2m} \left| \vec{k} + \vec{G}_e \right|^2 + E_0
\]
so we just shift the bands up and down by a constant. This
is satisfying because we expect
the bands to shift with the
application of an external potential
which we know moves the Fermi level.

The next level of complexity up from
the constant potential is to assume
that the matrix element \( M_{\vec{G}_e, \vec{G}_e} = E_1 \)
when \( \vec{G}_h \) and \( \vec{G}_e \) are
neighbors (i.e. \( \vec{G}_h = \vec{n}_1 b_1 + \vec{n}_2 b_2 + n_3 b_3 \)
and \( \vec{G}_e = \vec{n}_1 b_1 + \vec{n}_2 b_2 + n_3 b_3 \)).
Now we can pick an ordering for
the reciprocal lattice vectors and
write our equation like this
\[
\frac{\hbar^2}{2m} \left| \vec{k} + \vec{G}_e \right|^2 A_{\vec{G}_e}^0 + \sum_{\vec{G}_h} A_{\vec{G}_h}^0 M_{\vec{G}_h, \vec{G}_e} A_{\vec{G}_e}^0 = E(\vec{k}) A_{\vec{G}_e}^0
\]
with one such equation for each reciprocal lattice vector. Finally, we can arrange those equations as

$$\frac{\hbar}{2m} \left( \begin{array}{ccc} \hbar + G_1 & 0 & 0 \\ 0 & \hbar + G_2 & 0 \\ 0 & 0 & \hbar + G_3 \end{array} \right) \left( \begin{array}{c} \tilde{A}_{G_1} \\ \tilde{A}_{G_2} \\ \tilde{A}_{G_3} \end{array} \right) + \left( \begin{array}{c} 0 \\ M_{G_1} \tilde{G}_1 \\ 0 \\ M_{G_2} \tilde{G}_2 \\ 0 \\ \cdot \cdot \cdot \end{array} \right) = E(\tilde{\epsilon}) \left( \begin{array}{c} \tilde{A}_{G_1} \\ \tilde{A}_{G_2} \\ \tilde{A}_{G_3} \end{array} \right)$$

The zeros on the diagonal are because we already decided that diagonal elements don't do much — they just shift the energies up or down so we ignore them. Finally, we can arrange this as an eigenvalue problem:

$$\frac{\hbar^2}{2m} \left( \begin{array}{ccc} k^2 + G_1 & 0 & 0 \\ 0 & k^2 + G_2 & 0 \\ 0 & 0 & k^2 + G_3 \end{array} \right) \left( \begin{array}{c} \tilde{A}_{G_1} \\ \tilde{A}_{G_2} \\ \tilde{A}_{G_3} \end{array} \right) = E(\tilde{\epsilon}) \left( \begin{array}{c} \tilde{A}_{G_1} \\ \tilde{A}_{G_2} \\ \tilde{A}_{G_3} \end{array} \right)$$
What is the relationship between $M_{\mathbf{g}_1, \mathbf{g}_2}$ and $M_{\mathbf{g}_2, \mathbf{g}_1}$, or, in other words, what is the relationship between the matrix $\mathbf{M}$ and its transpose $\mathbf{M}^T$? Let us look at the definition:

$$M_{\mathbf{g}_1, \mathbf{g}_2} = \langle \mathbf{g}_1 | \mathbf{V} | \mathbf{g}_2 \rangle = \int_{\text{vol}} e^{-i \mathbf{g}_1 \cdot \mathbf{r}} \mathbf{V}(\mathbf{r}) e^{i \mathbf{g}_2 \cdot \mathbf{r}} d\mathbf{r} = \int_{\text{vol}} e^{-i \mathbf{g}_1 \cdot \mathbf{r}} e^{i \mathbf{g}_2 \cdot \mathbf{r}} d\mathbf{r} = M_{\mathbf{g}_2, \mathbf{g}_1}^*$$

They are complex conjugates of each other, so $\mathbf{M}^T = \mathbf{M}^*$ and the whole matrix is hermitian (equal to its complex conjugate transpose).

For our simple example of $1^{st}$ neighbors we get in 1d with lattice constant $a$:

$$\begin{pmatrix}
\frac{\hbar^2}{2m} k_x^2 & E_i^* \\
E_i & \frac{\hbar^2}{2m} k_x^2 + \frac{2\pi}{a} k_x^2 \\
E_i & 0 \\
E_i^* & 0 \\
\end{pmatrix}
$$

This band structure now looks similar to the free electron empty lattice approximation, but with a gap of size $2E_i$ opening at band crossings.
3.2 Pseudo potentials

In the more general case, we run up against the difficulty of defining the crystal potential. If we want to compute the bond structure of real crystals, the majority of the work will be in computing a suitable \( V(\mathbf{r}) \) which then completely defines the problem. The difficulty is in the fact that \( V(\mathbf{r}) \) is the effective potential which an electron "feels" and has to contain the effects of the electron interacting with all the other electrons, not just the bare nuclei of the atoms. Hence the potential does not have to be local meaning that \( V(\mathbf{r}) \) does not necessarily have to even be a function of only \( \mathbf{r} \) but could depend on other factors external to the electron. Hence we can consider the simplest case where \( V(\mathbf{r}) \) is indeed local and call this \( V(\mathbf{r}) \) a local pseudo potential because it represents not the real potential but an effective local potential which an electron "feels" and which gives us the correct bond structure.
There are also non-local pseudopotentials and also self-consistent — II —
but those are an extension of the local pseudopotentials which we will study here.

We will begin by using the periodicity (translational invariance) of \( V(\mathbf{r}) \) so that:

\[
V(\mathbf{r}) = \sum_l \upsilon_l (\mathbf{r} - \mathbf{R}_l)
\]

where \( \mathbf{R}_l \) goes over all atoms in the crystal. Next, we write our matrix element:

\[
M_{\mathbf{k}\ell} = \langle G_\mathbf{k} | V | G_{\mathbf{h}} \rangle
\]

as:

\[
M_{\mathbf{k}\ell} = \int \sum_l \upsilon_l (\mathbf{r} - \mathbf{R}_l) e^{-i (\mathbf{G}_{\mathbf{k}} - \mathbf{G}_{\mathbf{h}}) \cdot \mathbf{r}} d\mathbf{r}
\]

Since the integral and the matrix element only depend on the difference \( (\mathbf{G}_{\mathbf{k}} - \mathbf{G}_{\mathbf{h}}) \), we can define this difference as:

\[
\mathbf{G} = (\mathbf{G}_{\mathbf{k}} - \mathbf{G}_{\mathbf{h}})
\]

In addition, if we have materials like Si, Ge, InP, and GaN, they all have multiple atoms per basis. Let us write the position of the 2nd atom in the diamond/zinc-blende structure of Si, Ge, and InP, AsP materials as \( \mathbf{R}_2 \) which
signifies the displacement of the 2nd atom in the basis relative to the crystal lattice. Since each atom will have the same effective potential we can capture the effect of multiple atoms per basis using a so-called structure factor $S(\mathbf{G})$ which is defined as

$$S(\mathbf{G}) = \sum_{\mathbf{r}} e^{-i\mathbf{G} \cdot \mathbf{r}}$$

In our case of 2 atoms per basis this simplifies to

$$S(\mathbf{G}) = 1 + \exp(-i\mathbf{G} \cdot \mathbf{r})$$

Now we can write the matrix element as

$$M_{\mathbf{k}\mathbf{e}} = \sum_{\mathbf{r}} S(\mathbf{G}) \int e^{-i\mathbf{G} \cdot \mathbf{r}} \omega(\mathbf{r}) \, d\mathbf{r}$$

where "$k" now runs over all the primitive unit cells instead of all the atoms. Finally, it is standard to assume that the potential $\omega(\mathbf{r})$ is only non-zero inside the unit cell $\mathbf{r}$ so that the integral can be restricted to a single unit cell and the summation can be dropped to get the final matrix element as

$$M_{\mathbf{k}\mathbf{e}} = \sum_{\mathbf{r}} e^{-i\mathbf{G} \cdot \mathbf{r}} \int \omega(\mathbf{r}) \, d\mathbf{r}$$
Finally we recognize that the integral
\[ \int_{-\infty}^{\infty} \omega(\omega) d\omega, \]
is just a Fourier transform of the function \( \omega(\omega) \) over a unit cell. Cohen & Bergstresser proposed that only a few of these Fourier factors corresponding to the 1st few reciprocal lattice vectors are non-zero and capture the behavior of the pseudo-potential well. The first reciprocal lattice vectors of the FCC lattice have squared magnitudes 3 (from \((1,1,1)\) in units of \(2\pi/a\)) 4 (from \((2,0,0)\) in \(2\pi/a\)) 8 and 11. We often denote their Fourier coefficients as \( V_3, V_4, V_8, \) and \( V_{11} \). With these 4 parameters, the entire bandstructure is well represented. What Cohen & Bergstresser proposed was to vary these 4 parameters until experimentally measured gaps in the bandstructure were well reproduced by the calculated bands. This approach was termed "empirical pseudo potentials" because the input values were obtained empirically by fitting measured data on electron transitions.