In determining bandstructure, we take advantage of the natural periodicity of a solid. This allows us to derive the eigenvalues and eigenfunctions analytically.

- Repeated unit cell

\[ \begin{array}{cccc}
1 & \cdots & \times & \cdots & N \\
\end{array} \]

\[ \begin{array}{cccc}
\times & \cdots & \times & \cdots & \times & \cdots & N \\
\end{array} \]

\[ \begin{array}{cccc}
\times & \cdots & \times & \cdots & \times & \cdots & \times & \cdots & N \\
\end{array} \]

results in a periodic Hamiltonian

\[ H = \begin{bmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22} \\
\end{bmatrix} \]

- Recall that all \( H_{nm} \) are sub-matrices. The size of \( H_{nm} \) is directly dependent on the number of basis functions within a unit cell. Given \( b \) basis functions \( H_{nm} \) is of size \( b \times b \).

- As well, all basis functions

\[ \Psi_{n_i} \quad n = (1, \cdots, N) \quad i = 1 \cdots b \]

are grouped into

\[ \{ \Psi_{n_i} \} = \begin{bmatrix}
\Psi_{n_1} \\
\Psi_{n_2} \\
\vdots \\
\Psi_{n_b} \\
\end{bmatrix} \]
Finally, the Schrödinger Equation has the form
\[
\begin{bmatrix}
\phi_1 \\
\phi_2 \\
\vdots \\
\phi_N
\end{bmatrix}
\begin{bmatrix}
H_{11} & H_{12} & \cdots & \cdots \\
H_{21} & H_{22} & \cdots & \cdots \\
\vdots & \vdots & \ddots & \vdots \\
\vdots & \vdots & \vdots & \ddots \\
\end{bmatrix}
\begin{bmatrix}
\phi_1 \\
\phi_2 \\
\vdots \\
\phi_N
\end{bmatrix} = 0
\]
and
\[
E\phi_n = \sum_m H_{nm} \phi_m
\]
As shown earlier, these equations may be solved via the ansatz
\[
\{\phi_n\} = \{\phi_0\} e^{ikna}
\]
Such that,
\[
E\{\phi_0\} e^{ikna} = \sum_m [H_{nm}] e^{ikma} \{\phi_0\}
\]
or
\[
E\{\phi_0\} = \sum_m [H_{nm}] e^{ik(m-na)} \{\phi_0\}
\]
Let us define the matrix
\[
h(k) = \sum_m [H_{nm}] e^{ik(m-na)}
\]
where the eigenvalue problem is now defined by
\[
E\{\phi_0\} = [h(k)]\{\phi_0\}
\]
(Remember: \{\phi_0\} is a column vector and \{h(k)\} is a matrix of size bxb where b is the number of basis functions per unit cell)
Therefore $N$ lattice points, $N$ unit cells, and "$b$" basis functions will result in $b \cdot N$ eigenvalues.

To generalize, pick an origin and define the position of $n$ and $m$ by $d_n$ and $d_m$.

It is relatively straightforward to go from 1-Dimension to further dimensions. In the equation:

$$b(k) = \sum [H_{mn} \delta^{(k-nm)}]$$

from the $n^{th}$ unit cell we sum over all neighboring $m$ cells.

Beyond 1-Dimension
Now, given $\vec{a}_n$ and $\vec{a}_m$, we claim that the ansatz $\{\phi_n\} = \{\phi_0\} e^{i\vec{k} \cdot \vec{a}_n}$ Satisfies the Schrödinger equation. After substituting the above instead of eigenfunction, Sch. Eq. becomes:

$$E \{\phi_0\} = [h(\vec{k})] \{\phi_0\}$$

where

$$[h(\vec{k})] = \sum_m [H_{nm}] e^{i\vec{k} \cdot (\vec{a}_m - \vec{a}_n)}$$

which applicable to any number of dimensions!

(Don’t forget: the periodic nature of a lattice makes this all possible. Visually, one can stand at any $n^{th}$ unit cell, sum over all $m$ neighbors including itself, and the result will be the same)

We’ll use this general procedure for Graphite:

Graphite is made up of carbon atoms bonded in a hexagonal 2D plane.

But first, let’s gain familiarity with two dimensions, and consider a simple rectangular lattice.
• Assume **one** basis orbital per unit cell. So \(|\rho_0|\) and \([H_{nm}]\) become inx\times 1.

Want to evaluate: \(h(\vec{k}) = \sum_{m,n} H_{nm} e^{i\vec{k} \cdot (\vec{r}_m - \vec{r}_n)}\)

Evaluating \(H_{nn}\) results in \(E_0\) (self-energy) and evaluating \(H_{nm}\) results in a value that we call \(t\). So we have 5 terms in our summation:

\[
h(\vec{k}) = E_0 + \sum_{m=1}^{4} t e^{i\vec{k} \cdot (\vec{d}_m - \vec{d}_1)}
\]

• Take \(\vec{k} = k_x \hat{x} + k_y \hat{y} + \vec{z} + \vec{z}\) and set the origin as shown...

• Exponents of “e” for the four terms become:
  \[
  \vec{k} \cdot (\vec{d}_1 - \vec{d}_n) = \vec{k} \cdot \vec{d} = k_x = k_x, k_x
  \]
  \[
  \vec{k} \cdot (\vec{d}_n - \vec{d}_1) = k \cdot (-\vec{d}) = -k_x, k_x
  \]
  \[
  \vec{k} \cdot (\vec{d}_1 - \vec{d}_n) = \vec{k} \cdot \vec{b} = k_y, k_y
  \]
  \[
  \vec{k} \cdot (\vec{d}_n - \vec{d}_1) = k \cdot (-\vec{b}) = -k_y, k_y
  \]

• Thus, after adding all of them we get:
  \[
h(\vec{k}) = E_0 + 2t (\cos k_x a + \cos k_y b)
  \]
In any lattice we can look beyond nearest neighbor interactions to next-nearest neighbor interactions. For example, in the rectangular lattice...

\[ k(\vec{a}_m - \vec{a}_n) = (k_x \hat{x} + k_y \hat{y}) \cdot (a \hat{x} + b \hat{y}) \]

Now let's move onto Graphite. First identify the basic unit cell.
Next define two basis vectors, $\vec{a}_1$ and $\vec{a}_2$, such that the position of any cell in the lattice can be written as $\vec{R} = m\vec{a}_1 + n\vec{a}_2$ where $m$ and $n$ are integers.

Let $t$ denote the overlap between 2 adjacent (nearest neighbor) carbon atoms. Denote $n_1$ and $n_2$ the atoms of the unit cell under consideration. Thus, $H_{nn}$ is

$$H_{nn} = \begin{pmatrix} n_1 & n_2 \\ n_1^\dagger & t \\ n_2 & t & E_{\text{t}} \end{pmatrix}$$

Overlap outside the unit cell will involve 4 nearest atoms. i.e…

In order to calculate $\langle \psi_1 | \psi_2 \rangle$ assume 1 basis function per carbon atom. This gives two basis functions per unit cell, $\langle \psi_1 | \psi_2 \rangle$ will be a 2x2 matrix.
• Therefore, a total of 4 more matrices must be added (with phase factor!), they are:

\[
\begin{bmatrix}
0 & 0 \\
-1 & 0
\end{bmatrix} e^{ik \cdot \vec{a}_1} + \begin{bmatrix}
0 & t \\
0 & 0
\end{bmatrix} e^{ik \cdot (-\vec{a}_1)} + \\
\begin{bmatrix}
0 & t \\
-1 & 0
\end{bmatrix} e^{ik \cdot \vec{a}_2} + \begin{bmatrix}
0 & 0 \\
-1 & 0
\end{bmatrix} e^{ik \cdot (-\vec{a}_2)}
\]

• The final matrix looks like:

\[
\begin{bmatrix}
0 & 0 \\
-1 & 0
\end{bmatrix} e^{ik \cdot \vec{a}_1} + \begin{bmatrix}
0 & t \\
0 & 0
\end{bmatrix} e^{ik \cdot (-\vec{a}_1)} + \\
\begin{bmatrix}
0 & t \\
-1 & 0
\end{bmatrix} e^{ik \cdot \vec{a}_2} + \begin{bmatrix}
0 & 0 \\
-1 & 0
\end{bmatrix} e^{ik \cdot (-\vec{a}_2)}
\]

• If we let \( \vec{a} = a\hat{x} + b\hat{y} \) and \( \vec{a}' = a\hat{x} - b\hat{y} \) then \( |\psi(k)| \) simplifies to:

\[
\begin{bmatrix}
E_0 & h_0^*
\end{bmatrix}
\begin{bmatrix}
h_0 \\
E_0
\end{bmatrix}
\]

where

\[
h_0 = t\left(1 + e^{i(k_xa + k_yb)} + e^{i(k_xa - k_yb)}\right)
\]

• To find the eigenvalues of \( |\psi(k)| \) first recall the identity: given a matrix in the form

\[
\begin{bmatrix}
a & b^*
\end{bmatrix}
\begin{bmatrix}
b \\
a
\end{bmatrix}
\]

then its eigenvalues are \( a + |b| \) and \( a - |b| \)
• Thus the eigenvalues of $|h_0|$ are $E_0 + |h_0|$ and $E_0 - |h_0|$.

• What is $|h_0|$? Well, $h_0 = r(1 + 2e^{ik_x} \cos k_y b)$
  $\therefore h_0^* h_0 = r^2 (1 + 4 \cos k_x a \cos k_y b + 4 \cos^2 k_x b)$
  $= |h_0|^2$
  so, $|h_0| = r \sqrt{1 + 4 \cos k_x a \cos k_y b + 4 \cos^2 k_x b}$

• More formally we say,
  $$E(k) = E_0 \pm |h_0|$$

• Note, a plot of graphite energy reveals the exact symmetry of the two eigenvalues.

• Next lecture: Semiconductor Band Structure