BAND STRUCTURE IN 2D (continued...)

The molecular orbital with \( \vec{k} \) has energy

\[
E(\vec{k}) = \sum_{\vec{r}} e^{i \vec{k} \cdot (\vec{R} - \vec{R}')} \langle \vec{R}' | \hat{H} | \vec{R} \rangle \quad \text{where} \quad \vec{k} = \begin{bmatrix} k_x \\ k_y \end{bmatrix}
\]

The non-zero terms in this sum are

\[
\langle \vec{R}' | \hat{H} | \vec{R} \rangle = \alpha, \text{ the onsite energy}
\]

\[
\langle \vec{R}' | \hat{H} | \vec{R} \rangle = \beta, \text{ the hopping integral when } \vec{R}' \text{ & } \vec{R} \text{ are nearest neighbors.}
\]

If \( \vec{R}' \text{ & } \vec{R} \) are n.n., then

\[
\vec{R} - \vec{R}' = \begin{bmatrix} a \\ 0 \end{bmatrix}, \begin{bmatrix} -a \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ a \end{bmatrix} \text{ or } \begin{bmatrix} 0 \\ -a \end{bmatrix}
\]

\[
\Rightarrow E(\vec{k}) = \alpha + \beta \left[ e^{i k_x [a]} + e^{i k_x [-a]} + e^{i k_y [a]} + e^{i k_y [-a]} \right]
\]

\[
= \alpha + 2\beta \left( \cos k_x a + \cos k_y a \right)
\]
The plot shows a continuous surface. This makes sense when the 2D material has tens of thousands of atoms or more.

Regardless of big N or small N, it is important to recognize the discrete nature of \( \mathbf{k} \) that describe MOs.

**Example 1:** 4 x 4 Grid, Periodic B.C.s

**Sketch MOs in Real Space**

\[
\mathbf{k} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}
\]

\[
\mathbf{k} = \begin{bmatrix} \pi/a \\ 0 \end{bmatrix}
\]
There are 12 other M.O.s which I haven't sketched.

Each unique M.O. can be represented as a dot in the $k_x$-$k_y$ plane.

**EXAMPLE 2**: 8x8 Grid, Periodic B.C.'s $\Rightarrow$ 64 unique M.O.s
EXAMPLE 3: 100x100 grid, Periodic B.C.'s \( \Rightarrow 10,000 \) unique M.O.s.

This area of "k-space" is called the "First Brillouin Zone."

SPECIAL POINTS IN THE FIRST B.Z.

There are 4 equivalent places to draw \( \Gamma \), and 4 equivalent places to draw \( X \).

\[ \begin{align*}
\alpha &= 1 \\
\beta &= -0.3 \\
a &= 1 \\
E(k) &= \begin{cases} 
2 & \text{if } x = 0 \\
0 & \text{otherwise} 
\end{cases}
\]
Density of States

\[ \eta_{1d}(k) = 2 \frac{2k}{(2\pi)^{1/2}} \frac{Lk}{\pi} \]

where \( L = Na \) is length of the chain of atoms.

Now consider how this looks if \( N \to \) bigger and \( \Delta E \to \) smaller.

\( \eta_{1d}(k) \) is \# of states in this range.
How many states in the energy range $E \rightarrow E + dE$?

Answer: $\frac{dN}{dE}$

This is called Density of States, $D(E)$

$$D(E) = \frac{dN}{dE} = \frac{dN}{dk} \frac{dk}{dE}$$  \hspace{1cm} (Applying the chain rule from calculus)

$$= \frac{dN}{dk} / \frac{dE}{dk}$$

In this example, $E = \alpha + 2\beta \cos ka$

$$\frac{dE}{dk} = -2\beta a \sin ka$$

Therefore $D(E) = \frac{2L}{\pi} \frac{1}{2|\beta| a \sin ka}$

How do I express $\sin ka$ in terms of $E$?

$$\sin^2 ka = 1 - \cos^2 ka$$

$$= 1 - \frac{(E - \alpha)^2}{(2\beta)^2}$$

$$\sin ka = \sqrt{1 - \frac{(E - \alpha)^2}{4\beta^2}}$$

Final answer $D(E) = \frac{2L}{\pi a} \frac{1}{\sqrt{4\beta^2 - (E - \alpha)^2}}$
If $E$ depends only on $|k|^2$
we can follow a very similar protocol.

Circle of radius $k$ contains
this many states
$$\eta_{2d}(k) = 2 \frac{\pi k^2}{(\frac{2\pi}{L})^2}$$

Where $L$ is the dimension of
the grid of atoms in real space.

$$D(E) = \frac{d\eta_{2d}}{dk} / \frac{dE}{dk}$$