Electrons in 2d square lattice

(1) Assume zero lattice potential

\[ U_k = 0 \text{ for all } \mathbf{k}. \] Energy bands are:

\[ E_{\mathbf{k}} = \frac{\hbar^2}{2m} \left( \mathbf{\xi}^2 - \mathbf{k}^2 \right) \]

In the lowest bands:

\[ \mathbf{K}_0 = 0 \]
\[ \mathbf{K}_1 = \frac{2\pi}{a} \mathbf{a}_1 \]
\[ \mathbf{K}_2 = -\frac{2\pi}{a} \mathbf{a}_2 \]
\[ \mathbf{K}_3 = \frac{2\pi}{a} \mathbf{a}_3 \]
\[ \mathbf{K}_4 = -\frac{2\pi}{a} \mathbf{a}_4 \]

Rescale: \( \frac{\hbar^2}{2m} = 1, \frac{2\pi}{a} = 1 \)

In (101) direction, \( a_y = 0 \), \(-\frac{1}{2} \leq a_x \leq \frac{1}{2}\)

\[ E_{\mathbf{k},0} = a_x^2 \quad K_0 = (0,0) \]
\[ E_{\mathbf{k},1} = (a_x - 1)^2 \quad K_1 = (1,0) \]
\[ E_{\mathbf{k},2} = (a_x + 1)^2 \quad K_2 = (-1,0) \]
\[ E_{\mathbf{k},3} = a_x^2 + 1 \quad K_3 = (0,1) \]
\[ E_{\mathbf{k},4} = a_x^2 + 1 \quad K_4 = (0,-1) \]
A weak periodic potential will principally affect states that are
degenerate with other states, and where a matrix element of the electron-
ion potential connects the degenerate states. The equation is

\[(E_k \pm \epsilon) C_{\pm k} + \sum_{k'} U_{k-k'} C_{\pm k'} = 0\]

Here, we expect the degeneracies at \(kx = \frac{1}{2}\) and \(kx = -\frac{1}{2}\) to split, as well
as the multiple degeneracy at \(kx = 0\).

Let us consider the 4-fold degeneracy at \(kx = 0\). The matrix elements
of the electron-ion potential are \(U_{k_1-k_2}, U_{k_1-k_3}, U_{k_2-k_3}, \ldots\)

There are only two that are distinct:

\[k_1 - k_2 = (2, 0) \quad \text{Let } U_{k_1-k_2} = U_1\]
\[k_1 - k_4 = (1, 1) \quad \quad \quad \quad \quad \text{Let } U_{k_1-k_4} = U_2\]

We have \(1|k_1-k_2| = 2, 1|k_1-k_4| = \sqrt{2}\). So \(|k_1-k_2| > |k_1-k_4|\).

Smallest \(|k_1-k_j|\) has largest \(U_k\) (in absolute value). So we take

\[
\begin{align*}
U_{k_1-k_2} &= U_1 = -0.1 \\
U_{k_1-k_4} &= U_2 = -0.2
\end{align*}
\]

The matrix for the 4 bands that cross
at \(kx = 0\) is:

\[
H = \begin{pmatrix}
E_{k_1} & U_1 & U_2 & U_2 \\
U_1 & E_{k_2} & U_2 & U_2 \\
U_2 & U_2 & E_{k_3} & U_1 \\
U_2 & U_2 & U_1 & E_{k_4}
\end{pmatrix}
\]
At $h \times = 0$, we have $E_1 = E_2 = E_3 = E_4 = \mathcal{E}_0 = 1$.

So the matrix

$$H(\mathcal{E}_0) = \begin{pmatrix} \mathcal{E}_0 & U_1 & U_2 & U_3 \\ U_1 & \mathcal{E}_0 & U_2 & U_3 \\ U_2 & U_3 & \mathcal{E}_0 & U_1 \\ U_3 & U_2 & U_1 & \mathcal{E}_0 \end{pmatrix}$$

The eigenvalues can be found analytically:

$$
\begin{align*}
\mathcal{E}_1 &= \mathcal{E}_0 + U_1 + 2U_2 = \mathcal{E}_0 - 0.5 \\
\mathcal{E}_2 &= \mathcal{E}_0 + U_1 - 2U_2 = \mathcal{E}_0 + 0.3 \\
\mathcal{E}_3 &= \mathcal{E}_4 = \mathcal{E}_0 - U_1 = \mathcal{E}_0 + 0.1
\end{align*}
$$

(4) We diagonalize the matrix numerically and plot the bands (next page). The crossing near $h \times = \pm \frac{1}{2}$ is unphysical, it occurs because we didn't include the effect of the electron-electron potential in that regime.

In comparison with tight binding, the energies result from this calculation are:

$$
\begin{align*}
\mathcal{E} = (0,0) &: \quad \mathcal{E}_0 = 0, \quad \mathcal{E}_1 = 0.5, \quad \mathcal{E}_2 = \mathcal{E}_3 = 1.1, \quad \mathcal{E}_4 = 1.3 \\
\mathcal{E} = (\frac{1}{2},0) &: \quad \mathcal{E}_0 = 0.25, \quad \mathcal{E}_1 = 0.15, \quad \mathcal{E}_2 = 1.18, \quad \mathcal{E}_3 = 1.35, \quad \mathcal{E}_4 = 2.3
\end{align*}
$$
Tight binding model
Orbitals: $s, px, py, pz$

(e) List non-vanishing independent matrix elements: $E_{nn'}(R)$

$\bar{R}=0$ (on-site): $E_{ss}(0,0), E_{xx}(0,0) = E_{yy}(0,0) = E_{zz}(0,0)$

2 non-zero matrix elements:
$E_{sx}(0,0) = 0, E_{xy}(0,0) = 0$, etc. $E_{nn'}(0,0) = 0$ for all $nn'$

Nearest neighbors: 4 non-zero matrix elements:
$E_{ss}(1,0) < 0; E_{ss}(-1,0) = E_{ss}(1,0) = E_{ss}(0,1), ...$

$E_{sx}(1,0) > 0; E_{sx}(0,1) = 0$

$E_{sy}(0,1) = E_{sx}(1,0); E_{sz}(1,0) = 0 = E_{sz}(0,0)$

$E_{xx}(1,0) > 0 = E_{xx}(-1,0) = E_{yy}(0,1)$

$E_{yy}(1,0) = E_{xx}(0,1) < 0; E_{yy}(-1,0) = E_{yy}(1,0)$, etc.

$E_{zz}(1,0) = E_{yy}(1,0)$

Next-nearest neighbors: 4 independent matrix elements
$E_{ss}(1,1) < 0 = E_{ss}(1,-1)$, etc.

$E_{sx}(1,1) > 0; E_{sx}(-1,1) = -E_{sx}(1,1)$, etc.

$E_{sy}(1,1) = E_{sx}(1,1); E_{sz}(1,1) = 0$

$E_{xx}(1,1) > 0; E_{xx}(-1,1) = -E_{xx}(1,1)$, etc.

$E_{yy}(1,1) > 0; E_{yy}(-1,-1) = -E_{yy}(1,1)$, etc.

$E_{zz}(1,1) = 0$
The matrix elements $E_{xx}(1,1)$ and $E_{xy}(1,1)$ can be also written in terms of the $\sigma$ and $\pi$ bonds.

$$
\begin{align*}
\sigma & \quad \text{and} \quad \pi
\end{align*}
$$

by appropriate linear combinations, or vice versa.

The matrix element $E_{zz}(1,1)$ is the $\pi$ bond above, which we can write in terms of the $E_{xx}(1,1)$ and $E_{xy}(1,1)$ as

$$E_{zz}(1,1) = E_{xx}(1,1) - E_{xy}(1,1)$$

So there are 4 independent $nnn$ matrix elements.

Total matrix elements up to $nnn$: $2 + 4 + 4 = \boxed{10}$

Let's redefine them: $E_s$, $E_p$ in the $nn$-side $E_{ss}(0,0)$, $E_{xx}(0,0)$, and

$$
\begin{align*}
E_{ss}(1,0) & \equiv -t_s \\
E_{sx}(1,0) & \equiv t_{sx} \\
E_{xx}(1,0) & \equiv t_{xx} \\
E_{yy}(1,0) & \equiv -t_{\pi} \\
E_{ss}(1,1) & \equiv -t'_s \\
E_{sx}(1,1) & \equiv t'_{sx} \\
E_{xx}(1,1) & \equiv t'_{xx} \\
E_{xy}(1,1) & \equiv t'_{xy}
\end{align*}
$$

so that all the $t'$s and $t''$s are positive.

$$E_{zz}(1,1) = t'_{xx} - t'_{xy}$$
(d) Construct matrix elements $H_{mn'}(\vec{q})$.

$$H_{mn'}(\vec{q}) = \sum_{n} e^{i\vec{q} \cdot \vec{r}} E_{mm'}(\vec{q})$$

Let $T = a \lambda x$, $\eta = a \eta y$

$$H_{ss}(\vec{q}) = \varepsilon_s - T_s \left( e^{iT} + e^{-iT} + e^{i\eta} + e^{-i\eta} \right) - T_s \left( e^{i(\eta + \eta)} + e^{i(-\eta + \eta)} + e^{i(-\eta - \eta)} + e^{i(\eta - \eta)} \right) \Rightarrow$$

$$H_{ss}(\vec{q}) = \varepsilon_s - 2T_s (\cos \eta + \cos \eta) - 4T_s \cos \eta \cos \eta$$

$$H_{sx}(\vec{q}) = T_s x \left( e^{i\eta} - e^{-i\eta} \right) + T_s' x \left( e^{i(\eta + \eta)} - e^{i(\eta - \eta)} + e^{i(\eta + \eta)} - e^{i(-\eta - \eta)} \right) \Rightarrow$$

$$H_{sx}(\vec{q}) = 2iT_s x \sin \eta + 4iT_s x \sin \eta \cos \eta$$

$$H_{sy}(\vec{q}) = 2iT_s x \sin \eta + 4iT_s x \cos \eta \sin \eta$$

$$H_{xy}(\vec{q}) = 4T_s x \sin \eta \sin \eta$$

$$H_{xx}(\vec{q}) = \varepsilon_T + T_o \left( e^{i\eta} + e^{-i\eta} \right) + T \left( e^{i\eta} + e^{-i\eta} \right) +$$

$$+ T_{xx}' \left( e^{i(\eta + \eta)} + e^{i(\eta - \eta)} + e^{i(-\eta + \eta)} + e^{i(-\eta - \eta)} \right) \Rightarrow$$

$$H_{xx}(\vec{q}) = \varepsilon_T + 2T_o \cos \eta - 2T \cos \eta + 4T_{xx}' \cos \eta \cos \eta$$

$$H_{yy}(\vec{q}) = \varepsilon_T + 2T_o \cos \eta - 2T \cos \eta + 4T_{xx}' \cos \eta \cos \eta$$

$$H_{xy}(\vec{q}) = T_{xy}' \left( e^{i(\eta + \eta)} - e^{i(-\eta - \eta)} + e^{i(-\eta - \eta)} - e^{i(\eta - \eta)} \right) \Rightarrow$$

$$H_{xy}(\vec{q}) = 4T_{xy}' \sin \eta \sin \eta$$

$$H_{xz}(\vec{q}) = \varepsilon_T - 2T \cos (\cos \eta + \cos \eta) + 4 \left( T_{xx}' - T_{xy}' \right) \cos \eta \cos \eta$$
(g) For $E=0$, $\xi=\eta=0$ we have:

\begin{align*}
H_{ss}(0) &= E_5 - 4t_5 - 4t_5' \\
H_{sx}(0) &= H_{sy}(0) = H_{sz}(0) = 0 \\
H_{xx}(0) &= E_\rho + 2t_\sigma - 2t_\pi + 4t_{xx} = H_{yy}(0) \\
H_{zz}(0) &= E_\rho - 4t_\pi + 4(t_{xx} + t_{xy}) \\
H_{xy}(0) &= H_{xz}(0) = \ldots = 0
\end{align*}

so the matrix is diagonal. For any $\bar{\alpha}$, $H_{zz}(\bar{\alpha})$ is decoupled from the others.

(h) At $h=0$, we had from the nearly free electron calculation:

\begin{align*}
E_0 &= 0, \quad E_1 = 0.5, \quad E_2 = E_3 = 1.1
\end{align*}

Assume for simplicity non matrix elements are zero.

\begin{align*}
H_{ss}(0) &= E_5 - 4t_5 \\
H_{xx}(0) &= H_{yy}(0) = E_\rho + 2(t_\sigma - t_\pi) \quad \text{doubly degenerate} \\
H_{zz}(0) &= E_\rho - 4t_\pi
\end{align*}

The $z^2$ band dispersion upward: $H_{zz}(\bar{\alpha}) = E_\rho - 2t_\pi (1 + \cos \bar{\alpha})$

So this does not agree with result of nearly free electron calculation. Why?

Need different values in the $U$'s.

Assume: $U_1 = 0.2$, $U_2 = -0.1$

then:

\begin{align*}
E_0 &= 0 \\
E_1 &= 1.4 \\
E_2 &= 1.4 \\
E_3 &= E_4 = 0.8
\end{align*}
So assume
\[ E_s - 4t_s = 0 \]
\[ E_p + 2(t_\sigma - t_\pi) = 0.8 \]
Assume also \( t_{3x} = 0 \) in all phabs.
At \( \pi/4 \), we have:
\[ H_{ss} \left( \frac{\pi}{8} \right) = E_s - 2t_s + 2t_s = \boxed{E_s = 0.25} \]
\[ \Rightarrow \text{assume} \quad t_s = 0.0625 \]
\[ H_{xx} \left( \frac{\pi}{8} \right) = E_p - 2(t_\sigma + t_\pi) = 0.25 \]
\[ H_{yy} \left( \frac{\pi}{8} \right) = E_p + 2(t_\sigma + t_\pi) = 1.05 \]
\[ \Rightarrow \boxed{E_p = 0.65} \quad t_\sigma + t_\pi = 0.2 \]
\[ E_p + 2(t_\sigma - t_\pi) = 0.8 \Rightarrow 0.65 + 2(t_\sigma - t_\pi) = 0.8 \quad \Rightarrow \boxed{t_\sigma - t_\pi = 0.075} \]
\[ \Rightarrow t_\sigma = 0.1375, \quad t_\pi = 0.0625 \]
Plot tight binding bands (dashed lines) compared to nde bands:
\[ E_0^{tb}(\xi) = E_s - 2t_s - 2t_s \cos \xi \]
\[ E_3^{tb}(\xi) = E_p - 2t_\pi + 2t_\sigma \cos \xi \]
\[ E_4^{tb}(\xi) = E_p + 2t_\sigma - 2t_\pi \cos \xi \]
The 2nd band \( E_5^{tb}(\xi) = E_p - 2t_\pi - 2t_\pi \cos \xi \)
Assume \( E_p = 1.3 \) to fit 4th band.