Tight-Binding Method for Polyacetylene

We can write a generic tight-binding Bloch wavefunction as:

\[
\Phi(r) = \frac{1}{\sqrt{N}} \begin{pmatrix}
\sum_{\mathbf{R}_a} e^{i\mathbf{k} \cdot \mathbf{R}_a} u_1(r - \mathbf{R}_a) \\
\vdots \\
\sum_{\mathbf{R}_b} e^{i\mathbf{k} \cdot \mathbf{R}_b} u_1(r - \mathbf{R}_b)
\end{pmatrix}
\]

(1)

where \( \mathbf{a} = \mathbf{R}_a, ..., \mathbf{R}_b \) labels the position of the orbitals in the unit cell (e.g. orbitals on different basis sites). Because we have a set of orbitals in the unit cell represented by the vector above, the Hamiltonian is not guaranteed to be diagonal in this representation. Instead, we must explicitly form the Hamiltonian matrix using the vectors and then diagonalize it explicitly. This turns out to not be too difficult with the aid of a computer. Note that we can have indices for the atomic site and for the atomic orbital. Let us change notation to the Dirac bra-ket notation also. We now have:

\[
\frac{1}{N} \left( \sum_{\mathbf{R}_a} e^{i\mathbf{k} \cdot \mathbf{R}_a} \langle a | \sum_{\mathbf{R}_b} e^{i\mathbf{k} \cdot \mathbf{R}_b} \langle b | \right) H_{op} \left( \begin{array}{c}
\sum_{\mathbf{R}_a} e^{i\mathbf{k} \cdot \mathbf{R}_a} | a \rangle \\
\vdots \\
\sum_{\mathbf{R}_b} e^{i\mathbf{k} \cdot \mathbf{R}_b} | b \rangle
\end{array} \right) = E \left( \begin{array}{c}
\sum_{\mathbf{R}_a} e^{i\mathbf{k} \cdot \mathbf{R}_a} | a \rangle \\
\vdots \\
\sum_{\mathbf{R}_b} e^{i\mathbf{k} \cdot \mathbf{R}_b} | b \rangle
\end{array} \right)
\]

(2)

or in a more compact notation, we need to solve:

\[
\text{det}(H_{nm} - E S_{nm}) = 0
\]

(3)

where the notation should be self-explanatory. Let us then use the tight-binding approximation for polyacetylene. Polyacetylene is an organic molecule with a structure shown below with \( a = 1.5 \text{ Å} \):

One can see that a repeating unit has two inequivalent carbon 2p atoms. It should be noted that the relevant bands are 2p \( \pi \)-bands which will affect the sign of the matrix elements. Regardless, we can write the Hamiltonian matrix as:

\[
\frac{1}{N} \left( \sum_{\mathbf{R}_a} e^{i\mathbf{k} \cdot \mathbf{R}_a} \langle a | \sum_{\mathbf{R}_b} e^{i\mathbf{k} \cdot \mathbf{R}_b} \langle b | H_{op} \left( \begin{array}{c}
\sum_{\mathbf{R}_a} e^{i\mathbf{k} \cdot \mathbf{R}_a} | a \rangle \\
\vdots \\
\sum_{\mathbf{R}_b} e^{i\mathbf{k} \cdot \mathbf{R}_b} | b \rangle
\end{array} \right)
\]

(4)
Since $h_{aa} = h_{bb}$ and $h_{ab} = h_{ba}^*$, we really only need to evaluate two matrix elements:

$$
\begin{align*}
    h_{aa} &= \frac{1}{N} \sum_{R_a \neq R_a} e^{-i k \cdot R_a} e^{i k \cdot R_a} \langle a' | H_{op} | a \rangle \\
    h_{ab} &= \frac{1}{N} \sum_{R_a \neq R_b} e^{-i k \cdot R_a} e^{i k \cdot R_b} \langle a' | H_{op} | b \rangle
\end{align*}
$$

(5)

In the tight-binding approximation, we usually assume that the Hamiltonian can only cause transitions (or hoppings) to nearest-neighbors. Therefore, for the case of polyacetylene, where we assume that we have a linear chain of two inequivalent carbon atoms, the matrix elements end up working out like so:

$$
\begin{align*}
    h_{aa} &= \frac{1}{N} \sum_{R_a \neq R_a} e^{-i k \cdot R_a} e^{i k \cdot R_a} \langle a' | H_{op} | a \rangle \left( \delta_{R_a - R_a, 0} + 2 \delta_{n.n.} + \ldots \right) = E_{aa} + \ldots \\
    h_{ab} &= \frac{1}{N} \sum_{R_a \neq R_b} e^{-i k \cdot R_a} e^{i k \cdot R_b} \langle a' | H_{op} | b \rangle \left( \delta_{R_a - R_b, 2} + 3 \delta_{n.n.} + \ldots \right) \approx \frac{t}{N} \sum_{R_d} e^{-ik_d/2} + e^{ik_d/2} = 2 \cos \left( \frac{ka}{2} \right)
\end{align*}
$$

(6)

where $E_{aa} = \langle a' | H_{op} | a \rangle$ and $t = \langle a' | H_{op} | b \rangle$. Therefore the Hamiltonian matrix looks like:

$$
\begin{align*}
    h &= \begin{pmatrix}
        E_{aa} & 2 t \cos \left( \frac{ka}{2} \right) \\
        2 t \cos \left( \frac{ka}{2} \right) & E_{aa}
    \end{pmatrix}
\end{align*}
$$

(7)

The overlap matrix is computed similarly by disregarding next nearest neighbors. Many calculations approximate the overlap matrix as $\approx 1$. Here we calculate it for completeness:

$$
\begin{align*}
    S_{aa} &= \frac{1}{N} \sum_{R_a \neq R_a} e^{-i k \cdot R_a} e^{i k \cdot R_a} \langle a' | a \rangle \left( \delta_{R_a - R_a, 0} + 2 \delta_{n.n.} + \ldots \right) = 1 + \ldots \\
    S_{ab} &= \frac{1}{N} \sum_{R_a \neq R_b} e^{-i k \cdot R_a} e^{i k \cdot R_b} \langle a' | b \rangle \left( \delta_{R_a - R_b, 2} + 3 \delta_{n.n.} + \ldots \right) \approx \frac{s}{N} \sum_{R_d} e^{-ik_d/2} + e^{ik_d/2} = 2 s \cos \left( \frac{ka}{2} \right)
\end{align*}
$$

(8)

where $s = \langle a' | b \rangle$. Hence we must find the determinant of following matrix:

$$
\begin{align*}
    h - ES &= \begin{pmatrix}
        E_{aa} - E & 2 (t - s E) \cos \left( \frac{ka}{2} \right) \\
        2 (t - s E) \cos \left( \frac{ka}{2} \right) & E_{aa} - E
    \end{pmatrix}
\end{align*}
$$

(9)

This gives one the following expressions for the eigenvalues:

$$
\begin{align*}
    E_{\pm} &= \frac{E_{aa} \pm 2 t \cos \left( \frac{ka}{2} \right)}{1 \pm 2 s \cos \left( \frac{ka}{2} \right)}
\end{align*}
$$

(10)

The plot for this band dispersion can be seen below with the parameters set to $E_{aa} = 0$, $t = -1$, $s = 0$ (i.e. the zero of the energy has been set to $E_{aa} = 0$ and we have assumed that the overlap matrix is approximately one):
Now, in reality, the bonds in polyacetylene are not equivalent and the bond-lengths are not the same for the double and single bonds respectively. The “single bond” has length 1.7 Å⁻¹ and the “double bond” has length 1.3 Å⁻¹. In 1979, Su, Schrieffer and Heeger came up with a tight-binding model that changed not the bond lengths between the nearest neighbors, but actually changed the matrix elements (or hopping parameters).

\[
H_{a\bar{a}} = \frac{1}{N} \sum_{R_a R_{\bar{a}}} e^{-i k R_a} e^{i k R_{\bar{a}}} \langle a' | H_{op} | a \rangle \left( \delta_{R_a - R_{\bar{a}}, 0} + 2 n n. + \ldots \right) = E_{a\bar{a}} + \ldots
\]

\[
H_{b\bar{a}} = \frac{1}{N} \sum_{R_a R_{\bar{a}}} e^{-i k R_a} e^{i k R_{\bar{a}}} \langle a' | H_{op} | b \rangle \left( \delta_{R_a - R_{\bar{a}}, \pm} + 2 n n. + \ldots \right) = \frac{1}{N} \sum_{R_a} (t - \delta t) e^{-i \alpha a/2} + (t + \delta t) e^{i \alpha a/2} = (t - \delta t) e^{-i \alpha a/2} + (t + \delta t) e^{i \alpha a/2}
\]

\[
H_{a\bar{a}} = (t + \delta t) e^{-i \alpha a/2} + (t - \delta t) e^{i \alpha a/2}
\]

The Hamiltonian matrix then becomes:

\[
h = \begin{pmatrix}
E_{a\bar{a}} & (t - \delta t) e^{-i \alpha a/2} + (t + \delta t) e^{i \alpha a/2} \\
(t + \delta t) e^{-i \alpha a/2} + (t - \delta t) e^{i \alpha a/2} & E_{\bar{a} a}
\end{pmatrix}
\]

In the original paper by Su, Schrieffer and Heeger, they set the overlap matrix \( S_{m n} = 1 \), and we do the same here. Therefore we only need to diagonalize the matrix above. For \( E_{a\bar{a}} = 0 \), which we are free to choose (setting the zero of the energy), the eigenvalues are:

\[
E_s = \pm \sqrt{t^2 (1 + \delta)^2 + t^2 (1 - \delta)^2 + 2 t^2 (1 + \delta) (1 - \delta) \cos(k a)}
\]

Plotted below is the dispersion with \( \delta=0.15 \). The new qualitative feature is that the bands at the Brillouin Zone edge are now gapped. Therefore this model reproduces the qualitative behavior of the actual molecule which dimerizes under a Pierels distortion and also becomes gapped.
The Hamiltonian matrix can be expanded around $k = \pi/a$, and this is where this particular band theory begins to get interesting,

$$
    h = \begin{pmatrix}
    0 & t a q - 2 i t \delta \\
    t a q + 2 i t \delta & 0
\end{pmatrix} 
= d(q) \cdot \sigma
$$

(14)

where we have used the fact that $e^{i k a/2} |_{k = \pi/a} = i + q a/2 + ...$, $e^{-i k a/2} |_{k = \pi/a} = -i + q a/2 + ...$ and $q = \pi/a - k$.

This Hamiltonian can be written with the following (Pierels) substitution $q \rightarrow -i \partial_q$ and in terms of Pauli spin matrices as so:

$$
    h = -i \nu_F \partial_q \sigma_x + m \sigma_y
$$

(15)

We can identify $\nu_F = t a$ and $m = 2 t \delta$ and see that this expansion gives us a 1+1D Dirac equation. The topological aspect of this band theory occurs when we examine a domain wall between the two energetically equivalent systems, the one in the polyacetylene image above (A-phase), and the one with the double and single bonds switched (B-phase). At the domain wall between these two states (i.e. as $\delta$ OR $m > 0 \rightarrow \delta$ OR $m < 0$), we are guaranteed to have a zero mode. This can be seen explicitly as shown:

$$
    E_\pm = \pm |d(q)| = \pm \sqrt{\nu_F^2 q^2 + m^2} = \pm \sqrt{d_x^2 + d_y^2}
$$

(16)

Since $m \rightarrow 0$ at the boundary, the dispersion relation becomes in the vicinity of the domain wall:

$$
    E_\pm (\text{domain wall}) = \pm \nu_F q
$$

(17)

which signifies that the bands must cross and we get a zero mode. What is the significance of this zero mode? It appears because the two phases, the A- and B-phases, are topologically distinct. We know this because there is a Berry phase that results in going from one phase to another. This can be shown explicitly by writing the original Hamiltonian matrix as:

$$
    h = \begin{pmatrix}
    0 & (t - \delta t) e^{-i k a/2} + (t + \delta t) e^{i k a/2} \\
    (t + \delta t) e^{-i k a/2} + (t - \delta t) e^{i k a/2} & 0
\end{pmatrix}
$$

$$
    d_x(k) \sigma_x + d_y(k) \sigma_y = \begin{pmatrix}
    0 & d_x - i d_y \\
    d_x + i d_y & 0
\end{pmatrix}
$$

(18)
with \( d_x = 2 t \cos\left(\frac{k a}{2}\right) \) and \( d_y = 2 t \delta \sin\left(\frac{k a}{2}\right) \). Using the eigenvalues above, we can write the eigenvectors as:

\[
u_{\pm}(k) = \frac{1}{\sqrt{2}} \left( \frac{1}{ \mp e^{i\phi(k)} } \right) \tag{19}\]

where

\[
\phi(k) = \arctan\left(\frac{d_y}{d_x}\right) = \arctan\left(\frac{\delta \sin\left(\frac{k a}{2}\right)}{\cos\left(\frac{k a}{2}\right)}\right) = \arctan\left(\delta \tan\left(\frac{k a}{2}\right)\right) \tag{20}\]

Therefore, we can calculate the polarization change by using \( \delta = \pm 1 \) as \( \delta \) only needs to vary from positive to negative to obtain the polarization, but this particular choice makes the integral the easiest:

\[
\Delta P = e \int \frac{dk}{2\pi} A(k) \left|_{\delta=0}^{\delta=1} \right. = \frac{e}{2} \int \frac{dk}{2\pi} \nabla_k \phi(k) \left|_{\delta=-1}^{\delta=1} \right. = \frac{e}{2} \int \frac{dk}{2\pi} \left( \frac{a + a}{2} \right) = e a \tag{21}\]

where \( A_{\pm}(k) = i \langle u_{\pm}(k) | \nabla | u_{\pm}(k) \rangle \). We can therefore see that the polarization changes by \( e a / 2 \) just as we would naively expect. We can be more general by noting that:

\[
\Delta P = e \int \frac{dk}{2\pi} A(k) \left|_{\delta=0}^{\delta=1} \right. = \frac{e}{2} \int \frac{dk}{2\pi} \nabla_k \phi(k) \left|_{\delta=-1}^{\delta=1} \right. = \frac{e}{2} \int \frac{dk}{2\pi} \delta(1 + \tan^2(\frac{k a}{2})) \left|_{\delta<0}^{\delta>0} \right. = e a \tag{22}\]

The integral above has the remarkable property that:

\[
\int_{0}^{2\pi} \frac{d\chi}{2\pi} \frac{\delta(1 + \tan^2(\chi))}{1 + \delta^2 \tan^2(\chi)} = \begin{cases} +n & \text{for } \delta > 0 \\ -n & \text{for } \delta < 0 \end{cases} \tag{23}\]

From knowing this result, we can see that if the sign of \( \delta \) does not change (i.e. we do not have a domain wall), we do not obtain a polarization change. Only the sign of \( \delta \) matters and not the magnitude. Therefore the polarization change is a topological property.