1 Introduction

In the following we shall derive the band structure of polyacetylene (PA) assuming that:

1. C and H atoms are lumped in pairs of effective C-H “pseudo-atoms”, see Fig. 1. This is justified since we consider just the $p_z$ orbitals of the C atoms.

2. The electronic wavefunction, $\psi$, is defined on the “pseudo-atom” sites, only. This is justified by the fact the $p_z$ orbitals are localised about the “pseudo-atom” sites and not in the bonding regions. So, the probability of having an electron on the $i$-th “pseudo-atom” is given by $|\psi_i|^2$.

3. An integer number $L$ exists such that: $\psi_{i+L} = \psi_i$. This is known as Periodic Boundary Condition (PBC). Since the formula of polyacetylene is $[C_2H_2]_n$, we take $L$ even. In practice, one can get rid of $L$ at the end of the calculation by taking the limit $L \rightarrow \infty$. So, this assumption is just a trick to work out the algebra in a finite dimensional space, i.e., wavefunctions are now complex vectors of length $L$.

Here we also assume basic knowledge of Quantum Mechanics. In particular, one should know that by solving the (discretised) Schrödinger equation

$$\sum_{j=1}^{L} H_{i,j} \psi_j(k) = E(k) \psi_i(k)$$

one can obtain the band structure. It might be useful to write Eq. 1 explicitly as

Figure 1: PA model
where the entries of the Hamiltonian are
\[
\begin{cases}
H_{i,i} = \varepsilon \\
H_{i,i+1} = -t \\
H_{i,j} = 0 \text{ otherwise}
\end{cases}
\] (2)

The diagonal entries give the on-site energies and since all the \( p_z \) orbitals are equivalent, these entries are all equal to \( \varepsilon \). The off-diagonal entries give the hybridisation between \( p_z \) orbitals of different “pseudo-atoms”. Once again, since these orbitals are very localised and so we expect little hybridisation. So, we have included just nearest-neighbour entries. \( t \) is often called the transfer integral and the choice for its sign is just matter of definition. Since all the \( p_z \) are equivalent, it seems reasonable to set all the transfer integrals equal to \( t \). We shall discuss this point in Sec. 4.

2 Trial wavefunction

Solving Eq. 1 is generally a very difficult task. In practise, one is often guided by his/her previous experience. For instance, one can start from the wavefunctions of the free particle problem (see your favourite Quantum Mechanics textbook or http://en.wikipedia.org/wiki/Free_particle):
\[
\psi_j(k) = \frac{1}{\sqrt{L}} e^{ikj}.
\] (3)

These are called planewaves and \( k \) it is referred to as the wavenumber. As a consequence of the PBC, not all the real \( k \) are allowed:
\[
\psi_{j+L}(k) = \psi_j(k) \quad \forall j, k \Rightarrow e^{-ikL} = 1 \quad \forall k
\]
which is satisfied by
\[
k = \frac{2\pi}{L} n \quad n = 1, 2, \ldots, L.
\] (4)

We stop after \( L \) wavenumbers because the number of quantum states must be conserved and the number of \( p_z \) orbitals considered here is just \( L \). At the end of the calculation, by taking the limit \( L \to \infty \), one will see that the condition in Eq. 4 becomes \( k \in (0, 2\pi] \).
3 Solution

By plugging Eq. 3 in to Eq. 1, one obtains that
\[
\begin{pmatrix}
\epsilon & -t & 0 & \cdots & -t \\
-t & \epsilon & -t & \ddots & 0 \\
0 & \ddots & \ddots & \ddots & \vdots \\
\vdots & \ddots & -t & \epsilon & -t \\
-t & \cdots & 0 & -t & \epsilon
\end{pmatrix}
\begin{pmatrix}
e^{+ik} \\
e^{+2ik} \\
e^{+3ik} \\
\vdots \\
e^{+Lik}
\end{pmatrix}
= E(k)
\begin{pmatrix}
e^{+ik} \\
e^{+2ik} \\
e^{+3ik} \\
\vdots \\
e^{+Lik}
\end{pmatrix}
\]

which is equivalent to
\[
-te^{+ik(j-1)} + \epsilon e^{+ikj} - te^{+ik(j+1)} = E(k)e^{+ikj}.
\]

[check it!]. Finally, after getting rid of the factor \(e^{ikj}\) everywhere, one finds that
\[
-te^{-ik} + \epsilon - te^{+ik} = E(k).
\]

which can be rewritten in a more convecional way as
\[
E(k) = \epsilon - 2t \cos(k).
\]

This is the band structure following from our initial assumptions.

4 Discussion

As usual, the derivation of Eq. 5 is not the end of the story. We still have to understand the physical meaning of this equation. We start with noting that:

1. There is only one band, defined for \(k \in (0, 2\pi]\) (see Sec. 2) or \(k \in (-\pi, \pi]\), which is the same due to the periodicity of \(\cos(k)\). However, we expected at least two bands, one for the electrons (conduction band) and the other for the holes (valence band).

2. The only free parameter with a physical meaning is \(t\), the transfer integral, because energy can be always defined apart from an arbitrary constant, here \(\epsilon\). For instance, the bandwidth is equal to \(4t\).

A plot of the PA band structure as in Eq. 5 is reported in Fig. 2. In each of the \(L\) planewave levels (see Eq. 4) we can put two electrons, one with spin up and the other with spin down (see your favourite Quantum Mechanics textbook). Therefore, we ends with \(L/2\) occupied levels and \(L/2\) empty levels and a gap which goes to 0 as \(L\) goes to infinity. Of course, there is something wrong, because according to our band structure calculation, PA should be a metal!

Likely, there was something wrong in some of our initial assumptions. In fact, although all the \(p_z\) are equivalent, we also know that PA is a conjugated polymer, i.e., there is an alternation of single (long) and double (short) bonds.
So, it might be appropriate to introduce two different transfer integrals, $t_s$ and $t_d$, one for the single and the other for the double bonds. The band structure calculation for this case is left as homework assignment...

5 Homework

Solve the Schrödinger Eq. 1 when the (discrete) Hamiltonian is given by

\[
\begin{align*}
H_{i,i} &= \varepsilon \\
H_{i,i+1} = H_{i+1,i} &= -t_s \quad \text{if } i \text{ is odd} \\
H_{i,i+1} = H_{i+1,i} &= -t_d \quad \text{if } i \text{ is even} \\
H_{i,j} &= 0 \quad \text{otherwise}.
\end{align*}
\]

(6)

Obviously, you can follow the method you prefer, but one can also take advantage of what we discussed in Sec. 2. For instance, try the following trial wavefunction:

\[
\begin{align*}
\psi_j(k) &= e^{ikj} \quad \text{if } j \text{ is odd} \\
\psi_j(k) &= e^{ikj+i\phi} \quad \text{if } j \text{ is even}.
\end{align*}
\]

(7)

The phase factor $\phi$ is just another unknown quantity, along with the energy $E$. Therefore, by plugging Eq. 7 and Eq. 6 in to Eq. 1, one should obtain a system of two equations for two unknowns, one from the odd sites and the other from the even sites. The homework consists in solving this system to obtain the band structure and then computing the bandgap. Optionally, one can also calculate the effective masses for electrons and holes. [Hint: in the calculation, make use of the trigonometric identities, see http://www.tomzap.com/notes/Trigonometry/Identities.pdf].
In Fig. 3 the resulting band structure is plotted. Note that in this case $k \in (-\pi/2, \pi/2]$. This property could have been guessed just counting the number of quantum levels. Indeed, the wavefunction in Eq. 7 has been defined separately on even and odd “pseudo-atoms”, i.e., there are two nonequivalent sublattices. So, if one takes $L$ planewaves as in Sec. 2, the total number of levels will be $2L$. Therefore, it is correct to take just the first $L/2$ wavenumber in Eq. 4 which, after having taken the limit $L \to \infty$, finally leads to $k \in (0, \pi]$, or $k \in (-\pi/2, \pi/2]$ equivalently. [Check it after having derived the solution].

What we have found here is a general feature of one-dimensional systems known as Peierls instability: a chain of equispaced C-H “pseudo-atoms”, is unstable with respect to dimerisation, i.e., bond alternation. In other word, the dimerised solution in Fig. 3 gives a total energy smaller than the one of the undimerised solution in Fig. 2. Without working out the tedious integrals, one can guess it by comparing the energy of the higher occupied levels in the two cases.

In conclusion, we have verified once again that the physical properties of the system under consideration strongly depends on its structure (in this case, bond alternation). Being able to work out electronic structure calculations, analytically or numerically, is just half of the story. The other half is given by a careful discussion of the initial assumptions/approximations.