

More on One-Dimensional Crystals

Earlier, we saw earlier that the characters for the N irreducible representations of the one-dimensional translation group (\mathbf{T}_N) can be written as

	\mathbf{t}	\mathbf{t}^2	\mathbf{t}^3	...	\mathbf{t}^{N-1}	$\mathbf{t}^N = E$
$\Gamma(k)$	$e^{2\pi i(k \cdot a)}$	$e^{2\pi i(k \cdot 2a)}$	$e^{2\pi i(k \cdot 3a)}$...	$e^{-2\pi i(k \cdot a)}$	1

Where k takes on exactly N discrete values within the range $-1/(2a) < k \leq 1/(2a)$ and a is the unit cell length. This compressed “table” tells us all we need to know to discuss functions that form a basis for any of the irreducible representations of the \mathbf{T}_N group. For example, we know that if we operate on a function φ_k that forms a basis for the irreducible representation $\Gamma(k)$ with the translation operator \mathbf{t} , the result can be read directly from the character table:

$$\mathbf{t}\varphi_k = e^{2\pi i(k \cdot a)}\varphi_k.$$

More generally, if we operate on φ_k with any of the translation operators \mathbf{t}^m , we obtain

$$\mathbf{t}^m\varphi_k = e^{2\pi i(k \cdot ma)}\varphi_k.$$

It is also useful to note that the representation $\Gamma(-k)$ (with a corresponding basis function φ_{-k}) yields eigenvalues that are just the complex conjugates

$$\mathbf{t}\varphi_{-k} = e^{2\pi i(-k \cdot a)}\varphi_{-k} \quad \text{and} \quad \mathbf{t}^m\varphi_{-k} = e^{2\pi i(-k \cdot ma)}\varphi_{-k},$$

where $e^{2\pi i(-k \cdot a)} = (e^{2\pi i(k \cdot a)})^*$ and $e^{2\pi i(-k \cdot ma)} = (e^{2\pi i(k \cdot ma)})^*$. But, because the operator \mathbf{t} simply shifts the chain by one unit cell length (a) along the x - axis, this means that as functions that belong to the $\Gamma(k)$ and $\Gamma(-k)$ representations, φ_k and φ_{-k} have the important properties:

$$\varphi_k(x+a) = e^{2\pi i(k \cdot a)}\varphi_k(x) \quad \text{and} \quad \varphi_{-k}(x+a) = e^{2\pi i(-k \cdot a)}\varphi_{-k}(x). \quad (1)$$

Looking at these relations, we see that if we take the complex conjugate of φ_{-k} , the resulting function will form a basis for $\Gamma(k)$:

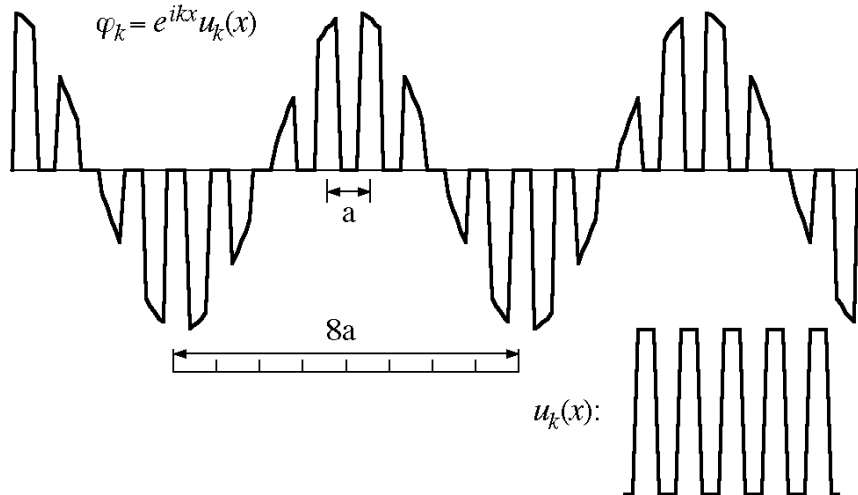
$$\varphi_{-k}^*(x+a) = e^{2\pi i(k \cdot a)} \varphi_{-k}^*(x) \text{ which implies } \mathbf{t}\varphi_{-k}^* = e^{2\pi i(k \cdot a)} \varphi_{-k}^*.$$

Thus, we can conclude that $\varphi_{-k}^* = \varphi_k$. The expressions (1) embody *Bloch's Theorem*, and are a direct result of the underlying translational symmetry of the system.

Any function $\varphi_k(x)$ that obeys Bloch's theorem can be written in the form:

$$\varphi_k(x) = e^{2\pi i k x} u_k(x)$$

where $u_k(x)$ is a periodic function that is identical in each unit cell of the crystal (i.e., $u_k(x) = u_k(x+a) = u_k(x+2a) = \dots$) and $e^{2\pi i k x}$ is a wave-like factor. With this form in mind, and making use of the fact that any electronic or vibrational wavefunction φ_k will be degenerate with its complex conjugate φ_{-k} , we can examine the characteristics of the *real* function $\varphi_k + \varphi_{-k}$ which varies sinusoidally with x . The plot below shows a Bloch function for $k = 1/8a$ and an arbitrary choice of the function $u_k(x)$.



We can see that because of the modulation provided by the factor of $e^{2\pi i k x}$, the function shown has an effective wavelength that is just $\lambda = 1/k = 8a$. The number of irreducible

representations, N , is just equal to the number of unit cells in the crystal, which we consider to be an arbitrarily large number. The variable k is then quasi-continuous and is often referred to as the *wavevector* of the Bloch function in question. It is nevertheless useful to remember that k takes on exactly N allowed values in the range $-1/(2a) < k \leq 1/(2a)$. This range of unique irreducible representations is referred to as the *First Brillouin Zone* or sometimes just the *Brillouin Zone*(BZ). Occasionally, it is convenient to consider the redundant representations for which k takes on values outside this range, but one should remember that for any value of k greater than $1/(2a)$ or less than $-1/(2a)$ there is an equivalent irreducible representation labeled by k' within the first BZ that is just found by computing $k' = k + n(1/a)$ where n is the appropriate integer.

Because the structure of the three-dimensional translation group is fundamentally analogous to the one-dimensional translation group, we will dispense with a discussion of the very cumbersome character table for $\mathbf{T}_{\mathbf{N}}^{3D}$. In general, the irreducible representations of $\mathbf{T}_{\mathbf{N}}^{3D}$ will behave in a way that parallels those for the one-dimensional translation group. For example, a function $\varphi_{l,m,n}$ which belongs to Γ^l of the $\mathbf{T}_{\mathbf{N}}^{\mathbf{a}}$ group, to Γ^m of the $\mathbf{T}_{\mathbf{N}}^{\mathbf{b}}$ group, and Γ^n of the $\mathbf{T}_{\mathbf{N}}^{\mathbf{c}}$ group will transform in a predictable way when operated upon by a three-dimensional translation operation:

$$\mathbf{t}^{\mathbf{R}}\varphi_{l,m,n} = \varepsilon^{u \cdot l + v \cdot m + w \cdot n} \varphi_{l,m,n} = e^{(2\pi i/N) \cdot (u \cdot l + v \cdot m + w \cdot n)} \varphi_{l,m,n}$$

$$\text{where } \mathbf{R} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

Just as we introduced the variable k in one-dimension, we can introduce a vector \mathbf{k} for three dimensions. Just as in one dimension, \mathbf{k} carries information about the irreducible representation in question for the three-dimensional translation group. There is a three-dimensional generalization of Bloch's Theorem:

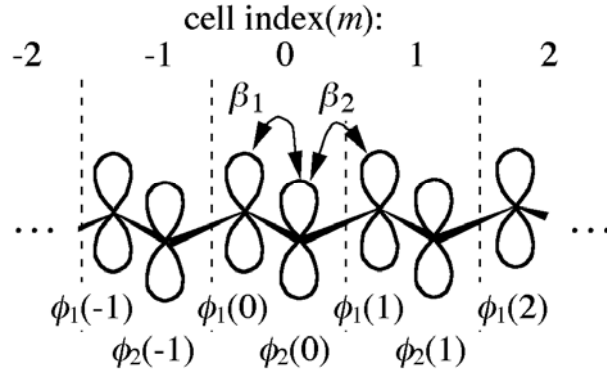
$$\varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{2\pi i \mathbf{k} \cdot \mathbf{R}} \varphi_{\mathbf{k}}(\mathbf{r})$$

where \mathbf{r} represents a position within the unit cell at the origin of our coordinate system, \mathbf{R} is a lattice vector between a pair of unit cells ($\mathbf{R} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$; $u, v,$ and w are integers). The dot product $\mathbf{k} \cdot \mathbf{R} = k_a u + k_b v + k_c w$, where the 3-dimensional wavevector $\mathbf{k} = k_a \mathbf{a}^* + k_b \mathbf{b}^* + k_c \mathbf{c}^*$ lies within the first Brillouin Zone. A fuller definition of \mathbf{k} will be given below. In two dimensions, Bloch's theorem is of the same nature as for one and three dimensions, and we will find 2-D examples in our treatment below. We emphasize that Bloch's Theorem is purely the result of the translational symmetry of crystals and when we specify a wavevector \mathbf{k} we are merely providing a label for a particular irreducible representation of the three-dimensional translation group.

Applications of Bloch's Theorem in One-Dimension

We begin by using Bloch's Theorem to solve for the Hückel orbitals and energies of polyacetylene. We will use a procedure that is exactly analogous to that used for molecular systems. First, we set up symmetry adapted linear combinations (SALCs) of the basis orbitals by use of projection

operators. We are considering the problem illustrated; there are two π orbitals per unit cell – each of which is related by a translation operation \mathbf{t}^m to equivalent orbitals in unit cells which we will index with the label m . Using



the formal machinery of projection operators, we can operate on each of the basis orbitals $\phi_1(0)$ and $\phi_2(0)$ with the projection operator for any representation to generate SALCs which extend over the entire chain (see Cotton, Sec. 6.2-6.3 and p. 145):

$$\hat{P}\phi_1(0) = \dots \chi(\mathbf{t}^{-2})\mathbf{t}^{-2}\phi_1(0) + \chi(\mathbf{t}^{-1})\mathbf{t}^{-1}\phi_1(0) + \chi(E)E\phi_1(0) \\ + \chi(\mathbf{t}^1)\mathbf{t}^1\phi_1(0) + \chi(\mathbf{t}^2)\mathbf{t}^2\phi_1(0) + \dots$$

$$\hat{P}\phi_2(0) = \dots \chi(\mathbf{t}^{-2})\mathbf{t}^{-2}\phi_2(0) + \chi(\mathbf{t}^{-1})\mathbf{t}^{-1}\phi_2(0) + \chi(E)E\phi_2(0) \\ + \chi(\mathbf{t}^1)\mathbf{t}^1\phi_2(0) + \chi(\mathbf{t}^2)\mathbf{t}^2\phi_2(0) + \dots$$

Now, we know that $\mathbf{t}^m \phi_1(0) = \phi_1(m)$ and $\mathbf{t}^m \phi_2(0) = \phi_2(m)$ and from Bloch's theorem we know that for a representation with wavevector k , the characters can be directly written as $\chi(\mathbf{t}^m) = e^{2\pi i k m a}$. Thus, the above expressions may be converted to read:

$$\hat{P}\phi_1(0) = \dots e^{-4\pi i k a}\phi_1(-2) + e^{-2\pi i k a}\phi_1(-1) + \phi_1(0) + e^{2\pi i k a}\phi_1(1) \\ + e^{4\pi i k a}\phi_1(2) + \dots = \sum_{m=-N/2+1}^{m=N/2} e^{2\pi i k m a} \phi_1(m)$$

$$\hat{P}\phi_2(0) = \dots e^{-4\pi i k a}\phi_2(-2) + e^{-2\pi i k a}\phi_2(-1) + \phi_2(0) + e^{2\pi i k a}\phi_2(1) \\ + e^{4\pi i k a}\phi_2(2) + \dots = \sum_{m=-N/2+1}^{m=N/2} e^{2\pi i k m a} \phi_2(m)$$

where we note that the summations run over all N cells of the chain. SALCs for any system with translational symmetry must be written in just the same way, so that in practice there is never any reason to actually refer to projection operators at all. SALCs that have been constructed using Bloch's theorem as above are referred to as a set of *Bloch basis* functions. We will label these as $\phi_{\mu}(k)$, where μ is a label that specifies the set of atomic orbitals with which we are concerned. We will normalize these basis orbitals by dividing by \sqrt{N} , and after changing the order of summation for typographical convenience, we write the general formula for a Bloch basis function:

$$\phi_{\mu}(k) = \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} e^{2\pi i k m a} \phi_{\mu}(m)$$

If we were faced with the problem of solving the Hückel secular determinant for the polyacetylene system *without* the use of symmetry factorization (i.e., we use the basis set of individual atomic orbitals, $\phi_{\mu}(m)$; $\mu = 1, 2$ and $m = 1, 2, \dots, N$) then we would have to solve a $2N \times 2N$ determinant. The use of the symmetry adapted Bloch basis block factors this determinant into N separate 2×2 determinants – one 2×2 determinant to solve for each of the N allowed values of k . This, in principle, is the kind of problem we face in all LCAO band structure calculations.

Let's set up the secular determinant we must solve for polyacetylene for each k . (This example proves to be simple enough that we can solve for the energies and obtain a solution in closed form.) We will assume that there are *two* resonance integrals involved in this problem, β_1 and β_2 , which represent a stronger(weaker) interactions between π orbitals that abut short(long) C-C bonds. Now we must evaluate the matrix element, $H_{12}(k)$, that involves the two Bloch basis orbitals for a given k :

$$\begin{aligned}
H_{12}(k) &= \langle \phi_1(k) | \mathcal{H} | \phi_2(k) \rangle = \left\langle \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} e^{2\pi i k m a} \phi_1(m) \middle| \mathcal{H} \middle| \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} e^{2\pi i k n a} \phi_2(n) \right\rangle \\
&= \frac{1}{N} \sum_{m=0}^{N-1} e^{-2\pi i k m a} \sum_{n=0}^{N-1} e^{2\pi i k n a} \langle \phi_1(m) | \mathcal{H} | \phi_2(n) \rangle = \frac{1}{N} \sum_{m=0}^{N-1} \sum_{n=0}^{N-1} e^{2\pi i k a (n-m)} \langle \phi_1(m) | \mathcal{H} | \phi_2(n) \rangle
\end{aligned}$$

This expression looks formidable, but can be made simpler. It is important to realize that the integral $\langle \phi_1(m) | \mathcal{H} | \phi_2(n) \rangle$ represents the Hamiltonian matrix element between $\phi_1(m)$ (ϕ_1 in the m^{th} unit cell) and $\phi_2(n)$ (ϕ_2 in the n^{th} unit cell); as such, it depends only the *difference* of the cell indices, $n - m$. As a result, each term in the double summation appears N times. (All N terms with $n = 3, m = 0$; $n = 4, m = 1$; $n = 5, m = 2$; ... are identical — this is more apparent by looking at the picture on the first page of this handout.) We can then eliminate one summation, introduce the shorthand $\langle \phi_1(m) | \mathcal{H} | \phi_2(n) \rangle = H_{12}^{n-m}$, and then change the remaining summation index by taking $p = n - m$. The matrix element then simplifies to read:

$$H_{12}(k) = \sum_{p=0}^{N-1} e^{2\pi i k a \cdot p} H_{12}^p.$$

The algebraic manipulations of the matrix element are to this point quite general and have nothing to do with Hückel theory. If we now introduce the assumptions of Hückel theory and use the notation above, we have the following: $H_{12}^0 = \beta_1$; $H_{12}^{-1} = \beta_2$ and all other terms are zero. We then obtain the simple expression:

$$H_{12}(k) = \beta_1 + \beta_2 e^{-2\pi i k a}$$

and the reader should verify that $H_{21}(k) = \beta_1 + \beta_2 e^{2\pi i k a} = H_{12}^*(k)$. As usual in Hückel theory we assign a value of α to the free atom $p\pi$ orbitals energy, so $H_{11}^0 = H_{22}^0 = \alpha$. For the special case of polyacetylene, there are no near neighbor interactions between atoms 1 and 2 with their symmetry equivalents across cell boundaries, so for all $p \neq 0$; $H_{11}^p = H_{22}^p = 0$. We then have the result

$$H_{11}(k) = H_{22}(k) = \alpha.$$

We can set up and solve the general k – dependent 2×2 secular determinant:

$$\begin{vmatrix} H_{11}(k) - E & H_{12}(k) \\ H_{21}(k) & H_{22}(k) - E \end{vmatrix} = \begin{vmatrix} \alpha - E & \beta_1 + \beta_2 e^{-2\pi i k a} \\ \beta_1 + \beta_2 e^{2\pi i k a} & \alpha - E \end{vmatrix} = 0$$

which, after expansion, yields

$$E_{\pm} = \alpha \pm \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos 2\pi k a}.$$

For each of the N allowed values of k , we obtain two eigenfunctions (chain orbitals) whose energies are given by the formula above. A usual procedure for presenting such results is to plot the energies as a function of wavevector for the range $0 \leq k \leq \pi/a$, since the range $-\pi/a \leq k \leq 0$ yields identical results (recall that $\psi_{-k}^* = \psi_k$, so $E(k) = E(-k)$). We can obtain the eigenfunctions by a procedure that continues to follow that used in molecular problems. For each k the chain orbitals are a linear combination of the two SALCs $\phi_1(k)$ and $\phi_2(k)$:

$$\psi_+(k) = c_{1+}(k)\phi_1(k) + c_{2+}(k)\phi_2(k)$$

$$\psi_-(k) = c_{1-}(k)\phi_1(k) + c_{2-}(k)\phi_2(k)$$

where the coefficients are found from the matrix equation:

$$\begin{bmatrix} H_{11}(k) - E_{\pm} & H_{12}(k) \\ H_{21}(k) & H_{22}(k) - E_{\pm} \end{bmatrix} \begin{bmatrix} c_{1\pm} \\ c_{2\pm} \end{bmatrix} = \begin{bmatrix} \mp \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos 2\pi k a} & \beta_1 + \beta_2 e^{-2\pi i k a} \\ \beta_1 + \beta_2 e^{2\pi i k a} & \mp \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos 2\pi k a} \end{bmatrix} \begin{bmatrix} c_{1\pm} \\ c_{2\pm} \end{bmatrix} = 0$$

These have particularly simple solutions when $k = 0$ or $1/2a$:

$$\begin{aligned} &\text{for } k = 0 \text{ or } k = 1/2a : \\ &c_{1+} = -c_{2+} \text{ (for } E_+); \quad c_{1-} = c_{2-} \text{ (for } E_-) \end{aligned}$$

We should stress that this does not mean that the crystal orbitals are the same for these two k points — because the Bloch basis functions are different for these two points:

$$\phi_{\mu}(k = 0) = \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} e^{i0m} \phi_{\mu}(m) = \frac{1}{\sqrt{N}} [\phi_{\mu}(0) + \phi_{\mu}(1) + \phi_{\mu}(2) + \dots]$$

$$\phi_{\mu}(k = 1/2a) = \frac{1}{\sqrt{N}} \sum_{m=0}^{N-1} (-1)^m \phi_{\mu}(m) = \frac{1}{\sqrt{N}} [\phi_{\mu}(0) - \phi_{\mu}(1) + \phi_{\mu}(2) - \dots]$$

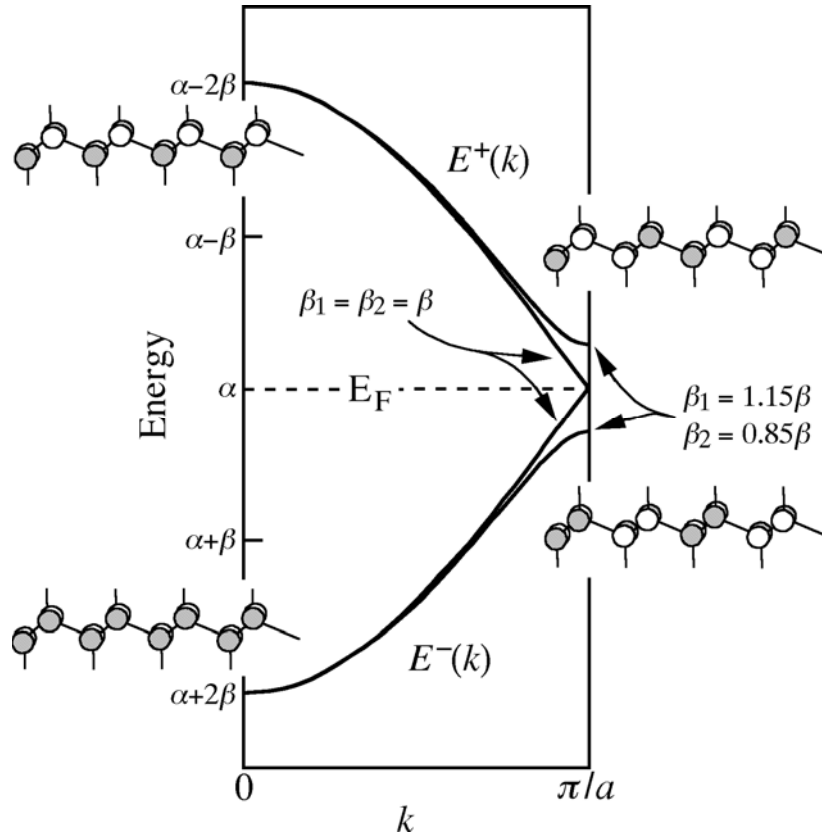
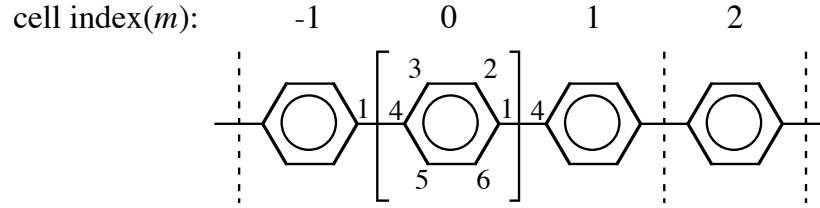


Figure 4. The Hückel π bands for polyacetylene, for two choices of β_1 and β_2 .

Pictorial representations of the chain orbitals at $k = 0$ and $1/2a$ reveal the origin of the energetic spreading (called *dispersion*) of the two bands. Just as we would expect, the most stabilized orbital is the totally bonding combination we see at $k = 0$ and the highest energy orbital is the maximally antibonding orbital that is also at $k = 0$. Figure 4 shows that neither of these orbitals are much affected by the presence of bond alternation in the chain because such an alternation stretches as many bonds as it shortens. For the

totally bonding chain orbital, this means that there are as many bonding interactions weakened as strengthened; for the completely antibonding orbital, as many antibonding interactions are increased as are decreased. The situation is quite different at $k = 1/2a$. Here, one of the orbitals is bonding across the bonds which are shortened and antibonding for those bonds which are lengthened; for the other orbital, just the opposite holds. The net result is that bond alternation introduces a band gap that is just equal to the energy difference between these two orbitals. Since the chain has one π electron per carbon center, two carbon atoms per unit cell, and N unit cells, there are $2N$ electrons to be placed into the N lowest energy chain orbitals. This is exactly the number of chain orbitals there are in each energy band (since there is one orbital per band for each of the N k - points). Therefore, the lowest energy band is entirely filled, while the upper band is unoccupied when the chain is in its lowest electronic state. The level to which electrons fill is called the *Fermi level* (E_F). Notice that if the polyacetylene chain did not exhibit bond alternation, there would be no band gap and the chain would be metallic. However, a glance at Figure 4 shows that the distortion stabilizes occupied levels while destabilizing only the unoccupied levels, leading us to conclude that the bond alternation should be energetically favorable. This special case of what is called *Peierls theorem*, which states that one dimensional systems are never metallic because they will always distort in such a way that a band gap is opened at the Fermi level.

Let us consider a problem with a bit more complexity — one where an analytical solution for all the bands may not be accessible and where it will be advantageous to account for more than just the translational symmetry. We will examine the π -electron (Hückel) problem for *p*-polyacene, which is just a polymer of biphenyl groups linked as shown below. Since there are six carbon atoms per unit cell we expect that without



further simplification, we will have to deal with k -dependent 6×6 secular determinants. However, if we use the proper basis of benzene fragment orbitals, the situation is considerably simplified. The polyacene chain has two mirror planes of symmetry beyond the mirror in which all the atoms lie. (Of course, it is the presence of the plane in which the atoms lie that enables us to separate the π electron problem from the σ electron problem in the first place.) These mirrors are respectively coincident with (σ_1) and perpendicular to the chain axis (σ_2). The benzene fragment orbitals (Figure 5) are a convenient starting point for analyzing the polymer because they are symmetry-adapted with respect to these mirror planes. Of the two mirror planes, σ_1 is the most useful for simplifying the problem before us. Because σ_1 contains the chain axis, any reflection of a Bloch orbital has no effect on its wavevector k . The wavevector k specifies the behavior of a Bloch orbital with respect to translational symmetry and a reflection operation through σ_1 commutes with any translation operation. Therefore, any Bloch orbital for this system can be labeled not only with a wavevector k , but also with a label that indicates its symmetry with respect to reflection through the σ_1 plane. (The same argument applies to the plane in which the atoms lie.) Of the labels attached to the benzene fragment orbitals, the first indicates the orbitals' σ_1 reflection symmetry — four of the orbitals are symmetric, two are antisymmetric. This means that we can now block-factor each of the k -dependent 6×6 secular determinants into a pair of 4×4 and 2×2 determinants.

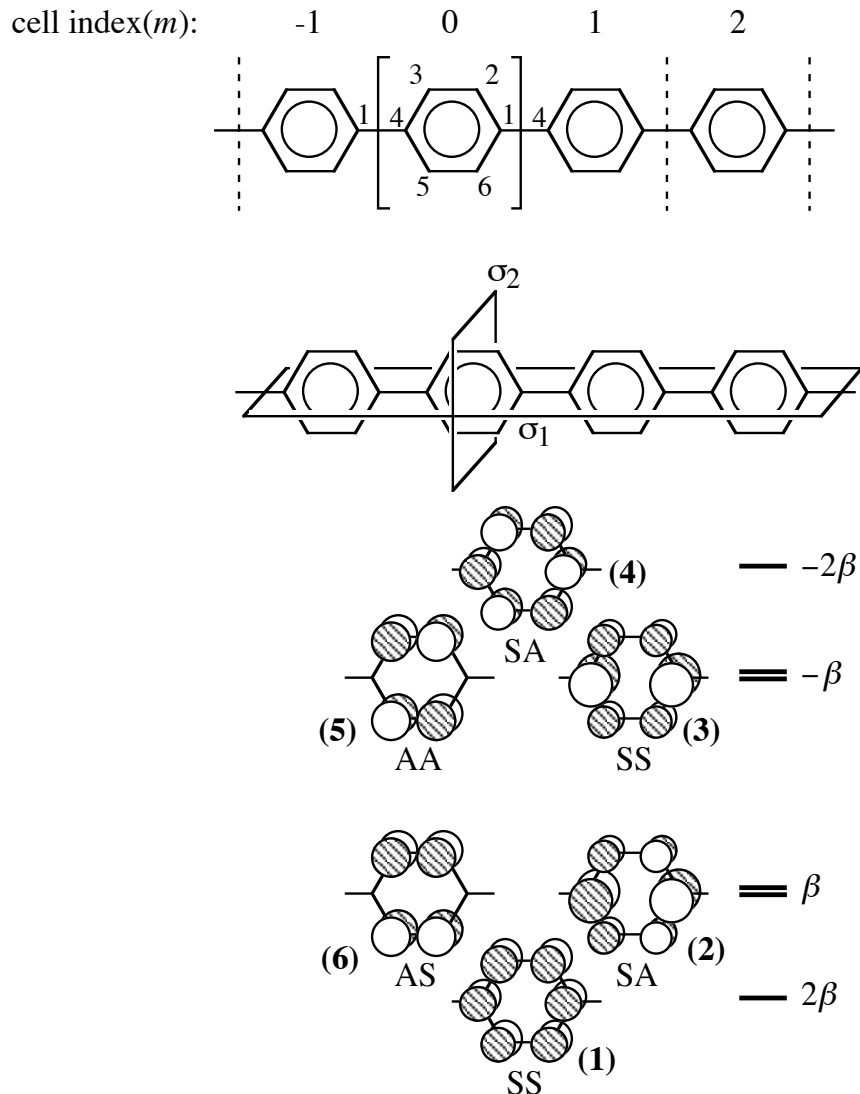
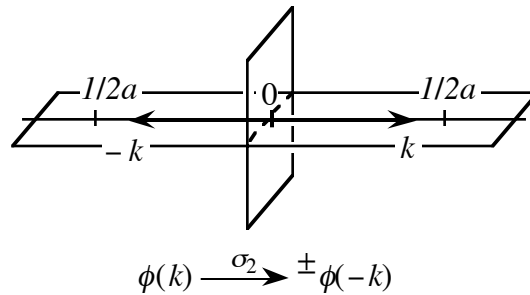


Figure 5. The benzene π orbitals used for building up the band structure of *p*-polyacene.

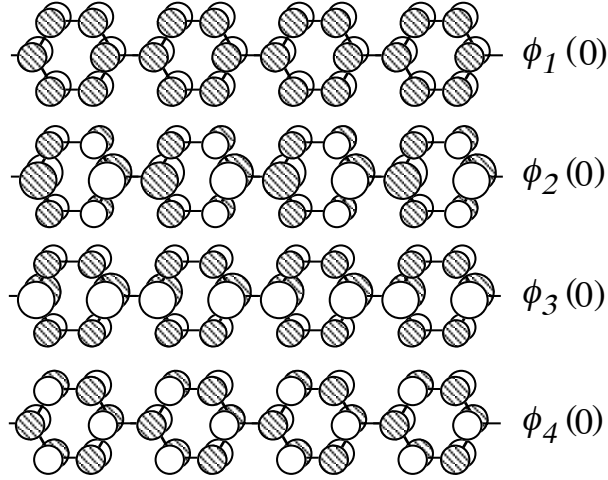
The two antisymmetric bands, built up from the benzene orbitals of AA and AS symmetry, are simply handled. Since neither of these fragment orbitals has a coefficient on the atoms that link the rings to their neighbors (atoms 1 and 4), when the 2×2 Hückel secular determinant is set up using these orbitals as a basis the off-diagonal matrix elements are zero. We know that there will be two bands which are completely flat (i.e., the $E(k)$ vs k curves will show no dispersion) and will lie at the same energies as the benzene orbitals from which they derive, β and $-\beta$.

The symmetric bands, for general k – points , are built from the benzene orbitals of SS and SA symmetry which have labels **1** through **4** in Fig. 5. A 4×4 secular determinant is analytically intractable, but there are special k – points , 0 and $1/2a$, where some simplification is possible. To understand how this occurs, its useful to look at the Bloch basis orbitals at these two k – points . For these special points, we can see that the Bloch basis orbitals are either symmetric or antisymmetric with respect to reflection in the σ_2 plane. For $k = 0$ or $1/2a$, $e^{2\pi ika} = 1$ or -1 , and this means that *only* for these k – points will the Bloch orbitals exhibit this symmetry. This is quite general and can be understood by noting that k , viewed as a vector in one dimension, is transformed to $-k$ after being reflected through the σ_2 plane. Viewed another way, we note that a Bloch function, $\phi(k)$, exhibits orbital coefficients in one cell which are the same as the previous cell after moving in the *positive x direction*, after multiplication by $e^{2\pi ikx}$. After reflecting through the σ_2 plane, the same pattern appears when we move in the *negative x direction*. Because of this behavior, the resulting function belongs to a representation at $-k$ — $\phi(k)$ is transformed to $\pm\phi(-k)$ by reflecting through a plane perpendicular to k .



For $k = 0$, this obviously implies that a reflection through the σ_2 plane leaves us with a function belonging to the same k – point . Because the points $k = 1/2a$ and $-1/2a$ really correspond to the *same* irreducible representation, this reflection is also “a good symmetry operation” for $k = 1/2a$ as well. In general, the set of operations which carry k onto k or an equivalent wavevector form a group that is called the “group of k ”.

$$k = 0 \quad \phi_{\mu}(k) \sim \phi_{\mu}(0) + \phi_{\mu}(1) + \phi_{\mu}(2) + \dots$$



$$k = 1/2a \quad \phi_{\mu}(k) \sim \phi_{\mu}(0) - \phi_{\mu}(1) + \phi_{\mu}(2) - \dots$$

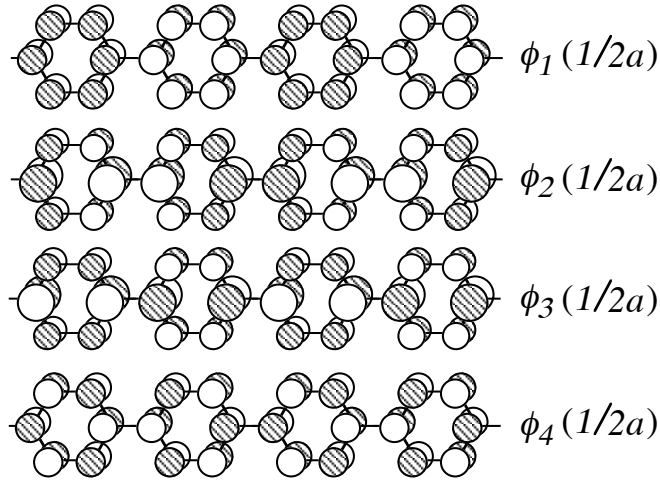


Figure 6. The Bloch basis functions for p -polyacene are shown for $k = 0$ and $1/2a$.

The discussion in the preceding paragraph indicates that at $k = 0$ and $1/2a$ we subdivide the 4×4 secular determinant for the symmetric bands into two 2×2 determinants, one for the bands built from SS symmetry orbitals (**1** and **3**) and the other for those built from SA symmetry orbitals (**2** and **4**). Using the numerical labels we will construct the appropriate matrix elements. From the benzene orbital energies we write: $H_{11}^0 = 2\beta$, $H_{22}^0 = \beta$, $H_{33}^0 = -\beta$, $H_{44}^0 = -2\beta$. Each of the ring orbitals interacts with its likeness in neighboring cells: $H_{11}^1 = H_{11}^{-1} = \beta/6$, $H_{22}^1 = H_{22}^{-1} = -\beta/3$, $H_{33}^1 = H_{33}^{-1} = \beta/3$,

$H_{44}^1 = H_{44}^{-1} = -\beta/6$. The nonzero off-diagonal matrix elements we will need are:
 $H_{13}^1 = H_{13}^{-1} = -\beta/3\sqrt{2}$, $H_{24}^1 = H_{24}^{-1} = -\beta/3\sqrt{2}$. With these we can get the $H_{ij}(k)$ matrix elements :

$$H_{11}(k=0) = \sum_p e^0 H_{11}^p = 2\beta + 2 \cdot (\beta/6) = 7\beta/3$$

$$H_{22}(k=0) = \beta + 2 \cdot (-\beta/3) = \beta/3$$

$$H_{33}(k=0) = -\beta + 2 \cdot (\beta/3) = -\beta/3$$

$$H_{44}(k=0) = -2\beta + 2 \cdot (-\beta/6) = -7\beta/3$$

$$H_{13}(k=0) = 2 \cdot (-\beta/3\sqrt{2}) = -2\beta/3\sqrt{2}$$

$$H_{24}(k=0) = 2 \cdot (-\beta/3\sqrt{2}) = -2\beta/3\sqrt{2}$$

$$H_{11}(k=\pi/a) = \sum_p (-1)^p H_{11}^p = 2\beta - 2 \cdot (\beta/6) = 5\beta/3$$

$$H_{22}(k=\pi/a) = \beta - 2 \cdot (-\beta/3) = 5\beta/3$$

$$H_{33}(k=\pi/a) = -\beta - 2 \cdot (\beta/3) = -5\beta/3$$

$$H_{44}(k=\pi/a) = -2\beta - 2 \cdot (-\beta/6) = -5\beta/3$$

$$H_{13}(k=\pi/a) = -2 \cdot (-\beta/3\sqrt{2}) = 2\beta/3\sqrt{2}$$

$$H_{24}(k=\pi/a) = -2 \cdot (-\beta/3\sqrt{2}) = 2\beta/3\sqrt{2}$$

Using the matrix elements above, we set up the secular equations for the SS and SA subblocks at $k=0$ and $1/2a$:

$k=0$:

$$\text{SS block: } \begin{vmatrix} H_{11}(k) - E & H_{13}(k) \\ H_{31}(k) & H_{33}(k) - E \end{vmatrix} = \begin{vmatrix} 7\beta/3 - E & -2\beta/3\sqrt{2} \\ -2\beta/3\sqrt{2} & -\beta/3 - E \end{vmatrix} = 0$$

$$\text{SA block: } \begin{vmatrix} H_{22}(k) - E & H_{24}(k) \\ H_{42}(k) & H_{44}(k) - E \end{vmatrix} = \begin{vmatrix} \beta/3 - E & -2\beta/3\sqrt{2} \\ -2\beta/3\sqrt{2} & -7\beta/3 - E \end{vmatrix} = 0$$

$k=\pi/a$:

$$\text{SS block: } \begin{vmatrix} H_{11}(k) - E & H_{13}(k) \\ H_{31}(k) & H_{33}(k) - E \end{vmatrix} = \begin{vmatrix} 5\beta/3 - E & 2\beta/3\sqrt{2} \\ 2\beta/3\sqrt{2} & -5\beta/3 - E \end{vmatrix} = 0$$

$$\text{SA block: } \begin{vmatrix} H_{22}(k) - E & H_{24}(k) \\ H_{42}(k) & H_{44}(k) - E \end{vmatrix} = \begin{vmatrix} 5\beta/3 - E & 2\beta/3\sqrt{2} \\ 2\beta/3\sqrt{2} & -5\beta/3 - E \end{vmatrix} = 0$$

The solutions are:

$$k=0: \quad \text{SS block: } E = \beta \pm \sqrt{2}\beta; \quad \text{SA block: } E = -\beta \pm \sqrt{2}\beta$$

$$k = \pi/a: \quad \text{SS block: } E = \pm\sqrt{3}\beta; \text{ SA block: } E = \pm\sqrt{3}\beta.$$

The energy bands for values of k between 0 and $1/2a$ are more difficult to calculate analytically, but symmetry considerations tell us how to connect the bands between these points. Quite simply, all Bloch basis orbitals that are symmetric with respect to reflection through σ_1 (built from SS *and* SA benzene fragment orbitals) will mix for intermediate values of k . This means that the energy bands must be connected without introducing any crossings among symmetric bands when moving from 0 to $1/2a$. The total π band structure is plotted in Figure 7.

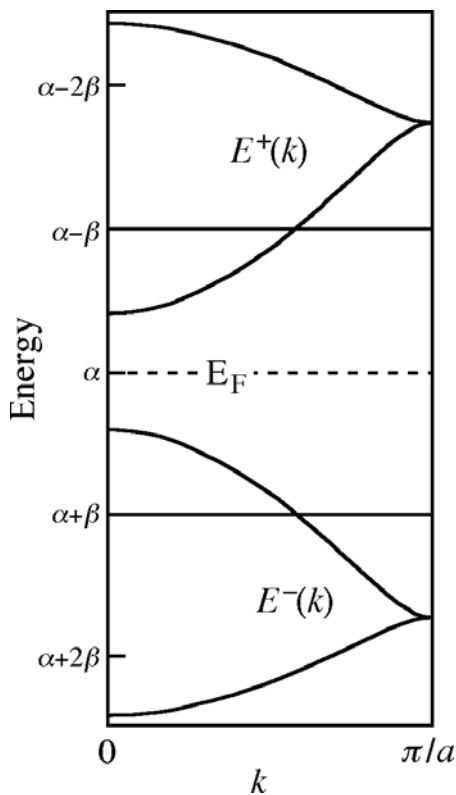


Figure 7. The π band structure for p -polyacene is shown. Note that there are six electrons per unit cell and so the bottom three bands are occupied. The presence of band gap between occupied and unoccupied bands indicates that this should be a semiconducting polymer.