Abstract
We discuss a conducting organic polymer named polyacetylene. First, we explain its structure by means of the tight binding approximation and the Peierls distortion. Then, we present the Su-Schrieffer-Heeger model of polyacetylene and point out its topological nature via the introduction of the winding number and edge states. We further elaborate on edge states in terms of chiral symmetry. Finally, we elucidate excitations of the model in the form of moving domain boundaries, hosting localized electronic states and touch on their analogy to solitons.
1 Introduction

Polymers – the term derives from the ancient Greek words polus meaning “many” and meros meaning “parts” – are large elongate molecules, composed of multiple repeating units. Although natural polymeric materials such as wood, bone or skin have been used by man since prehistoric time, and organic chemistry as a science dates back to the eighteenth century, polymer science on a molecular basis developed only in the twentieth century.

Because polymers first studied were saturated polymers, in which all of the four valence electrons of carbon are used up in covalent bonds, they were insulators and therefore regarded as uninteresting from the point of view of electronic materials. However, in conjugated polymers, in which one valence electron per carbon atom is left unpaired, the fundamentally different electronic configuration leads to charge carrier mobility along the backbone of the polymer. In 1976, American physicist Alan J. Heeger, American chemist Alan MacDiarmid and Japanese chemist Hideki Shirakawa discovered conducting polymers and the ability to dope these polymers over the full range from insulator to metal. They were awarded the 2000 Nobel Prize in Chemistry “for the discovery and development of conductive polymers” [1].

The representative example of a conducting polymer and the subject of this seminar is an organic polymer with the repeating unit \((C_2H_2)_n\) named polyacetylene. The Su-Schrieffer-Heeger model, put forward to understand its phenomena, is the simplest example of a (one-dimensional) topological insulator. In the last years, topological effects have become a hot topic in condensed-matter physics and in 2016, the Nobel Prize in Physics was awarded to British physicists David J. Thouless, F. Duncan M. Haldane and J. Michael Kosterlitz “for theoretical discoveries of topological phase transitions and topological phases of matter”.

2 The Structure of Polyacetylene

In polyacetylene, each carbon atom is sp\(^2\) hybridized and forms three covalent \(\sigma\) bonds in the \(xy\)-plane: two with the two neighbouring carbon atoms along the backbone of the polymer and one with a hydrogen atom.
In terms of the band structure theory, valence bands constructed from sp\(^2\) orbitals of carbon atoms and s orbitals of hydrogen atoms are completely filled, conduction bands are completely empty and there are band gaps of \(\sim 10\) eV separating valence bands and conduction bands. Since there are no partially filled bands and the band gap is large, electrons forming the \(\sigma\) bonds do not contribute to electrical conductivity of polyacetylene. The optimal bond angle of approximately 120° between the three \(\sigma\) bonds can be obtained by two possible arrangements of the carbon atoms, the trans and cis configuration, with two and four CH monomers per unit cell, shown in Fig. 1. It turns out that for trans polyacetylene, the ground state is degenerate, which is not the case with cis polyacetylene, as the hydrogen atoms break the symmetry. For this reason, only the trans configuration is considered in this seminar.

![cis-polyacetylene](image1.png) ![trans-polyacetylene](image2.png)

Figure 1: The two possible configurations of polyacetylene. Adapted from [7].

2.1 The Tight-Binding Method

The sp\(^2\) hybridization leads formally to one unpaired valence electron per carbon atom, occupying a 2p\(_z\) orbital – a \(\pi\) electron. The \(\pi\) electrons are considered within the tight-binding approximation, that deals with the case in which the overlap of the relevant atomic wave functions, centered at different atoms – in this case the 2p\(_z\) orbitals of carbon atoms – is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant [2]. It must be taken into account that the explicit Coulomb interactions between electrons are missing from the tight-binding approximation and the resulting tight-binding Hamiltonian is thus a one-electron Hamiltonian.

The tight-binding approximation is based on two assumptions, namely that in the vicinity of each point of the Bravais lattice the crystal Hamiltonian, \(\hat{H}\), can be approximated by the Hamiltonian of a single atom, \(\hat{H}_{\text{at}}\), located at the Bravais lattice point, \(\hat{H}(r) = \hat{H}_{\text{at}}(r) + \Delta U(r)\), and that the bound states of the atomic Hamiltonian are well localized. The term \(\Delta U(r) < 0\) contains all the corrections to the atomic potential required to produce the full crystal potential and is presumably small compared with the atomic potential, so that it can be viewed from the perspective of the first-order perturbation theory: to lift the degeneracy, \(\Delta \hat{U}\) is diagonalized in the basis of the relevant atomic bound states, centered at different points of the Bravais lattice.

Were the lengths of bonds along the backbone of a polyacetylene molecule equal, the tight-binding Hamiltonian with imposed periodic boundary conditions would have the approximate form

\[
\hat{H} = \sum_{j=1}^{N} (-t \langle j | j + 1 | h.c. \rangle + \text{const.}),
\]

where the sum runs over the sites of the carbon atoms, \(t = \langle j | -\Delta \hat{U} | j + 1 \rangle\) is the hopping integral, \(|j\rangle\) denotes the 2p\(_z\) orbital of the \(j\)-th carbon atom, and h.c. stands for Hermitian conjugation. Since the Hamiltonian is translationally invariant, it can be diagonalized by means of the Fourier transform,

\[
|j\rangle = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \exp \left( -in \frac{2\pi}{Na} j a \right) |n\rangle, \quad \frac{2\pi}{Na},
\]

where \(a\) is the distance between successive carbon atoms along the axis of the polymer, as shown in Fig. 3(a).
In the basis of the Bloch states, \( \{ |k \rangle ; \ k \in \text{the first Brillouin zone} \} \), the Hamiltonian is diagonal,

\[
\hat{H} = -2t \sum_k \cos k |k \rangle \langle k | + \text{const.} \quad (3)
\]

The band structure is shown in Fig. 2. It has been taken into account that, because p orbitals and corrections to the atomic potential are real, the hopping integral is also real. Since in polyacetylene, there are \( N \pi \) electrons altogether (one per carbon atom), half-filling of the band due to the twofold spin degeneracy would imply a metallic state. The fact that polyacetylene is not a metal is due to the Peierls instability.

\[\text{Figure 2: The band structure of the Hamiltonian, given by Eq. (3).}\]

2.2 The Peierls Instability

If the atoms in a chain are equidistant, with a distance \( a \), then all multiples of \( a \) are vectors of the Bravais lattice, and the first Brillouin zone is the interval \(-\pi/a < k < \pi/a\), containing \( N \) points, if \( N \) is the number of atoms. If the chain is distorted by displacing each atom a little, the displacement repeating every \( r \)th atom, the translational symmetry is reduced: the primitive cell of the distorted chain contains \( r \) atoms, only multiples of \( ra \) are vectors of the Bravais lattice and the first Brillouin zone is the interval \(-\pi/ra < k < \pi/ra\), containing only \( N/r \) points. For the number of one-electron eigenstates to remain the same, each band of the equidistant chain splits into \( r \) bands of the distorted chain.

\[\text{Figure 3: Upon displacement of every second carbon atom, the original Bravais lattice with a distance } a \text{ transforms into the Bravais lattice with a distance } 2a \text{ and a diatomic basis. Filled (empty) circles represent sites on sublattice A (B).}\]

In the case of a small displacement of every second atom, shown in Fig. 3(b), considering only first-order corrections to the hopping integral, \( t = t_0 \pm t_1 \), the tight-binding Hamiltonian reads

\[
\hat{H} = \sum_{j=1}^{N/2} \left[ -(t_0 + t_1) |j, A\rangle \langle j, B| - (t_0 - t_1) |j, B\rangle \langle j + 1, A| + h.c. \right] + \text{const.},
\]

where the sum runs over the vectors of the Bravais lattice, and \( A \) and \( B \) denote positions of atoms within the primitive cell. Upon application of the Fourier transform, the Hamiltonian becomes

\[
\hat{H} = \sum_k |k\rangle \langle k| \otimes \left[ -(t_0 + t_1) |A\rangle \langle B| - (t_0 - t_1) e^{ik2a} |A\rangle \langle B| + h.c. \right] + \text{const.} = \sum_k |k\rangle \langle k| \otimes \hat{H}(k)
\]

and the diagonalization of the bulk Hamiltonian \( \hat{H}(k) \) in the two-dimensional Hilbert space, spanned by \( |A\rangle \) and \( |B\rangle \), results in two bands, specified by the dispersion relation

\[
E_{1,2}(k) = \pm 2\sqrt{t_0^2 \cos^2(ka) + t_1^2 \sin^2(ka)}
\]

and separated by a band gap of \( 4t_1 \). The splitting into two separated bands is shown in Fig. 4. If the original band is completely filled, the total energy of the electrons will not be affected by the distortion.
But if the original band is half-filled, as is the case with polyacetylene, then the states which are displaced downwards in energy will be occupied, and the states which are raised will be empty, so that the total energy of the electrons will decrease. The competition between the reduction of the electronic energy and the increase in the elastic energy of the chain leads to an equilibrium modulation of the bond length.

It follows that for a one-dimensional metal with a partially filled band – as well as for polyacetylene – the equidistant chain structure will never be stable, since one can always find a distortion with a suitable value of \( r \) for which a band gap will occur at the Fermi level [3]. In polyacetylene, the Fermi level lies at \( k = \frac{\pi}{2a} \), the chain is dimerized with a modulation of the bond length of \( \pm 0.04 \) \( \AA \) (the average bond length is \( a = 1.22 \) \( \AA \)) and there is a band gap of \( 4t_1 = 1.4 \) eV (\( 4t_0 = 10 \) eV) [4].

3 The Su-Schrieffer-Heeger Model

The above model was proposed by American physicists Wu-Pei Su, John Robert Schrieffer (best known for the famous BCS theory of superconductivity which he proposed alongside John Bardeen and Leon Cooper) and Alan J. Heeger in 1979. Its construction was based on two fundamental assumptions: first, the \( \pi \) electrons can be treated in the tight-binding approximation. Secondly, because the displacements of carbon atoms are small compared with the average bond length, the hopping integrals are approximately linear functions of the distances between successive carbon atoms,

\[
t_{j+1,j} = t_0 - \alpha (u_{j+1} - u_j),
\]

where \( t_{j+1,j} \) is the hopping integral from site \( j \) to site \( j+1 \), \( u_j \) is the displacement of the \( j \)th carbon atom, and \( \alpha \) is the electron-phonon coupling constant. Bearing in mind that atoms are not static, the resulting Su-Schrieffer-Heeger (SSH) Hamiltonian is written as the sum of three terms:

\[
\hat{H} = -\sum_j (t_{j+1,j} |j + 1\rangle \langle j| + \text{h.c.}) + \sum_j \left[ \frac{1}{2} M \dot{u}_j^2 + \frac{1}{2} K (u_{j+1} - u_j)^2 \right],
\]

where \( M \) is the mass of the CH unit and \( K \) is the effective spring constant of the \( \sigma \) bond between successive carbon atoms. Due to the spontaneous symmetry breaking which results from the Peierls instability, \( \langle u_j \rangle = \pm (-1)^j u_0 \). Using the mean-field approximation, \( u_j \approx \langle u_j \rangle \), the Hamiltonian, given by Eq. (7), reduces to Eq. (4). Since \( u_0 \) and \(-u_0 \) both minimize the energy, the ground state is doubly degenerate. Consequently, one expects excitations to exist in the form of domain walls [4], which will turn out to be of vital importance for the existence of solitons in polyacetylene.

Defining the intracell and intercell hopping integrals \( v = -(t_0 + t_1) \) and \( w = -(t_0 - t_1) \) and omitting the constant term the SSH Hamiltonian becomes

\[
\hat{H} = v \sum_j |j, A\rangle \langle j, B| + w \sum_j |j, B\rangle \langle j + 1, A| + \text{h.c.},
\]

Figure 4: The band structure, given by Eq. (6), for \( t_1 = 0 \) in black colour (the same band structure as in Fig. 2) and for \( t_1/t_0 = 0.2 \) in red colour.

Figure 5: The geometry of the SSH model for a finite chain with open boundary conditions. Filled (empty) circles are sites on sublattice A (B). Taken from [5].
where $N$ is now half the number of carbon atoms and parameters $v$ and $w$ can be chosen nonnegative without loss of generality [5]. The geometry of the SSH model (for a finite chain with open boundary conditions) is shown in Fig. 5. Assuming periodic boundary conditions, the bulk Hamiltonian $\hat{H}(k)$ can be written as

$$\hat{H}(k) = (v + w \cos k) \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + w \sin k \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = d_x(k)\hat{\sigma}_x + d_y(k)\hat{\sigma}_y,$$

so that the structure within the primitive cell of the two one-electron eigenstates with crystal momentum $k$ is given by the direction of the vector $d(k)$, and the energy by its magnitude. Although the bulk Hamiltonian of any model with a diatomic basis is of the form $\hat{H}(k) = d(k) \cdot \hat{\sigma}$, the SSH Hamiltonian is somewhat special: the vector $d(k)$ has no $z$-component, and that in turn makes the SSH Hamiltonian exhibit chiral symmetry, which will be discussed in section 3.2.

As the crystal momentum runs over the first Brillouin zone, the vector $d(k)$ traces out a circle which due to chiral symmetry lies in the $d_xd_y$-plane. The circle is centered at $(d_x, d_y) = (v, 0)$ and has a radius of $w$, as shown in Fig. 6 for two different choices of the parameters. In the case of 2 electrons per unit cell, the SSH model describes an insulator as long as the circle avoids the origin: if there was a $k$ for which $d(k) = 0$, the gap would close at that $k$. The topology of the fully occupied valence band can be characterized by an integer representing the total number of times that a closed curve which the vector $d(k)$ traces out travels counterclockwise around the origin – a topological invariant called the winding number $\nu$. A topological invariant is an integer that can only be changed by a ferocious enough deformation of the object in question. The classic example is the number of holes an object has: in terms of topology, a coffee mug is identical to a donut, because they both have one hole, whereas a sphere can only be made into a torus, if a hole is drilled through it. In our case, all chiral symmetric bulk Hamiltonians with $\nu = 1$ are topologically equivalent, and all chiral symmetric bulk Hamiltonians with $\nu = 0$ are topologically equivalent, whereas the winding number of a chiral symmetric bulk Hamiltonian can only be changed by closing the band gap.

Sticking to the SSH model of polyacetylene, for $v > w$, $\nu = 0$ and the model describes a trivial insulator for the reason, which will be revealed in section 3.1. For $v < w$, $\nu = 1$ and the model describes a topological insulator. For $v = w$, however, the winding number remains undefined and the model describes a conductor. In order to continuously change the winding number, the circle has to meet the origin at some point during the deformation: if there exists an interface where a crystal interpolates between the trivial (which may as well be vacuum [6]) and the topological phase as a function of position, the energy gap has to vanish somewhere along the way, because it is otherwise impossible for the topological invariant to change.

There will therefore be electronic states with energy in the band gap bound to the region where the winding number changes – the edge states [6].

### 3.1 Edge States

A polyacetylene molecule not only has a bulk, which is considered translation invariant and can be treated with periodic boundary conditions, but also boundaries or edges. In the two completely dimerized limits, shown in Fig. 7, the trivial limit, $w = 0$, and the topological limit, $v = 0$, the chain does not need to be infinite to host unambiguously defined bulk and edge states.

The energy eigenstates of the bulk in the two completely dimerized limits can be chosen as even and odd superpositions of 2 $p_z$ orbitals, centered at the two different sites of each dimer: in the trivial limit,

$$\hat{H} (|j, A\rangle \pm |j, B\rangle) = \pm v (|j, A\rangle \pm |j, B\rangle) ; \quad j = 1 \ldots N,$$

...
and in the topological limit,
\[ \hat{H} (|j, B\rangle \pm |j+1, A\rangle) = \pm w (|j, B\rangle \pm |j+1, A\rangle) ; \quad j = 1 \ldots N-1. \] (11)

Figure 7: The two completely dimerized limits of the SSH model for a finite chain with open boundary conditions, the trivial (top) and the topological limit (bottom). Taken from [5].

In k-space, one gets delocalized energy eigenstates in two flat bands, separated by a band gap of 2|v − w|.
In the trivial limit, there are no edge states, because the winding number of the vacuum is zero as well, whereas in the topological limit, the two sites at the ends of the chain host one zero-energy edge state each: \( \hat{H} |1, A\rangle = \hat{H} |N, B\rangle = 0. \) An edge state can be either empty, singly or doubly occupied, again due to the twofold spin degeneracy.

Fig. 7 also provides an answer to the question why the trivial phase is actually termed trivial, namely because it is continuously connected to the molecular limit. On the other hand, if an open chain in the topological phase is broken into pieces by cutting the weaker bonds, the atoms at the ends of the chain are left unpaired.

Outside the completely dimerized limit, yet still in the topological phase, \( v < w \), the energies of the edge states remain very close to zero: because they lie inside the band gap of the bulk, the edge states have to be localized at the ends of the chain. It turns out [5] that in finite chains, the almost-zero-energy edge states are approximately even and odd superpositions of the zero-energy edge states of an infinite chain, exponentially localized at the left and right end of the chain, as shown in Fig. 8,

\[ |L\rangle = \sum_{j=1}^{N} a_j |j, A\rangle ; \quad a_j = (-1)^{j-1} e^{-(j-1)/\xi} \quad \text{and} \quad |R\rangle = \sum_{j=1}^{N} b_j |j, B\rangle ; \quad b_j = (-1)^{N-j} e^{-(N-j)/\xi}, \] (12)

where \( \xi = 1/\log(w/v) \) is a localization length.

Figure 8: Edge states of a chain of length \( N = 10 \) for \( v = 0.5, w = 1 \).

Due to the exponentially small overlap of the zero-energy edge states, localized at the ends of an infinite chain in a finite chain, the energies of the almost-zero-energy eigenstates are proportional to \( \exp(-N/\xi) \).
3.2 Edge States and Chiral Symmetry

Defining sublattice projectors

\[ \hat{P}_A = \sum_{j=1}^{N} |j, A \rangle \langle j, A| \quad \text{and} \quad \hat{P}_B = \sum_{j=1}^{N} |j, B \rangle \langle j, B| \]  

it can be easily seen that

\[ \hat{P}_A \hat{H} \hat{P}_A = \hat{P}_B \hat{H} \hat{P}_B = 0 \quad \text{and} \quad \hat{H} = \hat{P}_A \hat{H} \hat{P}_A + \hat{P}_B \hat{H} \hat{P}_B . \]  

These equalities are a direct consequence of the fact that the SSH Hamiltonian is bipartite, which means that it induces no transitions between sites on the same sublattice, and hold regardless of whether the hopping integrals depend on position. The two equalities of Eq. (14) can be combined into

\[ \left( \hat{P}_A - \hat{P}_B \right) \hat{H} \left( \hat{P}_A - \hat{P}_B \right) = -\hat{H} . \]  

The SSH Hamiltonian thus exhibits chiral symmetry, \( \hat{\Gamma} \hat{H} \hat{\Gamma} = -\hat{H} \), where \( \hat{\Gamma} = \hat{P}_A - \hat{P}_B \) is unitary and Hermitian, \( \hat{\Gamma} \hat{\Gamma}^\dagger = \hat{\Gamma}^2 = 1 \) \[5\].

The spectrum of a chiral symmetric Hamiltonian is symmetric: if \( |\psi\rangle \) is an eigenstate of \( \hat{H} \) with energy \( E \), \( \hat{\Gamma} |\psi\rangle \) is an eigenstate of \( \hat{H} \) with energy \(-E\), \( \hat{\Gamma} \hat{H} |\psi\rangle = -\hat{\Gamma} \hat{H} |\psi\rangle = -E \hat{\Gamma} |\psi\rangle \). Consequently, if a deformation of a perfectly dimerized chain brings a non-zero energy eigenstate \( |\psi\rangle \) to zero energy, \( \hat{\Gamma} |\psi\rangle \) moves simultaneously to zero energy (and vice versa). Bearing in mind that the dimension of the Hilbert space does not change given that the deformation does not affect the number of carbon atoms in the chain, edge states can only emerge (vanish) in pairs.

If \( |\psi\rangle \) is an eigenstate of \( \hat{H} \) with non-zero energy, \( |\psi\rangle \) and \( \hat{\Gamma} |\psi\rangle \) are orthogonal. As a result, the expected values of both sublattice projectors in state \( |\psi\rangle \) are equal,

\[ 0 = \langle \psi | \hat{\Gamma} | \psi \rangle = \langle \psi | \hat{P}_A | \psi \rangle - \langle \psi | \hat{P}_B | \psi \rangle . \]

On the contrary, a zero-energy eigenstate can be chosen as a superposition of 2 \( p_z \) orbitals of carbon atoms on only one sublattice:

\[ \hat{H} \hat{P}_A |\psi\rangle = \hat{H} \left( \hat{\Gamma} + \hat{P}_B \right) |\psi\rangle = \hat{H} \hat{P}_B |\psi\rangle \quad \text{or} \quad \langle \psi | \hat{P}_B \hat{H} \hat{P}_B |\psi\rangle = \langle \psi | \hat{\Gamma} |\psi\rangle = 0 . \]

Since \( \hat{P}_B \hat{H} \hat{P}_A \neq 0 \), the last equality allows for two different scenarios: if \( \hat{P}_B |\psi\rangle = 0 \) or \( \hat{P}_A |\psi\rangle = 0 \), \( |\psi\rangle \) is already a superposition of orbitals on only one sublattice. The other way round, \( \hat{P}_A |\psi\rangle \) and \( \hat{P}_B |\psi\rangle \) are orthogonal zero-energy eigenstates.

As a consequence, if each zero-energy edge state is chosen as a superposition of 2 \( p_z \) orbitals on only one sublattice, the number of zero-energy edge states on one sublattice minus the number of zero-energy edge states on the other sublattice is another topological invariant of the SSH model: because zero-energy edge states can only emerge (vanish) in pairs, the creation (annihilation) of a pair of zero-energy edge states results in an increase (a decrease) of one zero-energy edge state on each sublattice \[5\].

3.3 Domain Walls as Solitons

Edge states do not only occur at ends of an open chain, but also at interfaces between different insulating domains within the chain. The concept is again easy to grasp in the completely dimerized limit, shown in Fig. 9. There are two types of domain walls, both of which host zero-energy edge states: those containing isolated sites and those containing trimers. On a trimer, the zero-energy edge state is an odd superposition of 2 \( p_z \) orbitals, centered at the two end sites. Since a domain wall converts one phase into another, domain walls can only emerge (vanish) in pairs.

Outside the completely dimerized limit, the almost-zero-energy edge states of a pair of domain walls at a finite distance will be approximately even and odd superpositions of the zero-energy edge states of a pair of infinitely separated domain walls, localized exponentially at each domain wall.

\[1\] According to the first equality of Eq. (16).
In an electrically neutral polyacetylene molecule, the negative-energy edge state will be doubly occupied and the positive-energy edge state will be empty. For a large enough separation of a pair of domain walls, they can be viewed as non-interacting, hosting one zero-energy edge state each. Although the concept of the domain wall has been introduced as an abrupt change from one phase to another, in agreement with the predictions of the SSH model, given by Eq. (7), experiments indicate that the structural relaxation in the vicinity of a domain boundary extends over approximately 14 carbon atoms [1].

Because the energy of the system is – as long as the separation of domain walls is large enough – independent of the positions of domain walls, they can move freely along the chain. In view of the fact that a domain wall hosting an edge state is a localized shape preserving excitation which propagates freely, it has been historically referred to as a soliton.

For a neutral soliton, the edge state is singly occupied, so that the negative charge of the electron neutralizes (together with the three electrons forming the \( \sigma \) bonds) the positive charge of the carbon nucleus. Since an electron has a half spin and all the valence states in an electrically neutral polyacetylene molecule are spin paired, it follows that a neutral soliton has spin 1/2. Since a half-spin object would be expected to carry charge \( \pm e_0 \), as in the case of an electron or a hole, the excitation is in fact very unusual. Equally unusual is that if the edge state is empty (doubly occupied), a soliton carries positive (negative) charge of magnitude \( e_0 \) and has zero spin, rather than spin 1/2 as an electron or a hole. These reversed spin-charge relations are a fundamental feature of the soliton model of polyacetylene and are supported by experiment [7]. In usual semiconductors, electrons (holes) in partially filled (empty) bands exclusively account for electrical conductivity. But in polyacetylene, it turns out that the formation of a pair of solitons is energetically more favourable. In intrinsic polyacetylene, solitons are neutral. But in n-doped (p-doped) polyacetylene, solitons are negatively (positively) charged and are actually the predominant mobile charge carriers [4]. To get a more detailed insight into the role solitons play for the electrical conductivity of (doped) polyacetylene, the reader should refer to Appendix A.

4 Conclusion

Polyacetylene is an organic polymer, in which one valence electron per carbon atom is left unpaired. Due to the Peierls instability, the band obtained from the \( 2p_z \) orbitals of carbon atoms splits into two bands, separated by a band gap. In the ground state, the valence band is completely filled and the conduction band is completely empty. Because the ground state is degenerate, excitations exist in the form of moving domain walls, which separate phases with different winding numbers. The winding number is a topological invariant and since the only way of changing a topological invariant of a chiral symmetric Hamiltonian is by closing the band gap, electronic states with energy in the band gap appear. They are localized at domain walls. These edge states can be either empty, singly or doubly occupied. If the edge state is singly occupied, the soliton is neutral and has spin 1/2. If the edge state is empty (doubly occupied), a soliton carries positive (negative) charge of magnitude \( e_0 \) and has zero spin. Because the formation of a pair of solitons is energetically more favourable than the semiconductor-type of excitation, charged solitons are the predominant mobile charge carriers in doped polyacetylene.

References

Appendix A  Excitations of a Polyacetylene Molecule

An easily imaginable means of obtaining a pair of domain walls is by shifting a piece of the chain with respect to the rest of the chain: sticking to the completely dimerized limit of the SSH model, a pair of domain walls consists of an isolated site hosting a zero-energy eigenstate and a trimer, as shown in Fig. 9. A trimer not only hosts one zero-energy edge state, but also one eigenstate with (negative) energy $-\sqrt{2}t$, if $t > 0$ is the hopping integral, and another one with (positive) energy $\sqrt{2}t$. Considering one-electron excitations of a neutral molecule, an electron can jump from the valence band at energy $-t$ into the conduction band at energy $t$ upon an energy input of $2t$, as in usual intrinsic semiconductors. On the other hand, a pair of solitons may form: in this case, two states of the valence band and another two of the conduction band vanish, and one eigenstate with energy $-\sqrt{2}t$, two zero-energy edge states and one eigenstate with energy $\sqrt{2}t$ appear instead, as shown in Fig. 10(b). In a neutral molecule, the negative-energy eigenstates are doubly occupied, the zero-energy edge states host two electrons altogether, and the positive-energy eigenstates are empty: a pair of solitons forms at the energy cost of $2(2 - \sqrt{2})t < 2t$. Thus, the formation of a pair of solitons is the energetically more favourable type of excitation.

If an electron is added to a neutral molecule, it either jumps into the conduction band, so that the energy of the system is $-(N-1)t$, if $N$ is the number of carbon atoms, or one neutral and one negatively charged soliton form, so that the energy of the system is $-N - 2(2 - \sqrt{2})t > -(N-1)t$. Thus, the semiconductor-type of excitation is energetically more favourable in the case of one additional electron.

If a second electron is added, its jumping into the conduction band raises the energy of the soliton-free chain for another $2t$, while the energy of the chain, now containing a pair of negatively charged solitons, is left unchanged. The situation is similar if electrons are removed from a neutral molecule. Thus, unlike in usual semiconductors, where electrons (holes) in partially filled (empty) bands exclusively account for electrical conductivity, in n-doped (p-doped) polyacetylene, negatively (positively) charged solitons are the predominant mobile charge carriers.