The semiconducting state of conjugated polymers

Miguel Lagos

Facultad de Ingeniería, Universidad de Talca, Campus Los Niches, Camino a los Niches km 1, Curicó, Chile

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Recently a variety of \( \pi \)-conjugated polymers have been developed and essayed for a number of applications such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and sensors. Some of them are now in mass production. Is central for these applications the semiconductor character of the pure materials, which can turn into metallic conductivity by local oxidation or reduction. The issue is that \( \pi \)-electrons are paired in covalent highly localized stable orbitals and interact strongly between them and with the ionic cores, thus being far from the extended quasi-free independent electron states assumed by the theory of inorganic semiconductors. A model yielding a mechanism for many-body conduction of charge and semiconducting properties of the undoped material is introduced here.

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Conjugated polymers are polymers constituted by chains of identical molecular structures held together by a sequence of bonds that alternates single and double covalent bonds. The double bonds combine a \( \sigma \)- and a \( \pi \)-bond, whereas the single ones are \( \sigma \)-bonds. Hence the backbone is essentially the more stable uniform sequence of \( \sigma \)-bonds. The simplest conjugate polymer is polyacetylene, for which the periodic molecular structure is just a carbon atom with one of its valence electrons in covalent bond with an hydrogen atom. The metallic state is reached by doping through local oxidation or reduction. Thin films of conjugated polymers are attracting considerable interest because of their varied actual and potential applications in electronic and optoelectronic devices, such as transistors, photodiodes, organic photovoltaic (OPV) devices, organic light-emitting diodes (OLEDs) and many others, combined with their versatility and ease low cost fabrication. Even the use of paper as a substrate for organic transistors is now being investigated \cite{1}. Devices combining the injected electrons from one electrode and holes from the other electrode of a two-layer organic emitting diode were found to have a good electroluminescent efficiency with appropriately low operation voltages \cite{2,3}. Now the use of organic materials as the active semiconductors in electronic flat panel displays are in large scale production and commercialization. Conjugated polymers are intrinsically stable upon excitation by an applied voltage or photon capture in either light emission or harvesting devices. The alternating \( \pi \)-bonds participate actively in the electronic processes leaving intact the primary structure, constituted by the uniform backbone of \( \sigma \)-bonds. This backbone provides the necessary stability against degradation by the energy transfers demanded by the operation of the devices.

In opposition to the importance of these applications, the underlying science that governs the properties that give rise to them is yet in an early stage of understanding. In comparison with inorganic semiconductors, relatively little is known about the physical origin of the electronic properties of the conjugated polymers, and even the precise nature of the semiconductor excitations remains yet uncertain. Inorganic semiconductors are characterized by the long range spatial order of a single crystal, where delocalized non-interacting quasi-free electrons evolve in the periodic field of the crystalline lattice. On the contrary, in organic semiconductors the strict spatial order is often reduced to one dimension because the different polymeric chains are rarely in ordered arrays. More importantly, the electrons are paired in covalent highly localized \( \sigma \)- or \( \pi \)-orbitals which interact strongly between them and with the ionic cores, and are then far from being in delocalized free or quasi-free states.

In general, carbon atoms of the backbone take electrons from neighboring atoms to constitute pairs with their four valence electrons in order to form particularly stable octets. Hence the spatial electronic pairing inherent to the \( \pi \)-bonds is a primary condition of the conjugate polymers. Models for the charge transport along the polymer chain must take this into account, and presume that the occurrence of any one-electron elementary process demands a too large activation energy. Bearing this in mind, I propose here an essentially many-body mechanism of charge transport which meets the conditions posed by the structure of the conjugated polymers much better than the conventional scheme developed for inorganic conductors and semiconductors.

The Hamiltonian of the polymer chain is written as

\[
H = H_0 + H_C + H_T, \tag{1}
\]

where

\[
H_0 = \sum_l \epsilon (n_{l\uparrow} + n_{l\downarrow}), \tag{2}
\]

\( \epsilon \) denotes the energy per electron of the two-electron \( \pi \)-orbital and \( n_{l\uparrow} = c_{l\uparrow}^\dagger c_{l\uparrow}, n_{l\downarrow} = c_{l\downarrow}^\dagger c_{l\downarrow} \), are the occupation operators of the two one-electron states at sites

*Electronic address: mlagos@utalca.cl
\( l = -N/2, -N/2 + 1, \ldots, N/2 \). The term \( H_C \) stems from the Coulomb repulsion between \( \pi \)-orbitals located in adjacent sites of the polymer chain

\[
H_C = \sum_l U(n_{l+1\uparrow} + n_{l+1\downarrow})(n_{l\uparrow} + n_{l\downarrow}).
\]

The hopping term

\[
H_T = \sum_l V(c_{l+1\downarrow}c_{l\uparrow}c_{l\downarrow}c_{l+1\uparrow} + c_{l\uparrow}c_{l\downarrow}c_{l+1\downarrow}c_{l+1\uparrow})
\]

accounts for quantum fluctuations of the \( \pi \)-bonds between neighbouring sites. The underlying principle is that the low energy \( N \)-electron states of the chain can be expressed as combinations of two-electron \( \pi \)-states localized every other site along the chain. Hence any term of the Hamiltonian not having this general structure will give vanishing contribution when operating on the paired states.

The transformed new dynamical variables

\[
s_1(l) = \frac{1}{2}(c_{l\uparrow}c_{l\downarrow} + c_{l\downarrow}c_{l\uparrow})
\]

\[
s_2(l) = \frac{1}{2i}(c_{l\uparrow}c_{l\downarrow} - c_{l\downarrow}c_{l\uparrow})
\]

\[
s_3(l) = \frac{1}{2}(n_{l\uparrow} + n_{l\downarrow} - 1)
\]

satisfy commutation relations of the components of an angular momentum

\[
[s_1, s_2] = is_3 \quad [s_2, s_3] = is_1 \quad [s_3, s_1] = is_2.
\]

As just full occupation will be considered, the first sum in the right hand side of this equation is a constant and can be disregarded.

The use of fermion or angular moment operators are two formally equivalent alternatives to deal with the model put forward here. Translating them into the fermion scheme, the published techniques for dealing with the anisotropic Heisenberg antiferromagnetic chain \([13] \), can be applied here. In this spirit define first the operators

\[
\phi_e^\dagger = \sqrt{\frac{2}{N}} \sum_{l \text{ even}} c_{l+1\uparrow}c_{l\downarrow}c_{l\uparrow}c_{l+1\downarrow} + \frac{\alpha}{2} \sqrt{\frac{N}{2}},
\]

\[
\phi_o^\dagger = \sqrt{\frac{2}{N}} \sum_{l \text{ odd}} c_{l\uparrow}c_{l\downarrow}c_{l+1\downarrow}c_{l+1\uparrow} + \frac{\alpha}{2} \sqrt{\frac{N}{2}},
\]

where \( \alpha = V/(2U) \), which have the commutation properties

\[
[\phi_e, \phi_o^\dagger] = \frac{2}{N} \sum_{l \text{ even}} [n_{l\uparrow}n_{l\downarrow}(1 - n_{l+1\uparrow} - n_{l+1\downarrow})
- n_{l+1\uparrow}n_{l+1\downarrow}(1 - n_{l\uparrow} - n_{l\downarrow})],
\]

\[
[\phi_o, \phi_e^\dagger] = -\frac{2}{N} \sum_{l \text{ odd}} [n_{l\uparrow}n_{l\downarrow}(1 - n_{l+1\uparrow} - n_{l+1\downarrow})
- n_{l+1\uparrow}n_{l+1\downarrow}(1 - n_{l\uparrow} - n_{l\downarrow})],
\]

\[
[\phi_e, \phi_o] = 0,
\]

\[
[H_C, \phi_o^\dagger] = 2U \sqrt{\frac{2}{N}} \sum_{l \text{ even}} c_{l+1\dagger}c_{l\dagger}c_{l\uparrow}c_{l+1\downarrow}
\times (n_{l\downarrow} + n_{l+1\dagger} - n_{l+1\downarrow} - n_{l\uparrow} + n_{l\uparrow} - n_{l\downarrow} - n_{l-1\dagger} - n_{l-1\downarrow} - 2),
\]

and

\[
[H_C, \phi_e^\dagger] = 2U \sqrt{\frac{2}{N}} \sum_{l \text{ odd}} c_{l\dagger}c_{l\dagger}c_{l+1\dagger}c_{l+1\downarrow}
\times (-n_{l+1\uparrow} - n_{l+2\dagger} + n_{l+1\dagger} + n_{l+1\downarrow} - n_{l\uparrow} + n_{l\downarrow} + n_{l-1\dagger} + n_{l-1\downarrow} - 2).
\]

The commutators \([10] \) and \([11] \) go to Bose commutation relations

\[
[\phi_e, \phi_e^\dagger] = [\phi_o, \phi_o^\dagger] = 1
\]

in the asymptotic limit of high conjugation.
Also, in the same limit,

$$[H_C, \phi_{e,o}^\dagger] = 4U \left( \phi_{e,o}^\dagger - \frac{\alpha}{2} \sqrt{\frac{N}{2}} \right).$$

(18)

Hence in the limit of strong conjugation (17) the operators $\phi_{e,o}$ are ladder operators. The ground state $|g\rangle$ of $H$ must satisfy

$$\phi_e|g\rangle = \phi_o|g\rangle = 0.$$  

(21)

Defining now $|N\rangle$ as the chain of bare $\pi$–electronic states (the Néel state in the spin representation)

$$|N\rangle = \prod_{\text{even } l} c_{l+1}^\dagger c_l^\dagger |0\rangle, \tag{22}$$

where $|0\rangle$ is the vacuum, and

$$\Lambda = \sqrt{\frac{N}{2}} (\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o)$$

$$= \sum (\sqrt{2} \phi_e^\dagger c_{l+1}^\dagger c_{l+1} c_l c_l^\dagger - \phi_o^\dagger c_l^\dagger c_{l+1} c_l c_{l+1}^\dagger), \tag{23}$$

it can be shown that the ground state of $H$ in the asymptotic limit (17) is

$$|g\rangle = \exp \left( - \frac{\alpha}{2} \Lambda \right) |N\rangle.$$  

(24)

To demonstrate this, notice that it can be proven by complete induction that in the limit (17) one has that

$$[\phi_{e,o}, (\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o)^n] = n(\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o)^{n-1}, \tag{25}$$

hence for any analytic function $F$ with derivative $F'$

$$[\phi_{e,o}, F(\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o)] = F'(\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o). \tag{26}$$

Applying this property with $F$ substituted by the exponential function appearing in Eq. (24) and the definitions (19) and (20), it can be readily shown that $|g\rangle$ satisfies Eqs. (21) and is then the ground state in the limiting case (17). Notice that the ground state (24) is not perturbative because of the large factor $\sqrt{N/2}$ multiplying the sum (23) defining $\Lambda$.

To determine the ground state energy consider the commutation property of $\Lambda$

$$[c_{l+1}^\dagger c_l^\dagger, \Lambda]$$

$$= (-1)^l (c_{l+1}^\dagger c_l^\dagger + c_l^\dagger c_{l+1}^\dagger) (n_{l+1} - n_l - 1), \tag{27}$$

which after iterating $\nu$ times in the asymptotic limit (17) reads

$$[[[\cdots [c_{l+1}^\dagger c_l^\dagger, \Lambda], \Lambda], \cdots, \Lambda]_{\nu \text{ times}}$$

$$= (-1)^l (-1)^{l(l+1)/2} (\tau + \tau^{-1})^\nu c_{l+1}^\dagger c_l^\dagger, \tag{28}$$

where $\tau$ is the translation operator to the next site:

$$\tau c_l = c_{l+1} \quad \tau^{-1} c_l = c_{l-1}, \quad s = \uparrow, \downarrow. \tag{29}$$

Combining this with the identity

$$e^{-B} A e^B = A + \frac{1}{1!} [A, B] + \frac{1}{2!} [[A, B], B]$$

$$+ \frac{1}{3!} [[[A, B], B], B] + \cdots, \tag{30}$$

the generating function of the modified Bessel functions $I_\nu(z)$

$$\exp \left( \frac{z}{2} (\tau + \tau^{-1}) \right) = \sum_{\nu=-\infty}^{\infty} I_\nu(z) \tau^\nu, \tag{31}$$

and the property $J_\nu(z) = i^{-\nu} J_\nu(iz)$, where $J_\nu$ is the unmodified Bessel function, it can be shown that

$$\exp \left( -\frac{\alpha}{2} \Lambda \right) c_{l+1}^\dagger c_l^\dagger \exp \left( -\frac{\alpha}{2} \Lambda \right)$$

$$= \sum_{\nu=-\infty}^{\infty} (-1)^l (-1)^{l(l+1)/2} J_\nu(\alpha) c_{l+\nu}^\dagger c_{l+\nu}. \tag{32}$$

Eq. (32) together with Eq. (24) are useful to calculate expectation values, as the mean occupation of a $\pi$–orbital

$$\langle g | (n_{l+1} + n_l) | g \rangle = 1 + (-1)^l J_0(2\alpha), \tag{33}$$

or the short range correlation coefficient
The bosonic operators $\phi$ and the set of vectors
\[ |n_e, n_o\rangle = \frac{(\phi_e^\dagger)^{n_e} (\phi_o^\dagger)^{n_o}}{\sqrt{n_e!} \sqrt{n_o!}} |g\rangle, \quad n_e, n_o = 0, 1, 2, 3, \ldots \]
are a set of eigenvectors of $H$, with eigenenergies
\[ E_{n_e, n_o} = 4(n_e + n_o)U + E_g. \]

The theoretical framework described up to this point would not be complete without observing that the ground state is twofold degenerate. In effect, the state
\[ |g\rangle = \exp \left( \frac{\alpha}{2} \Lambda \right) |N\rangle, \quad |N\rangle = \prod_{\text{odd } l} c_{l \uparrow}^\dagger c_{l \downarrow}^\dagger |0\rangle, \]
is also an eigenvector of $H$ with the same energy eigenvalue $E_g$. The bosonic operators $\phi_e$ and $\phi_o$ turn to creation operators when operating on $|g\rangle$.

Certainly the system may have other degrees of freedom, additional to the ones described by the operators $\phi_e$ and $\phi_o$, e.g. the solitons firstly invoked by Su, Schrieffer and Heeger [10] for polyacetylene, and then generalized to other conjugate polymers [12]. However the serendipitous finding explained next confers to the excitations associated with the operators $\phi_e$ and $\phi_o$ a particular importance. As it has been assumed that one-electron processes involve too large activation energies, the momentum operator $\vec{P}$ must be written as a two-particle operator, in the way
\[ \vec{P} = -i\hbar q \hat{i} \sum_{l} \left( c_{l \uparrow} c_{l+1 \downarrow}^\dagger - c_{l \downarrow}^\dagger c_{l+1 \uparrow} \right), \]
when written in terms of the electron field operator
\[ \Psi(\vec{r}, t) = \sum_{l} c_{l \uparrow} w_{s}(\vec{r} - a \hat{i}). \]

Here $\nabla'$ and $\nabla$ are the gradient operators with respect to $\vec{r}'$ and $\vec{r}$, and $w_{s}(\vec{r} - a \hat{i})$ represents the one-particle wave function of an electron in a $\pi$ covalent state at site $l$, $a$ is the distance between two adjacent sites of the polymer chain, and $\hat{i}$ is the unitary vector along the chain direction. Because of analytical reasons and the small overlap of functions $w_{s}$ centered in neighboring sites
\[ \int d^3 \vec{r} w_{s}^* (\vec{r} - l' \hat{\alpha}) \nabla w_{s} (\vec{r} - a \hat{i}) = \begin{cases} 0, & \text{if } l = l' \\ q \hat{i} & \text{if } l' = l + 1 \\ -q \hat{i} & \text{if } l' = l - 1 \\ 0, & \text{otherwise.} \end{cases} \]

Inserting Eqs. (11) and (12) as they are written into Eq. (10), the resulting expression for $\vec{P}$ finally reduces to the same standard equation for the one-particle momentum operator. However, one must recall that the backbone of the polymer is not rigid and the alternating occupied and unoccupied $\pi$–orbitals should cause a dimerization of the polymer chain. Hence the occupied and virtual $\pi$–orbitals are expected to have a finite difference, simply because of the broken periodicity of the distance between the positive charges involved in the chemical bonds. In Eq. (12) the parameter $a$ takes slightly different values if the accompanying index $l$ is even or odd. When taking this into consideration the momentum operator splits into a one-particle term and a two-particle one, taking the general form
\[ \vec{P} = -i\hbar q i \sum_{l} \left( c_{l \uparrow} c_{l+1 \downarrow}^\dagger - c_{l \downarrow}^\dagger c_{l+1 \uparrow} \right) + \text{adjoint operator}, \]
where $\gamma$ is a coefficient proportional to the shift $\delta a$ in the bond lengths of the dimerized chain. The first term of $\vec{P}$ in general destroys pairs and the second one always conserves them. As $H$ and the eigenstates [24, 37] and [39] involve just paired electrons, consistently with the principle that one-electron processes involve too large activation energies we can retain only the second term and write $\vec{P}$ as
\[ \vec{P} = -i\hbar q i \sum_{l \text{ odd } l} \left( c_{l \uparrow} c_{l+1 \downarrow}^\dagger - c_{l \downarrow}^\dagger c_{l+1 \uparrow} \right), \]
and the Heisenberg picture
\[ \frac{d^2 P}{dt^2} = -\frac{1}{\hbar^2} [H, [H, P]]. \]
Replacing Eqs. (44) and (20) one has that
\[
\frac{d^2 P}{dt^2} = -\frac{4U^2}{\hbar^2} P.
\] (46)

Eq. (46) shows that the operators \( \phi^\dagger_\varepsilon \) and \( \phi^\dagger_o \) excite modes of the collective motion of the charges involved in the \( \pi \)-bonds present in the chain. The collective oscillation involves charge displacement and has an angular frequency \( \omega = 2U/\hbar \), independent of the length of the polymer chain. Hence resonances favouring charge transfers with the neighbouring chains are expected to occur.

Although the frequency \( \omega = 2U/\hbar \) of the predicted charge waves are expected to be much higher than the vibrational frequencies of the polymeric chain, a next step in the development of the model is the introduction of the dynamics of the ionic cores. Phonons and the electron–phonon interaction sure would enrich the model, particularly in the last part when chain dimerization was introduced. The requirement of phase correlations between the \( \pi \)-orbitals introduces more modes, but the procedure was dismissed here because their frequencies do not have dispersion and do not give significant contribution in the present stage.

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