The semiconducting and metallic phases of conjugated polymers

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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, organic field-effect transistors, organic photovoltaics, and sensors. Is central for these applications the semiconductor character of the pure materials, which can turn into metallic conductivity by local oxidation or reduction. Many very recent experiments show two characteristic peaks in the UV–Vis excitation spectra of the conjugated polymers of interest, both lying in the gap between the energies of the bonding $\pi$ and antibonding $\pi^*$ bands and having excitation energies in a ratio ranging from 1.4 to 1.7. The issue is that $\pi$-electrons are paired in covalent orbitals which interact strongly between them and with the ionic cores, thus being far from the extended quasi–free independent one–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. The model yields two new flat bands of excited bonding states of Bose–Einstein statistics able of charge transport. The two bands explain well the characteristic pair of maxima of the UV–Vis excitation spectra of the conductive conjugated polymers.

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In opposition to the importance of their potential or actual applications [1], the underlying science that give rise to the semiconducting and conducting properties of conjugated polymers 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.

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 [2]. 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 [3][4]. 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 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, it is proposed 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 results

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agree well with direct observations of the electronic structure of polymer conductors and semiconductors by the absorption of UV–Vis photons \[7\] 12.

The model put forward here is consistent with the pioneer ideas of Su, Schrieffer and Heeger \[13\] 15, but with explicit recognition of the importance of the electrostatic repulsion between π-orbitals in neighboring sites \[16\]. Chain dimerization is taken as granted and included as an implicit condition. Charge carriers in the conducting states have the same structure than the solitons of Su, Schrieffer and Heeger, but with some subtle differences. The model Hamiltonian for 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 \(l = -N/2, -N/2 + 1, \ldots, N/2\). The term \(H_C\) stems from the Coulomb repulsion between \(\pi\)-orbitals located in adjacent sites of the polymer chain. Zhang et al. has proven that the \(\pi-\pi\) electrostatic repulsion has significant effect in conjugated systems, and the \(\pi-\pi\) Pauli repulsion plays a secondary but nonnegligible role \[16\]. Hence

\[
H_C = \sum_l U (n_{l+1\uparrow} + n_{l+1\downarrow}) (n_{l\uparrow} + n_{l\downarrow}). \tag{3}
\]

The two–electron tunneling term

\[
H_T = \sum_l V (c_{l+1\uparrow}^\dagger c_{l\downarrow} + c_{l+1\downarrow}^\dagger c_{l\uparrow} + c_{l\uparrow}^\dagger c_{l+1\downarrow} + c_{l\downarrow}^\dagger c_{l+1\uparrow}) \tag{4}
\]

accounts for quantum fluctuations of the \(\pi\)-bonds between neighboring 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

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

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

\[
s_3(l) = \frac{1}{2} (n_{l\uparrow} + n_{l\downarrow} - 1)
\]
satisfy commutation relations of the components of an angular momentum

\[
[s_1, s_2] = is_3, \quad [s_2, s_3] = is_1, \quad [s_3, s_1] = is_2. \tag{6}
\]

As the number operators \(c_{l\uparrow}^\dagger c_{l\downarrow}\) have eigenvalues 0 and 1, the eigenvalues of \(s_3\) are \(-1/2, 0\) and \(1/2\). The eigenvalue 0 conveys the breaking of a covalent bond, which has a large energy cost. Taking it as infinite the operators \(s_1, s_2, \) and \(s_3\) behave as the components of a spin \(1/2\). The Hamiltonian \(H\) then takes the general form of the Hamiltonian of an anisotropic spin \(1/2\) antiferromagnetic Heisenberg model

\[
H = (\epsilon + 2U) \sum_l [2s_3(l) + 1] + 4U \sum_l \left( s_3(l + 1)s_3(l) \right.
\]

\[
+ \frac{V}{2U} \left[ s_1(l + 1)s_1(l) + s_2(l + 1)s_2(l) \right] \right)
\]

which in terms of the ladder operators \(s_+ = s_1 + is_2\) and \(s_- = s_1 - is_2\) can be rewritten as

\[
H = (\epsilon + 2U) \sum_l [2s_3(l) + 1] + 4U \sum_l \left( s_3(l + 1)s_3(l) \right.
\]

\[
+ \frac{V}{4U} \left[ s_+(l + 1)s_-(l) + s_+(l)s_-(l + 1) \right]. \tag{8}
\]

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 \[17\] 19, can be applied here. In this spirit define first the operators

\[
\phi_{\epsilon}^l = \sqrt{\frac{2}{N}} \sum_{\text{even } l} c_{l\uparrow}^\dagger c_{l+1\downarrow} c_{l+1\uparrow} + \frac{\alpha}{2} \sqrt{\frac{N}{2}}, \tag{9}
\]

\[
\phi_{\epsilon}^l = \sqrt{\frac{2}{N}} \sum_{\text{odd } l} c_{l\uparrow}^\dagger c_{l+1\downarrow} c_{l+1\uparrow} + \frac{\alpha}{2} \sqrt{\frac{N}{2}}, \tag{10}
\]

where \(\alpha = V/(2U)\). Recalling the elementary identities \([A, BC] = [A, B]C + B[A, C]\) and \([A, BC] = \{A, B\}C - B\{A, C\}\) between commutators and anticommutators in standard notation, one can readily show they have the commutation properties

\[
[\phi_{\epsilon}, \phi_{\epsilon}^l] = \frac{2}{N} \sum_{\text{even } l} \left[ n_{l\uparrow} n_{l\downarrow} (1 - n_{l+1\uparrow} - n_{l+1\downarrow}) \right.
\]

\[
- n_{l+1\uparrow} n_{l+1\downarrow} (1 - n_{l\uparrow} - n_{l\downarrow}) \right]. \tag{11}
\]
\[ [\phi_e, \phi_o] = -\frac{2}{N} \sum_{l \text{ odd}} \left[ n_{l\uparrow} n_{l\downarrow} (1 - n_{l+1\uparrow} - n_{l+1\downarrow}) - n_{l+1\uparrow} n_{l+1\downarrow} (1 - n_{l\uparrow} - n_{l\downarrow}) \right], \quad (12) \]

\[ [\phi_e, \phi_o] = 0, \quad (13) \]

\[ [H_C, \phi_o] = 2U \left( \sum_{l \text{ even}} c_{l+1\uparrow} c_{l+1\downarrow} c_{l\uparrow} c_{l\downarrow} - \sum_{l \text{ odd}} c_{l\uparrow} c_{l\downarrow} c_{l+1\uparrow} c_{l+1\downarrow} \right) \times (n_{l+2\uparrow} + n_{l+2\downarrow} - n_{l+1\uparrow} - n_{l+1\downarrow} + n_{l\uparrow} + n_{l\downarrow} - n_{l-1\uparrow} - n_{l-1\downarrow} - 2), \]

and

\[ [H_C, \phi_e] = 2U \left( \sum_{l \text{ even}} c_{l\uparrow} c_{l\downarrow} c_{l+1\uparrow} c_{l+1\downarrow} - \sum_{l \text{ odd}} c_{l\uparrow} c_{l\downarrow} c_{l+1\uparrow} c_{l+1\downarrow} \right) \times (-n_{l+2\uparrow} - n_{l+2\downarrow} + n_{l+1\uparrow} + n_{l+1\downarrow} - n_{l\uparrow} - n_{l\downarrow} + n_{l-1\uparrow} + n_{l-1\downarrow} - 2). \]

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

\[ [\phi_e, \phi_e^\dagger] = [\phi_o, \phi_o^\dagger] = 1 \quad \text{in the asymptotic limit of high conjugation} \]

\[ n_{l\uparrow} = n_{l\downarrow} \rightarrow \begin{cases} 1, & \text{if } l \text{ even} \\ 0, & \text{if } l \text{ odd}. \end{cases} \]

Also, in the same limit,

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

Noticing that

\[ H_T = \sqrt{\frac{N}{2}} V(\phi_e^\dagger + \phi_o^\dagger + \phi_e + \phi_o) - N\alpha V, \]

disregarding \( H_0 \) one has from Eqs. (1), (18) and (19) that

\[ [H, \phi_e^\dagger] = 4U \phi_e^\dagger, \quad [H, \phi_o^\dagger] = 4U \phi_o^\dagger. \]

Hence in the limit of strong conjugation (17) the operators \( \phi_e \) and \( \phi_o \) are ladder operators.

The ground state \( |g\rangle \) of \( H \) must satisfy

\[ \phi_e|g\rangle = \phi_o|g\rangle = 0. \]

Defining now \( |\mathcal{N}\rangle \) as the chain of bare \( \pi \)-electronic states (the Néel state in the spin representation)

\[ |\mathcal{N}\rangle = \prod_{\text{even } l} c_{l\uparrow}^\dagger c_{l\downarrow}^\dagger |0\rangle \quad (22) \]

where \(|0\rangle\) is the vacuum, and

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

\[ = \sum_{l} (-1)^l (c_{l+1\uparrow} c_{l\downarrow} c_{l\uparrow} c_{l\downarrow} - c_{l\uparrow} c_{l\downarrow} c_{l+1\uparrow} c_{l+1\downarrow}), \quad (23) \]

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

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

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

\[ [\phi_e,o, F(\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o)] = F(\phi_e^\dagger + \phi_o^\dagger - \phi_e - \phi_o). \]

Applying this property with \( F \) substituted by the exponential function appearing in Eq. (24) and the definitions (9) and (10), 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 \( \Lambda \)

\[ [c_{l\uparrow}^\dagger c_{l\downarrow}^\dagger, \Lambda] \]

\[ = (-1)^l (c_{l+1\uparrow} c_{l\downarrow}^\dagger c_{l\uparrow}^\dagger + c_{l-1\downarrow} c_{l\uparrow}^\dagger c_{l\downarrow}^\dagger) (n_{l\uparrow} + n_{l\downarrow} - 1), \]

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

\[ [[\ldots [c_{l\uparrow}^\dagger c_{l\downarrow}^\dagger, \Lambda], \ldots, \Lambda]_{\nu \text{ times}} = (-1)^{l\nu} (-1)^{\nu(\nu+1)/2} (\tau + \tau^{-1})^\nu c_{l\uparrow}^\dagger c_{l\downarrow}^\dagger, \]

where \( \tau \) is the translation operator to the next site:

\[ \tau c_{ls} = c_{l+1s} \quad \tau^{-1} c_{ls} = c_{l-1s} \quad s = \uparrow, \downarrow. \]

Combining this with the identity
\[ e^{-B} A e^B = A + \frac{1}{1!} [A, B] + \frac{1}{2!} [[A, B], B] + \cdots , \] (30)

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

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

\[ \exp \left( \frac{\alpha}{2} A \right) c^\dagger_l c^\dagger_{l+1} \exp \left( -\frac{\alpha}{2} A \right) = \sum_{\nu = -\infty}^{\infty} (-1)^\nu (-1)^{\nu+1/2} J_\nu(\alpha) c^\dagger_{l+\nu} c^\dagger_{l-\nu} . \] (32)

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

\[ \langle g | (n_{l\uparrow} - n_{l\downarrow}) | g \rangle = 1 + (-1)^l J_0(2\alpha) , \] (33)

or the short range correlation coefficient

\[ \frac{1}{N} \langle g | \sum_l (n_{l-1\uparrow} + n_{l-1\downarrow})(n_{l\uparrow} + n_{l\downarrow}) | g \rangle \]

\[ = 1 - [J_0(2\alpha)]^2 , \] (34)

or the energy of the ground state \( E_g = \langle g | (H_C + H_T) | g \rangle \)

\[ E_g = NU \left[ 1 - (J_0(2\alpha))^2 + 2\alpha J_1(2\alpha) \right] . \] (35)

In obtaining Eqs. (33), (34) and (35) use was made of Neumann’s addition formulas of the Bessel functions and Graf’s generalization of them [20]. The previous results expressed in terms of the Bessel functions look elegant, but care must be taken in that they hold in the asymptotic limit [17], which occurs for small enough \( \alpha \). Up to the second order in \( \alpha \) one has that

\[ E_g = 4NU(\alpha^2 + 0(\alpha^4)) . \] (36)

By the properties [20] of the ladder operators \( \phi^\dagger_e \) and \( \phi^\dagger_o \) the set of vectors

\[ |n_e, n_o\rangle = (\phi^\dagger_e)^{n_e} (\phi^\dagger_o)^{n_o} |g\rangle , \quad n_e, n_o = 0, 1, 2, 3, \ldots \] (37)

are a set of eigenvectors of \( H \), with eigenenergies

\[ E_{n_e n_o} = 4(n_e + n_o)U + E_g . \] (38)

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

\[ |g\rangle = \exp \left( \frac{\alpha}{2} A \right) |\bar{\mathcal{N}}\rangle , \quad |\mathcal{N}\rangle = \prod_{\text{odd } l} c^\dagger_l c^\dagger_{-l} |0\rangle \] (39)

is also an eigenvector of \( H \) with the same energy eigenvalue [35]. The bosonic operators \( \phi_e \) and \( \phi_o \) turn to creation operators when operating on \( |g\rangle \).

\[ \begin{array}{c}
\text{π*-band} \\
\text{LUMO}
\end{array} \]

\[ \begin{array}{c}
\text{Flat band of Bose-Einstein charged excitations} \\
\text{Flat band of Bose-Einstein charge wave excitations}
\end{array} \]

\[ \begin{array}{c}
\text{π-band} \\
\text{HOMO}
\end{array} \]

\[ \begin{array}{c}
\text{2U} \\
4U
\end{array} \]

FIG. 1: The π–π repulsion give rise to two energy levels of Bose–Einstein excitations whose energies are 4\(U\) and 6\(U\) above the energy of the highest occupied molecular orbital (HOMO).

Figure 1 shows a schematic diagram of the energy spectrum of the molecular chain. The π–π repulsion yields a novel energy level of Bose–Einstein excitations located in between the energies of the HOMO and the LUMO. Hence the conduction band in this framework is not constituted by electrons in extended anti–bonding states, but of electronic pairs excited to the novel flat band of energy 4\(U\). Certainly the system 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 [13] for polyacetylene, and then generalized to other conjugate polymers [15]. They give rise to the flat band of energy 6\(U\) in Figure 1 which will be adressed with some detail after showing how the excitations associated with the operators \( \phi_e \) and \( \phi_o \) transport momentum and energy. As it has been assumed that one–electron processes involve too large activation energies, the momentum operator \( \hat{P} \) must be written as a two–particle operator, in the way
\[ \vec{P} = -\frac{i\hbar}{2} \int d^3\vec{r} d^3\vec{r}' \Psi^\dagger(\vec{r}', t) \Psi(\vec{r}', t)(\nabla' + \nabla) \Psi(\vec{r}, t) \Psi(\vec{r}, t) + \text{adjoint operator}, \]  

(40)

when written in terms of the electron field operator

\[ \Psi(\vec{r}, t) = \sum_{ls} c_{ls} w_s(\vec{r} - lai). \]  

(41)

Here \( \nabla' \) and \( \nabla \) are the gradient operators with respect to \( \vec{r}' \) and \( \vec{r} \), and \( w_s(\vec{r} - lai) \) 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 \( i \) is the unitary vector along the chain direction. Because of analytical reasons and the small overlap of functions \( w_s \) centered in neighboring sites

\[ \int d^3\vec{r} w_s^\dagger(\vec{r} - l'ai) \nabla w_s(\vec{r} - lai) = \begin{cases} 0, & \text{if } l = l' \\ q \hat{c}_{l}^\dagger \hat{c}_{l} & \text{if } l' = l + 1 \\ -q^* \hat{c}_{l} \hat{c}_{l}^\dagger & \text{if } l' = l - 1 \\ 0, & \text{otherwise.} \end{cases} \]  

(42)

Inserting Eqs. (41) and (42) as they are written into Eq. (40), 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. (42) the parameter \( a \) takes slightly different values if the accompanying index \( i \) 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

\[ \vec{P} = -i\hbar q \frac{1}{2} \sum_{ls} \left( c_{l+1s}^\dagger c_{ls} - c_{ls}^\dagger c_{l+1s} \right) \]  

(43)

\[ -i\hbar \gamma q i \sum_{l} \left( c_{l+1l}^\dagger c_{l+1l}^\dagger c_{l1l} - c_{l1l}^\dagger c_{l+1l}^\dagger c_{l+11l}^\dagger \right), \]

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 \( |g\rangle \) and \( |g\rangle \) 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

\[ \vec{P} = -i\hbar \gamma q i \sqrt{\frac{N}{2}} \left( \phi_{e}^\dagger - \phi_{o}^\dagger - \phi_{e} + \phi_{o} \right). \]  

(44)

In the Heisenberg picture

\[ \frac{d^2 P}{dt^2} = -\frac{1}{\hbar^2} [H, [H, P]]. \]  

(45)

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 \( \phi_{i}^\dagger \) and \( \phi_{i} \) 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.

The model worked out in the preceding paragraphs shows that the dynamical effect of the \( \pi \– \pi \) repulsion in conjugate polymers is a set of degenerate excited states able of transporting charge along the polymer chain. The novel states obey Bose–Einstein statistics and have energy eigenvalues forming a flat band located at an energy \( 4U \) over the ground state, in the gap between the HOMO and the LUMO. The model assumed in this step is a natural reply to the question of how the repulsion between the \( \pi \)–orbitals may affect the dynamics of the system, however is yet a bit too simple. An important conclusion is that the single frequency \( \omega = 2U/\hbar \), common to all the polymeric chains in a sample, no matter their lengths, which is expected to produce resonances that enhance the probability of mutual charge transfers.

\[ |\psi_1(l)\rangle = |l\rangle \]  

\[ |\psi_2(l)\rangle = |l\rangle \]  

FIG. 2: Circles represent monomers and lines the \( \pi \)–bonds. The black filling of a circle is only for reference. The two first lines represents the states \( |\psi_1\rangle \) and \( |\psi_2\rangle \), the third line shows the configuration of one of the two degenerate ground states.

The metallic phase is constituted by a set of excited states similar to those introduced by Su, Schrieffer and Hoeger [14 15]. At a site \( l \) the occupation of the \( \pi \)–orbitals changes from even to odd sites, or vice–versa. The monomer in between marks a frontier between the two degenerate ground states, \( |g\rangle \) and \( |g\rangle \), prevailing at each side of it. The energy of such a state can be inferred from an heuristic argument instead of a formal one. Consider first a class of excited states of the form...
\[
(|\psi_1(l)| \pm |\psi_2(l)|)/\sqrt{2}, \text{ where } |\psi_1(l)| \text{ and } |\psi_2(l)| \text{ are the states represented schematically in Figure 2. As the interaction between the orbitals is circumscribed to nearest neighbors, for small enough } \alpha \text{ the mutual perturbation of the states in the two sides of } l \text{ is small. Hence the contribution to the energy of both sides sum approximately } 4U, \text{ and the central parts of } |\psi_1(l)| \text{ and } |\psi_2(l)| \text{ contribute } 4U \text{ and } 0, \text{ in the zeroth order in } \alpha. \text{ Hence the mean energy of the state is } 6U. \text{ This class of excited states configures the flat band of charged excitations represented in Figure 1. The excitations have charge } \pm 2e \text{ and an energy } 6U \text{ over the energy of the highest occupied molecular orbital (HOMO). The metallic phase is constituted by the set of linear combinations of the form}
\]

\[
|k\rangle = \frac{1}{N} \sum_{l=-N/2}^{N/2} \exp(ikl)|\psi_{1,2}(l)|, \quad k = \frac{2\pi}{N} n, \\
n = \frac{N}{2}, \ldots, -1, 0, 1, 2, \ldots, \frac{N}{2}.
\]

The predictions made here on the energy bands can be readily identified in the light absorption spectra. The two flat bands of Figure 1 are quite characteristic because their energies are in the ratio 3/2. A recent paper [2] shows the measured absorption spectra of electromagnetic radiation of wavelengths in the interval 300–800 nm of the conjugated polymer FBT-Th\(_4\)(1,4). The target polymer was in solid films of 60 nm thick and so-target polymer was in solid films of 60 nm thick and so-}

\[
\lambda_2 = 453 \text{ nm were observed in the film. The energies in eV are } \epsilon_1 = 1.792 \text{ eV and } \epsilon_2 = 2.737 \text{ eV and their ratio is}
\]

\[
\frac{\epsilon_2}{\epsilon_1} = 1.527,
\]

which is quite close to the predicted value 3/2. The precision of the agreement is quite unexpected because the real energy of the transitions are shifted from the spectral maxima by a Stokes shift. However the Stokes shifts are expected to be very similar for the two maxima, which can explain such precision. The rest of the experimental spectrum agrees very well with the scheme of Figure 1 with the maxima in between a plateau and a null region evidencing the energy gap.

More recent observations of the UV–Vis excitation spectra of many conjugated polymers of interest show results similar to those of Chen et al. [7], with the ratio of Eq. (48) ranging from approximately 1.4 to 1.7 [8–12]. The spectra show two main peaks centered typically at \( \lambda_1 \approx 700 \text{ nm} \) and \( \lambda_2 \approx 450 \text{ nm} \) with full half width of about 100 nm. The peak of higher wavelength has always a shoulder. In general the spectra exhibit two main peaks clearly attributable to the two flat bands derived from the model solved here. The obtention of precise values for the discrete energy levels over the energy of the HOMO from the UV–Vis excitation spectra demands to deconvolute the vibrational modes, which widens the spectral maxima [21].

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