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Introduction to Organic Electronic Devices

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Preface

Organic materials, according to conventional wisdom, are carbon-based insulators that lack the optical, electrical, and magnetic properties of conductors or semiconductors. The discovery of conducting polymers in the late 1970s ushered in the emerging field of organic electronics. Organic electronics has since grown in importance as a research field and is still flourishing. The optical, electrical, and magnetic properties of organic materials have steadily been recognized, and researchers have advocated their use in various electronic devices. Particularly in the last 30 years, semiconductor materials and electronic devices based on organic molecules have advanced fast. They have progressed from pure scientific research to the practical stage and are moving toward industrialization. For example, organic electroluminescent materials and devices are not only used in digital cameras, mobile phone screens, thin-film large-screen displays, but also in solid-state lighting. Besides, organic semiconductor materials have also achieved rapid development in photovoltaic cells, thin-film sensors, thin-film field-effect transistors, and other devices.

The most common characteristic of organic molecular materials is that they have delocalized π electronic structures and weak intermolecular forces. The solid phase of organic materials is mainly formed due to non-bonding interactions such as van der Waals forces. Therefore, the properties of the material depend essentially on the nature of the molecule itself and the condensed structure. Compared with the limited inorganic semiconductor materials, a wide variety of molecular materials can be synthesized by chemical methods, and their functions can be rationally modulated through chemical synthesis and modification, making it easier to meet different functional requirements. Organic molecular materials can realize information display, sensing, storage, solar energy conversion, and other functions of inorganic semiconductors such as silicon. More importantly, they are relatively inexpensive and can produce lightweight and thin devices at low cost through printing methods. Most of them can be prepared on foldable flexible substrates to create thin-film devices with special shapes. This not only can complement and expand inorganic semiconductor devices, but also have unlimited potential in the application of electronic devices in the future. If these devices can be made into all organic, it will be a profound revolution in electronic devices. It will also play a huge role in developing new energy and solving environmental pollution. In addition, since organic materials are more compatible with living organisms than inorganic materials, they can be used as a bridge between inorganic materials and biological systems.

The authors have written this book based on years of experience in research work in this field. The aim is to introduce the research status, important progress, and application prospects of organic molecular materials to readers from the perspective of materials and devices. The book systematically introduces the characteristics of molecular materials and their working mechanisms different from inorganic semiconductors. By summarizing both the results from both theoretical analysis and experimental data, it describes the application of organic molecular materials in thin-film devices such as organic electroluminescence devices, organic photovoltaics, organic field-effect transistors, and organic sensors. One of the hot topics of current research, organic–inorganic hybrid materials with perovskite crystal structure, is also systematically discussed. Chapters 1, 2, 7, and 10 of this book were written by Shunpu Li, Chaps. 3, 5, and 6 were written by Guangye Zhang, Chaps. 4, 8, and 9 were written by Chen Xie, and Chap. 11 by Peng You. We would like to thank Lihong Wang for her dedication to the drawing, formatting, and proofreading of some of the chapters this book.

The research on organic electronic materials and devices is developing rapidly. New concepts and new achievements are emerging all the time, so some of the new topics and new results may miss and mistakes certainly remain in the book. Nonetheless, we hope that this book paints a reasonable picture of what organic electronics are and can provide a reference for the researchers engaged in molecular materials and device research, as well as graduate students in colleges and universities. We sincerely hope that readers will provide valuable comments.

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Chapter 1
Electronic Process in Organic Semiconductor Materials

The nature of bonding in organic molecule semiconductors is fundamentally different from inorganic semiconductors. In polymer materials and organic crystals, the molecules are bonded by van der Waals force implying a weaker intermolecular bonding as compared to inorganic semiconductors, like silicon, where the atoms are strongly bonded covalently. The weak bonding property can be seen from their mechanical and thermodynamic properties. In organic materials, a much weaker delocalization of electronic wave functions among neighbor molecules brings a strong impact on the optical and electrical properties.

1.1 Semiconductor Property of Conjugated Polymers

1.1.1 Fermi Surface of One-Dimensional System

Organic semiconductor materials are the premise of development of organic electronics. An understanding of conducting mechanism in conjugated molecules is important for designing new organic semiconductors and device fabrication. Therefore, we start from discuss about conducting property of conjugated polymer: why is an intrinsic conjugated polymer a semiconductor, not a conductor?

Taking a one-dimensional (1D) system with length L contains N free electrons. Electrons are moving with momentum p in the system. The electron wavelength λ and momentum p follow the de Broglie relation:

$$\lambda = \frac{h}{p} \tag{1.1}$$

where h is plank constant. The wavelength is often replaced with wavenumber k.

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$$k = \frac{1}{\lambda} = \frac{p}{h}, p = \text{hk} \tag{1.2}$$

If free electrons are moving in direction x, the wave function is a plane wave and can be expressed as:

$$\psi_p(x) = \frac{1}{L} e^{\frac{i}{\hbar} px}, (\hbar = h/2\pi) \tag{1.3}$$

$$\psi_k(x) = \frac{1}{L} e^{i2\pi kx} \tag{1.4}$$

When an electron is moving in a chain with length L, the wave function is satisfying the boundary condition $\psi_k(L) = \psi_k(0)$. Inserting Eq. (1.4) to the boundary condition, we have

$$e^{i2\pi kL} = 1 \tag{1.5}$$

Thus, kL can only be an integer and

$$k = m/L(m = 0, \pm 1, \pm 2 \cdots) \tag{1.6}$$

As $k = p/h$, the k (or p) can only take a series of discrete points in momentum space, and the interval between two neighbor states is:

$$\Delta k = \frac{1}{L}, \tag{1.7}$$

Kinetic energy of a free electron:

$$E(k) = \frac{p^2}{2m} = \frac{h^2k^2}{2m} \tag{1.8}$$

From (1.8), we know that the energy (E) is a quadratic function of wavenumber (k) (Fig. 1.1). Each momentum state can be occupied by two electrons (spin-up and spin-down), N electrons in the 1D system will sequentially fill into these states from low momentum to high momentum, and the maximum momentum is p_F. The corresponding maximum wavenumber is k_F ($p_F = \text{hk}_F$). The p_F is named as Fermi momentum below which ($|p| \le p_F$) all states are occupied without any holes. In contrast, all states with $|p| > p_F$ are empty (Fig. 1.1).

The electron density in the 1D system is $n = N/L$, and from Fig. 1.1, we see that the occupied region in the momentum space is $2k_F$and the number of states occupied is $2k_F/\Delta k = 2k_FL$. The number of occupied electrons is $4k_FL = N$ (each state contains two electrons with anti-parallel spins), and we have the Fermi momentum of 1D system:

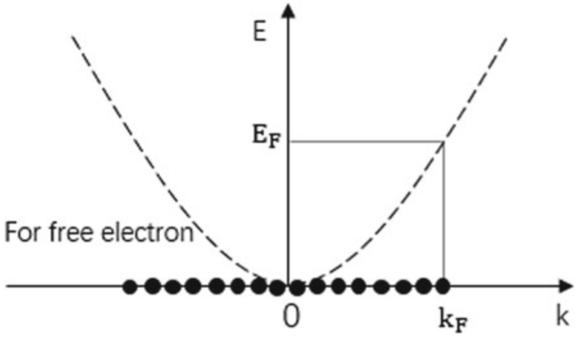


Fig. 1.1 Schematic illustration of momentum states and energy of free electrons in 1D system

$$k_F = \frac{N}{4L} = \frac{n}{4}, \tag{1.9}$$

The corresponding maximum energy, i.e., Fermi energy, is

$$E_F = \frac{h^2 k_F^2}{2m}, \tag{1.10}$$

1.1.2 Brillouin Zone in One-Dimensional Lattice and Peierls Transition

We have discussed free electrons in one-dimensional system without lattice of crystal. In a practical material, the electrons are moving in crystal lattice and the lattice will influence the energy states of the system. We consider N atoms which are equally spaced in a line to form one-dimensional lattice. If the distance of two neighbor atoms (i.e., lattice constant) is a, then the length of the system is $L = Na$ (strictly speaking, $L = a(N-1)$, for $N >> 1$ we take $L = N$a). If each atom provides one valence electron to contribute conductance, there are N conduction electrons in the system. As described above, the wave function can only take certain discrete values. At ground state of the system, the N electrons occupy momentum space below Fermi momentum $[-k_F, +k_F]$. For the weak interaction between the electrons and lattice atoms, the energy of an electron is mainly contributed by kinetic energy (free electron):

$$E_0(k) = \frac{h^2 k^2}{2m} \tag{1.11}$$

The plot of energywavenumber has a parabolic form as depicted in Fig. 1.2a (dashed line), which is similar to the case of free electrons (Fig. 1.1). Such an energy-wavenumber relation $E(k)$ is called energy spectrum.

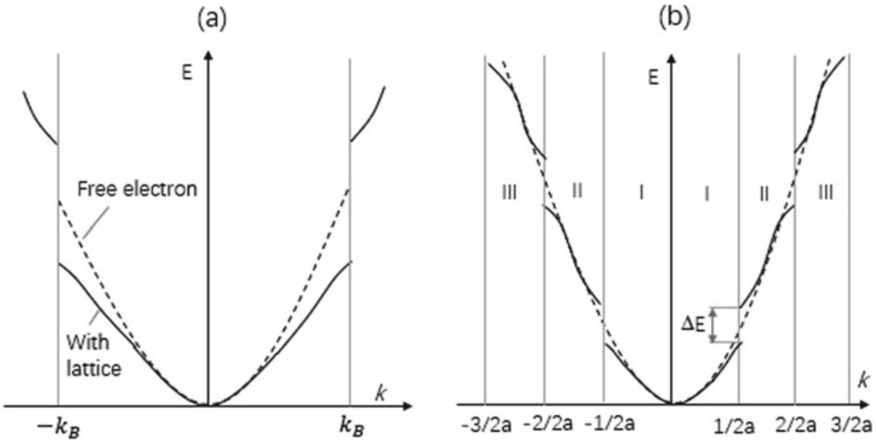


Fig. 1.2 Schematic illustration of energy spectrum of 1D crystal and Brillouin zones

When each atom provides one conduction electron, the linear density of electrons is:

$$n = \frac{N}{L} = \frac{1}{a} \tag{1.12}$$

From Eq. (1.9), we have the Fermi momentum of electrons:

$$k_F = \frac{n}{4} = \frac{1}{4a}, \tag{1.13}$$

This indicates that for such a one-dimensional system, the electrons occupy the states in the region [−1/4a, 1/4a], and those states outside the region are empty.

Next, we discuss the influence on the energy spectrum caused by the atom lattice. An electron with wavelength $\lambda = 1/k$ propagates in a 1D crystal, and the plane wave experiences scattering from atoms as shown in Fig. 1.3 where the solid line expresses the forward propagated wave and the dashed lines express reflective waves from atoms in the crystal lattice. Let us examine the situation at point A. The wave paths of the waves reflected from different atoms are different. As the lattice constant is a, the path difference of reflected waves from any two neighbored atoms is $\Delta l = 2a$ [e.g., path (ACA)-path (ABA) = $2a$]. Therefore, the phase difference between the two reflected waves from neighbored atoms is:

$$\Delta\varphi = 2\pi\frac{\Delta l}{\lambda} = 2\pi\frac{2a}{\lambda}, \tag{1.14}$$

For electrons with long wavelength, $\lambda >> a$, $\Delta\varphi << 2\pi$. Hence, at point A, the phase differences for waves reflected from all atoms in the chain are distributed in the range $[0, 2\pi]$, and this leads to a cancelation of the reflected waves which means

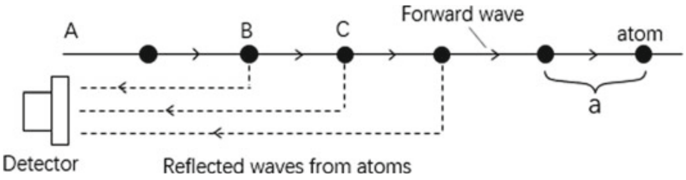


Fig. 1.3 Schematic illustration of electron wave propagation and reflection in 1D crystal

that the waves of electrons can propagate forward without attenuation by the lattice atoms. Thus, for electrons with small momentum, the energy spectrum is close to that of free electrons $E_0(k)$.

For electrons with large momentum (i.e., small wavelengths) from Eq. (1.14), one can see that the phase difference of reflected waves from two neighbor atoms $\Delta\varphi$ increases. In this case, the reflected waves will not cancel each other completely. The energy spectrum of electrons $E(k)$ start deviate from that of free electrons $E_0(k)$. In Fig. 1.2a, the solid curve expresses actual energy spectrum. When k is small, the solid cure is close to the dashed curve (free electrons). With decreasing of wavelength, the deviation between the two curves increases, especially in the case $\lambda = 2a$. From Eq. (1.14), one can see that all reflected waves are in phase and the reflected waves are strengthened by superposition. This indicates that the waves with $\lambda = 2a$ cannot propagate in the 1D lattice. The wavenumber (k_B) that corresponding to $\lambda = 2a$ defines a boundary of wave propagation.

$$k_B = \frac{1}{\lambda} = \frac{1}{2a}, \tag{1.15}$$

The electrons with wavevector k_B will experience a strong scattering from lattice atoms which leads a gap at k_B for the energy spectrum (Fig. 1.2a).

More generally, when $\lambda = 2a/m$ ($m = \pm 1, \pm 2, \pm 3, \ldots$), $\Delta\varphi = 2m\pi$ (see Eq. 1.14), the reflective waves from lattice atoms are in phase. The energy spectrum is discontinuous at following wavenumbers:

$$k_B^m = \frac{m}{2a}, \quad (m = \pm 1, \pm 2, \pm 3, \ldots) \tag{1.16}$$

It is obvious from Eq. (1.16) that because the existing of lattice atoms, there is series of special points k_B^m in the momentum space where the energy spectrum is discontinuous (Fig. 1.2b). These points define many regions in the momentum space. In each region, the energy spectrum is continuous, and at the boundary between any two neighbored regions (k_B^m), an energy gap exists. Each continuous region forms an energy band, and the energy gap between two neighbored regions is called band gap. The regions that are divided by k_B^m form Brillouin zones, where the region with small momentum is the first Brillouin zone. With increasing momentum, other regions are named second Brillouin zone, third Brillouin zone in turn.

For each Brillouin zone, the width is $1/a$, and the energy spectrum in each Brillouin zone form an energy band. The points k_B^m are the boundaries of Brillouin zones. For 1D crystal lattice, the two boundary points of the first Brillouin zone are $\pm\ 1/2a$, where a is the lattice constant.

Next, let us evaluate the number of states in each Brillouin zone. For 1D system, the interval of two neighbor momentum states is $\Delta k = 1/L$ in the momentum space (Eq. 1.7), while the momentum region in one Brillouin zone is $1/a$. The total state number in a Brillouin zone is:

$$\left(\frac{1}{a}\right)/\left(\frac{1}{L}\right) = \frac{L}{a} = N_c \tag{1.17}$$

where N_c is the state number in the first Brillouin zone of 1D crystal. When the atoms are equally spaced (Fig. 1.4a), the lattice constant "a" equals the average distance of atoms "$\overline{a}$", i.e., each unit cell only contains single atom. In this case, the number of states (Eq. 1.17) equals the number of atoms Nc $= N$. As each state can occupy two electrons, 2 N electrons are needed for each Brillouin zone (or energy band) to be fully occupied. If each atom provides one free electron, only N free electrons in the system. Therefore, the fermi momentum locates in the middle of the first Brillouin zone, i.e., the corresponding energy band is partially filled, and the system is metallic. If atoms are arranged pairwise in the chain (or dimerized), one unit cell contains two atoms, $a = 2\ \overline{a}$ (Fig. 1.4b). The state number in the Brillouin zone is $N_\mathrm{c} = L/a = L/2\ \overline{a} = N/2$, i.e., N electrons can be occupied. If each atom provides one free electron, the Fermi momentum coincides with the boundary of first Brillouin zone, i.e., the energy band is fully occupied. In this case, the 1D system is semiconductor or insulator. Such lattice change-induced transition from conductive phase to semiconductor (or insulator) phase is called Peierls transition [1].

1.2 Semiconductor Property of Conjugated Molecules

In the polyacetylene, the basic unit is CH and each CH provides one p electron as the carbon is sp^2 hybridized. In principle, such a structure is expected to behave as an intrinsic conductive polymer. However, pure polyacetylene is not conductive which is explained by the π-electron overlap in an alternating fashion, i.e., the CH units arrange pairwise in the polymer chain. In such 1D structure the first Brillouin zone (or lowest energy band) is fully occupied and the higher energy bands are empty. This specifies that the polyacetylene is intrinsic semiconductor.

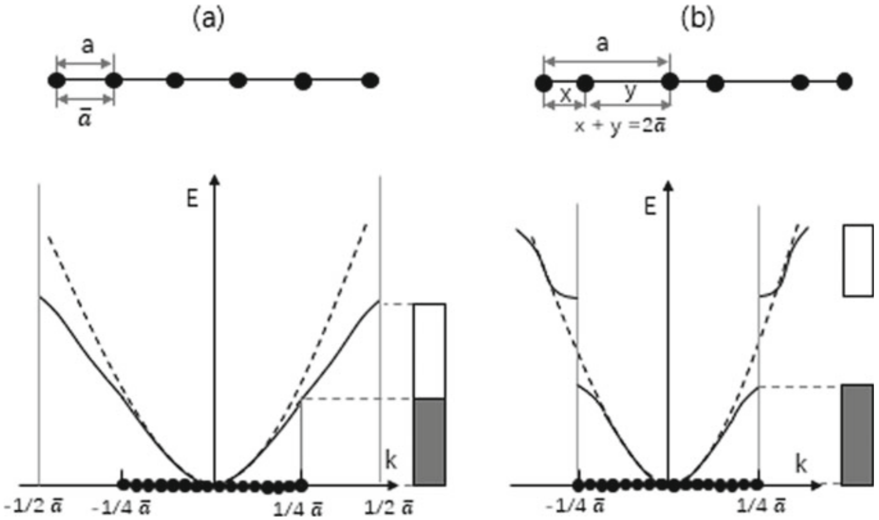


Fig. 1.4 Schematic illustration of energy spectrum of 1D crystal for equally spaced atoms (**a**) and paired atoms (**b**)

1.2.1 *Solitons in Polyacetylene*

As described above, polyacetylene is intrinsic semiconductor which is not conductive in pure state. After doping of donor impurity (Li, Na, K…) or acceptor impurity (Cl, I, Br, AsF_5, PF_5, BCl_3 …), it became conductive. After such doping, the conductance of polyacetylene has increased for 10 orders of magnitude from $10^{-9}(\Omega^{-1}\ \mathrm{cm}^{-1})$ to 10 $(\Omega^{-1}\ \mathrm{cm}^{-1})$ [2], which indicate that there are many mobile charges in the polyacetylene. If these charges are electrons or holes, one can use spin resonance technique to measure spin momentum of the charges, i.e., magnetic susceptibility $\chi > 0$. Experiment showed that when the impurity concentration is less than 6%, the magnetic susceptibility is zero as shown in Fig. 1.5 [2–4]. This indicates that the charge carriers are spinless. When the impurity concentration is larger than 6%, there is a phase transition in the system: from semiconductor to conductor and χ increases drastically. The spinless charge carriers indicate that the carriers in the polyacetylene are not electrons or holes. To understand the electrical conduction mechanism, W. Su, J. R. Schrieffer and A. Heeger have proposed a new theory [5]. It is suggested that the charge carriers are solitons which can carry positive charges and negative charges with zero spin. This theory can nicely explain many observed properties in polyacetylene.

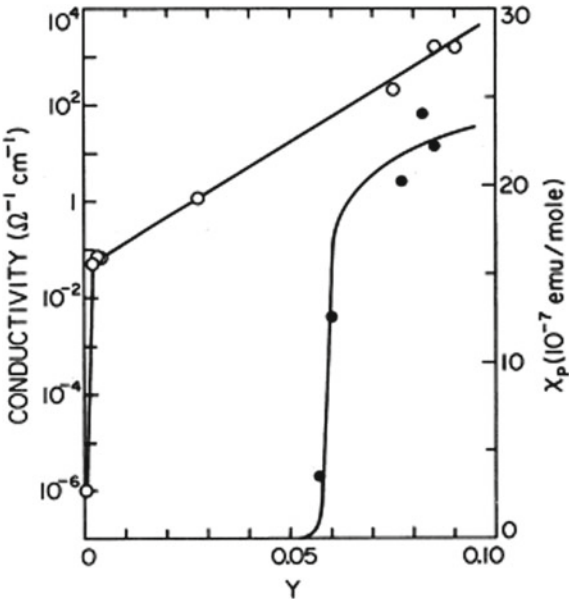


Fig. 1.5 Impurity content dependence of conductivity and susceptibility measured from trans-$(CH)_x$ doped with sodium (Adapted from ref [2])

1.2.1.1 Degenerate /Non-degenerate Ground States in Conjugated Polymers

For a given sequence of polyacetylene chain (with carbon atoms numbered as 1, 2, 3⋯), there are two ways of dimerization of carbon atoms as shown in Fig. 1.6.

Odd numbered atoms displace to the right direction for u_0, while the even numbered atoms displace to left direction for u_0 as shown in (a);

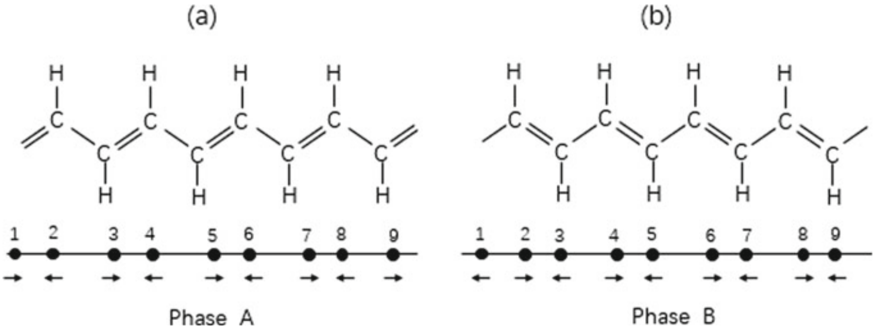


Fig. 1.6 Phase A and phase B in trans-polyacetylene

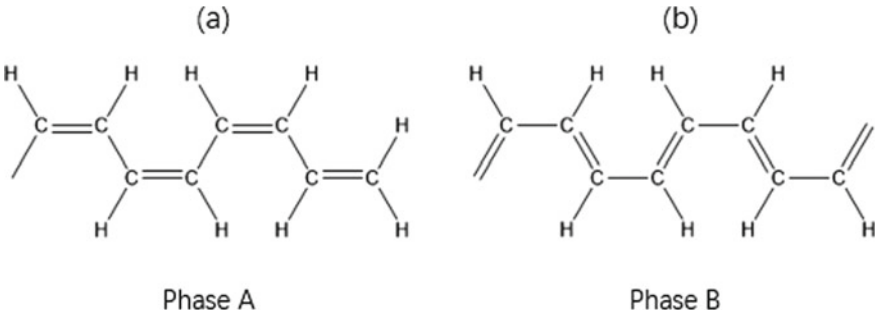


Fig. 1.7 Phase A and phase B in cis-polyacetylene

In contrast to (a), odd numbered atoms displace to the left direction for u_0, while the even numbered atoms displace to right direction for u_0 as shown in (b);

We specify the dimerization structure (a) as phase A and the structure (b) as phase B. If we interchange the positions of singe bond and double bond in phase A, it becomes phase B. The same is for the transition from phase B to phase A. For trans-polyacetylene, the two phases are shown in Fig. 1.6, while for cis-polyacetylene, the two phases are shown in Fig. 1.7. In the trans-polyacetylene, the phase A and phase B are completely equivalent and the ground energies of the two phases are degenerate. For the cis-polyacetylene, the phases A and B are inequivalent, and the energies of the two phases are non-degenerate. Therefore, the cis-polyacetylene has only one ground state which is the phase A. For other polymers, like polyparaphenylene, polythiophene, polypyrrole, etc., all have energy non-degenerate states: phase A (rings are linked by single bonds) and phase B (rings are linked by double bonds) (Fig. 1.8). For polyparaphenylene, the two phases are well known as aromatic and quinoid phase. For these polymers, the phases A and B are isomers with different structures where the energy of phase B is higher than phase A [6]. The ground state degeneracy/non-degeneracy will determine the type of excited states of a conjugated polymer. When there are degenerate ground states of phase A and B, solitons might exist in the polymer chains. In contrast, when the grounds are non-degenerate, the solitons cannot exist and polarons can be formed in the polymer chains (detailed in future sections).

1.2.1.2 Solitons in Trans-Polyacetylene

In the dimerized ground state of trans-polyacetylene (phase A or B), the displacement u_0 of any two neighbor atoms has opposite directions (Fig. 1.6). The atom displacement in a chain can be described with an order parameter ϕ_n:

$$\phi_n = (-1)^n u_n, \tag{1.18}$$

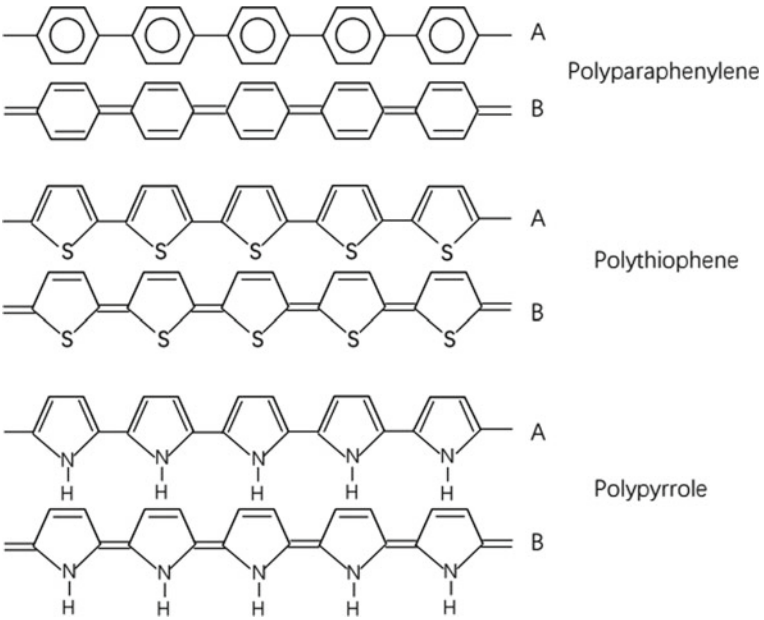


Fig. 1.8 Schematic molecule structures of phase A and phase B for polyparaphenylene, polythiophene, and polypyrrole

where u_n is the physical displacement of n-th atom. It is convenient to use ϕ_n to express a dimerized polymer chain instead of using u_n. For phase A, $\phi_n = -u_0$, and for phase B, $\phi_n = u_0$.

Assuming a trans-polyacetylene chain was in phase A originally, and a sequence of it has changed to phase B through thermal excitation or irradiation (Fig. 1.9). The excitation process requires certain energy $2E_s$. In the left part, a transition from phase A to phase B is seen, and this transition region is named as positive domain wall. Similarly, in the right part, a negative domain wall exist which is formed from transition from phase B to phase A. Because the energy degeneracy of the phases A and B, the energy spent for excitation is mainly used for domain wall formation (i.e., the energy is stored in the domain walls). The energy in the regions outside the domain walls does not change after the excitation. The domain walls are neither phase A nor phase B, where the links between carbon atoms are neither a single bond nor a double bond (indicated with dotted lines in Fig. 1.9). In a positive domain wall, the order parameter ϕ_n varies from $-u_0$ to u_0 across the domain wall (Figs. 1.10 and 1.11).

The domain wall is an elementary excitation which can move along the chain and the domain wall configuration does not change during the movement. We name such a domain wall as soliton. A positive domain wall is named as soliton (expressed as S) and negative domain wall is named as anti-soliton (expressed as $\overline{S}$).

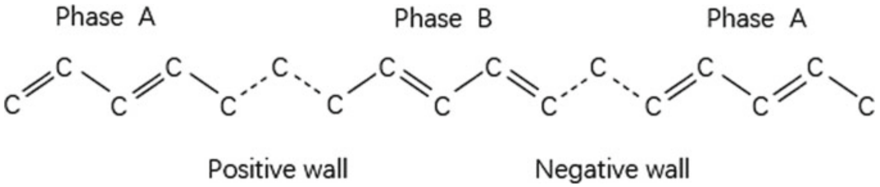


Fig. 1.9 Domain walls in trans-polyacetylene

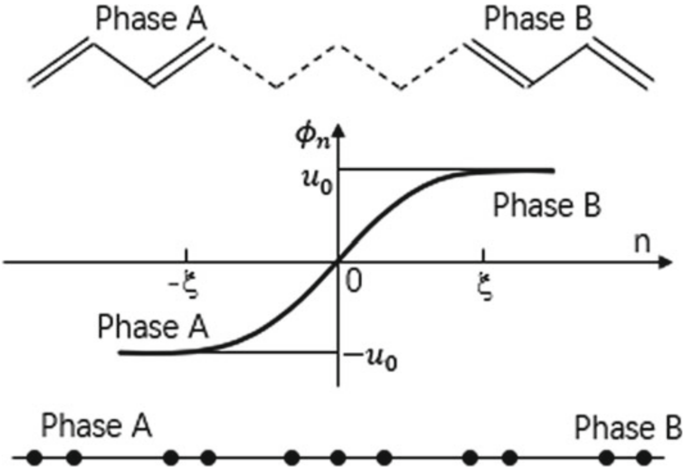


Fig. 1.10 Schematic structure of positive domain wall

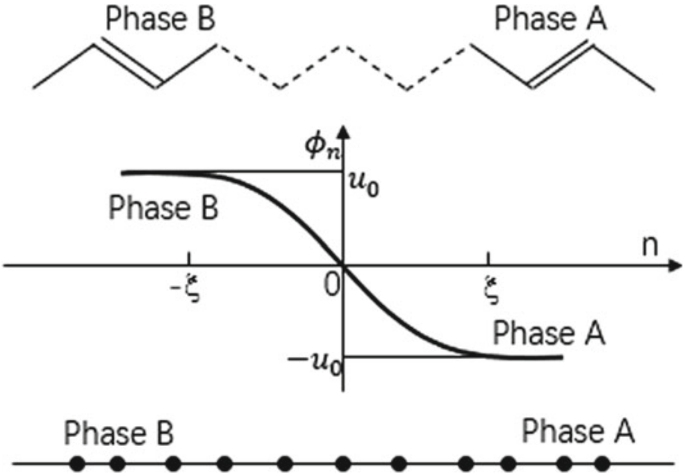


Fig. 1.11 Schematic structure of negative domain wall

In a dimerized polymer chain, a soliton as a localized distortion of lattice generates local potential, like the impurity in crystal of semiconductor. Thus, a soliton can generate a localized state around it and the energy level of the localized state is discrete and located in the middle of the band gap [5, 7]. The energy level of the localized soliton state is called soliton level ε_s which has been found experimentally [8, 9].

1.2.1.3 Electrical Charge and Spin of Soliton

A polymer chain with π-electrons of N can forms N energy levels. The dimerization induces two energy bands with a band gap between them, i.e., valence band (VB) and conduction band (CB). Each band contains $N/2$ levels. Each level contains two electrical states and can be occupied by two electrons with different spin orientations (spin-up and spin-down). The valence band is fully occupied by electrons and the conduction band is empty. For clear description, we draw the band diagram separately for different spin orientations in Fig. 1.12a where each line represents one electrical state and can be occupied with one electron.

The soliton generation does not change the numbers of atoms and π-electrons in the polymer chain. The total electrical states will not change in the system owing to the soliton generation. Thus, with the soliton state generation, the valence band needs to deficit of one-half a state for each spin, as does the conduction band (Fig. 1.12b). We consider spin-up ($s = 1/2$, right) and spin-down ($s = -1/2$, left) states separately. For spin-up state (right of Fig. 1.12b), to generate a soliton state in the gap, a deficiency of one state from valence and conduction band is needed. Because the soliton state located in the middle of gap and the symmetry of the band structures, the reduced number of states from valence and conduction band are the same. This requires a reduction of "one-half state" from both valence and conduction band. For better

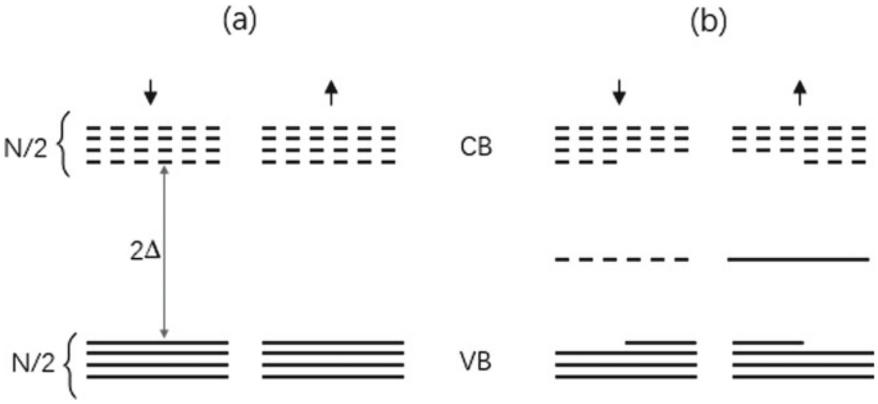


Fig. 1.12 Schematic illustration of energy level distribution for dimerized polymer molecule (**a**) and soliton energy level (**b**)

visualization, we illustrate the bottom of the conduction band with half dashed line and illustrate the top of the valence band with half solid line. These two "half states" are moved to the middle of gap to form a soliton state with spin-up oriented electron. The same is happened for the states with spin-down electrons, where a reduction of "one-half of spin-down state" from both valence and conduction band.

For pure polyacetylene, the number of π-electrons N does not change after the soliton generation. Before the soliton generation, there are N electrical states which are occupied with N electrons. After soliton generation, one state (one-half for spin-up and one-half for spin-down) is donated from valence band. Thus, only $N-1$ electrons can be accommodated in the valence band, and the remaining one electron needs to fill in the soliton state with either spin-up or spin-down. We assume that it occupies the spin-up state, therefore the spin-up soliton state is illustrated with solid line and the spin-down soliton state is illustrated with dashed line.

Let us examine the charge and spin of the soliton. Because the number of electrons does not change after the soliton generation, the system remains neural. Therefore, the soliton is non-charged. In the valence band, the occupation condition is identical for the two spin orientations and the total spin is zero. There is neither electron nor spin in the conduction band. On the soliton level, there is only one electron occupied in the spin-up state (the spin-down state is empty); hence, the total spin is $+1/2$. Therefore, the soliton has no charge but has spin 1/2, i.e., neutral soliton has spin $\pm 1/2$. Experiment showed that a kind of "defect" exists in polyacetylene which is neutral electrically, but they carry spin [10]. Such neutral defects with nonzero spin are solitons.

From Fig. 1.12b, we see that in pristine trans-polyacetylene, only one soliton state from the two is occupied. Therefore, the empty soliton state can be occupied with the electron donated by the donor impurity, if donor impurity exists in the polyacetylene. In this case, the two soliton states are illustrated with two solid lines (Fig. 1.13a). In this case, at all energy levels (valence band, conduction band, soliton level), the electron occupation conditions are identical for both spin-up and spin-down states. The total spin is zero which indicates that the negatively charged soliton has zero spin.

If an acceptor impurity is introduced into the polyacetylene, the impurity will remove the electron from the soliton and the two soliton states became empty as shown in Fig. 1.13b. The two empty states of the soliton level are illustrated with two dashed lines. As an electron is taken, the soliton is positively charged, and the net spin is zero. A summary of charge/spin of soliton is listed in Table 1.1 along with the electron/hole for comparison.

It seems that the above mentioned "one-half state" violated the basic principle of quantum mechanics. An electron is described by a quantum state and cannot occupy one-half state. The reason is that the anti-soliton $\overline{S}$ needs to be considered here, as the soliton and anti-soliton are paired in the polymer chain. The soliton and anti-soliton can be treated as two wave packages in a whole state. Consider a soliton and anti-soliton pair (Fig. 1.14), where the left part is energy band structure for the soliton, while the right part is the energy band structure for the anti-soliton. In the valence band there are four "half state" (two with soliton and another two with anti-soliton),

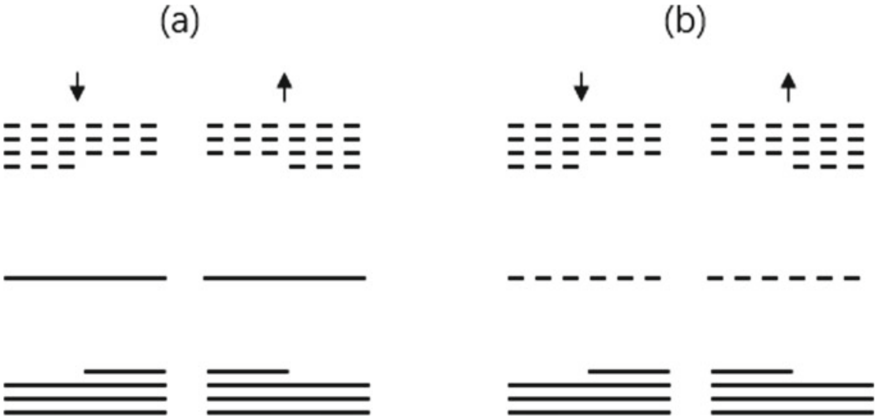


Fig. 1.13 Schematic illustration of energy levels for negative soliton $q = -\mathrm{e}$ and $s = 0$ (**a**), and positive soliton $q = +\mathrm{e}$ and $s = 0$ (**b**)

Table 1.1 The charge and spin of soliton

	Charge q	Spin S
Neutral soliton	0	$\pm\frac{1}{2}$
Positive soliton	+e	0
Negative soliton	−e	0
Electron	−e	$\pm\frac{1}{2}$
Hole	+e	$\pm\frac{1}{2}$

and two of them are occupied with spin-up electron and another two with spin-down electron. Two from the four “half state” form a whole spin-up state, and other two form a spin-down state. The two spin-up “half state” represent two wave packages of one wave function, i.e., the two spin-up “half state” form one whole spin-up state. The same description is applied for the two spin-down “half state.” The two “half state” are coupled together and occupied by one electron which is indicated with dashed curves in Fig. 1.14.

1.2.2 *Polarons in Conjugated Polymers*

1.2.2.1 The Formation of Polarons

Soliton and anti-soliton are simultaneously generated in a polymer chain. When they get close to each other an interaction is expected. The soliton and anti-soliton have three charging conditions which possess different interaction between the soliton and

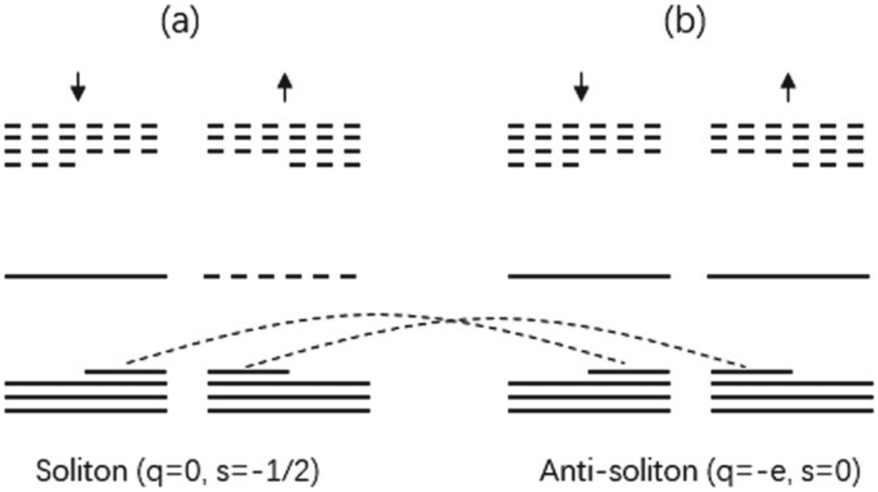


Fig. 1.14 State distribution of a $S - \overline{S}$ pair

anti-soliton. According to the total charges carried by the $S - \overline{S}$ pair, three different situations can be considered for investigating the soliton/anti-soliton interaction:

(i) The $S - \overline{S}$ pair has zero total charge, where soliton and anti-soliton carry opposite charges, or both are neutral.
(ii) The $S - \overline{S}$ pair has total charges ±2e, where the soliton and anti-soliton carry charges with the same sign.
(iii) The $S - \overline{S}$ pair has total charges ±e, where one carries charge (e or −e) and another is neutral for soliton and anti-soliton.

In the case (i), the soliton and anti-soliton attract each other. They approach each other under attraction force to reduce phase B gradually, and the soliton and anti-soliton annihilate eventually as shown in Fig. 1.15.

In the case (ii), as the soliton and anti-soliton carry charges with same sign, they repel each other. Therefore, no new local state will form.

In the case (iii), when the soliton and anti-soliton are apart with far distance, they attract each other, and the system energy is the total energy of soliton and anti-soliton $4\Delta_0/\pi$ (Δ_0 is the energy required to generate a hole). However, when

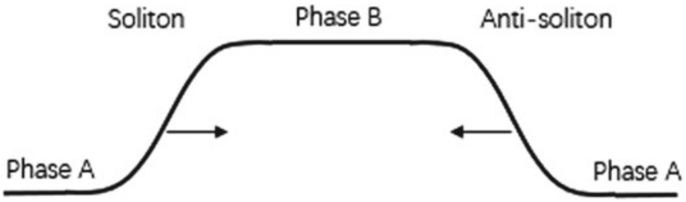


Fig. 1.15 Annihilation of soliton and anti-soliton

they are very close, a repelling force exists. Therefore, a balanced distance (1.24 ξ_0, where ξ_0 is called half width of the soliton) exists at which the net force between the soliton and anti-soliton is zero. While, the energy of the system is minimized which is $2\sqrt{2}\Delta_0/\pi$ [11, 12]. If the soliton and anti-soliton overlap for any reason to become single phased chain. The dimerized A (or B) phase will carry one charge (hole or electron) which will increase the energy of the system to Δ_0. Thus, soliton and anti-soliton can form a bound state with energy $2\sqrt{2}\Delta_0/\pi$. For this bound state the distance between the soliton and anti-soliton is 1.24 ξ_0, and the overlap between the soliton and anti-soliton is so huge that the profiles of the individual soliton and anti-soliton cannot be recognized. This newly formed bound state is stable and is termed as polaron.

1.2.2.2 The Structure and Property of Polarons

Polaron is a bound state formed with soliton and anti-soliton. Therefore, the polaron structure could be evolved from the structures of soliton and anti-soliton. The structure of polaron includes two aspects: distribution of atoms and energy band structure.

(1) The distribution of atoms in polaron

As stated earlier, the distribution of atoms is described with order parameter $\phi_n = (-1)^n u_n$. The coordinates at the centers of soliton and anti-soliton are x_0 and $-x_0$, respectively. When the length of $S-\overline{S}$ pair $2x_0$ is much large than width of soliton($2x_0$ >> $2\xi_0$), there is no overlap between the soliton and anti-soliton. Three regions exist on the chain as shown in Fig. 1.16a which is assumed that phase A is excited in phase B. If one is charged in the $\overline{S} - S$ pair, the soliton and anti-soliton attract each other, and the region A is shrinking as shown in Fig. 1.16b. At $2x_0 = 2\xi_0$, the soliton and anti-soliton overlap, the phase A disappears as shown in Fig. 1.16c. With further narrowing the phase A, an equilibrium position $2x_0 = 1.24\xi_0$ is reached where the ϕ_n is no longer being negative (Fig. 1.16d). Under this condition, the ϕ_n represents the order parameter of polaron. From the shape of ϕ_n, one can see that after the formation of polaron the chain is in single phase. The dent on the curve represents a small charged region with structure deformation from equilibrium, i.e., polaron. In the polaron formation process described in Fig. 1.16, the phase A is generated in phase B where anti-soliton is on the left and the soliton on the right. The polaron is formed in the phase B. Similarly, a polaron can be created in phase A and the process is shown in Fig. 1.17. In this case, the soliton is on the left and the anti-soliton on the right. The order parameter of the polaron is negative.

Polaron is a local lattice distortion in a uniform dimerized chain. The region of the distortion is around $4\xi_0$ where the displacements of atoms are not uniform (the values of u_n are different). Such a lattice distortion forms bound state located in the energy gap between the valence and conduction bands.

Fig. 1.16 Schematic illustration of polaron formation and polaron structure in phase B

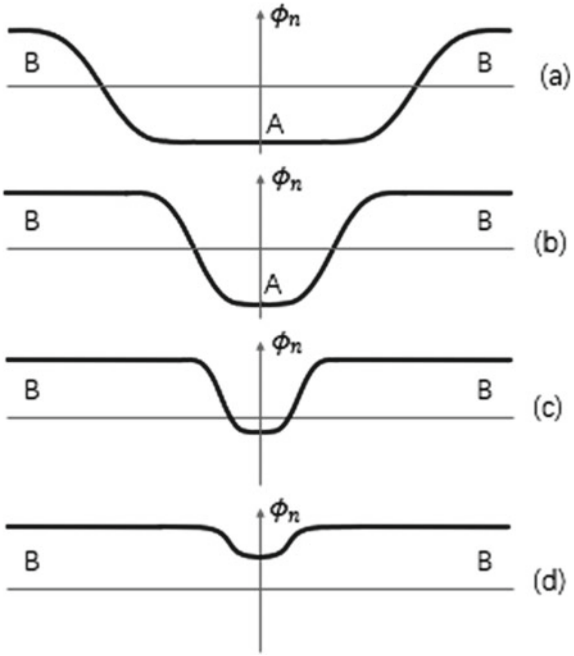
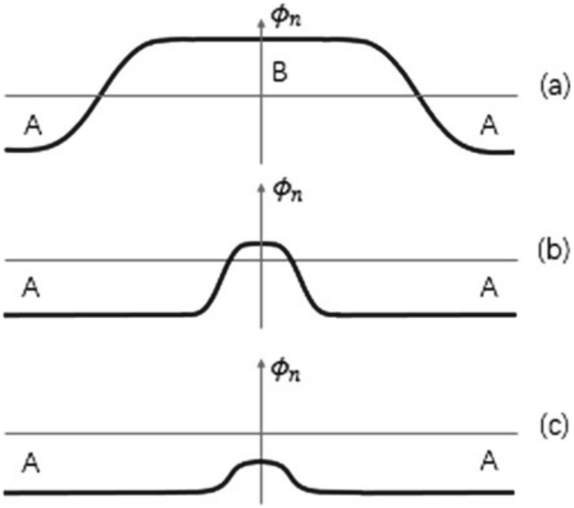


Fig. 1.17 Schematic illustration of polaron formation and polaron structure in phase A



(2) The energy levels of polaron

As the polaron can be viewed as a bound state of a $S-\overline{S}$ pair, the energy levels of the polaron could be evolved from soliton states. We examine the states of a $S-\overline{S}$ pair as shown in Fig. 1.18. For simplicity, only the spin-up states are considered (for the

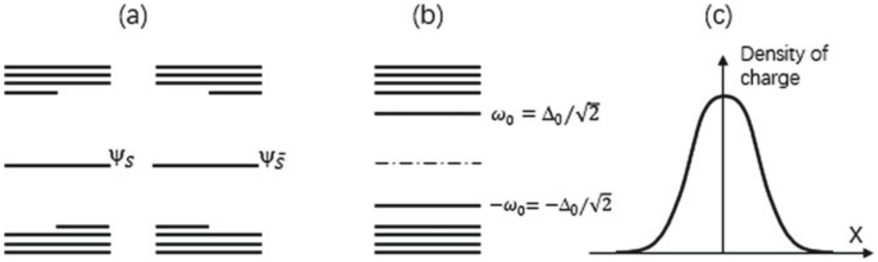


Fig. 1.18 Electrical spectrum and charge density distribution of polaron

spin-down states, the energy spectrum is symmetric with the spin-up states). When the soliton and anti-soliton are far apart ($2x_0 >> 4\xi_0$) they are less interacted, and the state of the soliton (ψ_S) and the state of anti-soliton ($\psi_{\bar{S}}$) are located in the center of energy gap (Fig. 1.18a, only spin-up state is drawn). Each state of the ψ_S and $\psi_{\bar{S}}$ is formed by splitting off one-half state from the valence band and conduction band. The states ψ_S and $\psi_{\bar{S}}$ are degenerate when the soliton and anti-soliton are far apart. When the soliton and anti-soliton approach to each other and partially overlapped, because the overlap of the wave packages of the soliton and anti-soliton, the two "one-half states" on the two conduction band edges of soliton and anti-soliton will merge together to become a whole state of the conduction band. The same is happened for the valence band. Therefore, in the polaron no "one-half state" exist as shown in Fig. 1.18b. The overlap of soliton and anti-soliton will bring huge impact to the gap states ψ_S and $\psi_{\bar{S}}$. The states ψ_S and $\psi_{\bar{S}}$ are degenerate when the soliton and anti-soliton are well apart. When the soliton and anti-soliton overlap, the interaction of them will cause the splitting of the degenerated ψ_S and $\psi_{\bar{S}}$, i.e., the ψ_S and $\psi_{\bar{S}}$ will mix and form two new states: bonding state and anti-bonding state. The bonding and anti-bonding states have different energies which appear as two separated energy levels in the band gap. As the soliton and anti-soliton are mirror symmetric the newly formed bonding and anti-bonding states are symmetrical about the gap center. The bonding state is below the gap center line for ω_0, and the anti-bonding is above the line for ω_0. Thus, for the polaron there two separated energy levels in the energy gap which are ω_0 and $-\omega_0$. The value of the ω_0 is $\Delta_0/\sqrt{2}$ [7]. These two localized states are bound states of electron in the potential of the lattice distortion, and the charge localization is schematically shown in Fig. 1.18c.

1.2.2.3 The Charge and Spin of the Polaron

From the energy spectrum shown in Fig. 1.18, we can discuss the charge and spin of the polaron. The two energy levels $-\omega_0$ and $+\omega_0$ in the energy gap are split off from the valence and electron band, respectively. For the neutral ground state, the states in valence band and $-\omega_0$ level are occupied completely, while the $+\omega_0$ level and conduction band are empty. For trans-polyacetylene, a stable polaron can