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Photoinduced Phase Transitions in Polyacene and Its Heterocyclic Analogs

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ABSTRACT

Photoinduced structure phase transitions in polyacene, paracyanogen and boron-nitride acene are studied. In each compound, there exist two degenerate lattice-distorted structure: double bonds in a *cis* pattern and those in a *trans* pattern. In polyacene and paracyanogen, *cis* patterned lattice configurations have the mirror symmetry while the *trans* ones have the C_{2z} rotation invariance. In boron-nitride acene, either *cis* patterns or *trans* patterns have no definite symmetries. We argue that the symmetry properties will strongly affect the optical properties and lead to contrast optical conductivities between the *cis* and *trans* patterns in polyacene, paracyanogen and boron-nitride acene.

By using the time-dependent Hartree-Fock method, we simulate the lattice evolution process in polyacene, paracyanogen and boron-nitride acene after they are photoexcited. We find that any kind of photons can not break the symmetry of the initial state. Due to this symmetry-preserving law, phase transitions in polyacene and paracyanogen behave as the *one-way* switchings: Only *trans* patterns can be well converted into *cis* ones, but the reverse conversions are forbidden. Since boron-nitride acene has no definite symmetries in any lattice configuration, the symmetry-preserving law does not work and the phase transitions between *cis* and *trans* patterns are bidirectional.

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Chapter 1

Introduction and background

1.1 Photoinduced phase transitions

The phenomena of photoinduced phase transitions (PIPTs) have attracted a lot attentions in the past decade. Fundamentally, at low temperature, materials stay in their stable equilibrium ground state. However, some other transient states having higher energy than the ground state, may also be locally stabilized and long-lived. They are just the so-called metastable states which are effectively the same as the equilibrium ones. Photoexcitation is proved to be powerful to search these possible metastable states.¹ Nowadays, the great development of experiment techniques have already been able to provide sub-10-fs pulses, which makes the observation of fast dynamics after photoexcitation is realizable.

An ultrafast pulse is able to effectively pump the ground state electrons to high-lying energy levels (Fig.2.3), providing the absorption of photons with the energy scale of eV and forming electron-hole pairs. A sudden change of the charge distributions may induce a motion of the crystal lattice surrounding the excited electrons, which is called the lattice relaxation process just after the photoexcitation. Such a relaxation finally stabilize the crystal into a equilibrium phase, although it might be local stable with a substantial energy barrier separated with the other equilibrium state.

Meanwhile, multiple degrees of freedom are nowadays becoming hot candidates to study photoinduced phase transitions. Photoinduced nonequilibrium processes have been widely investigated in the system of charge density waves (CDWs), spin density waves

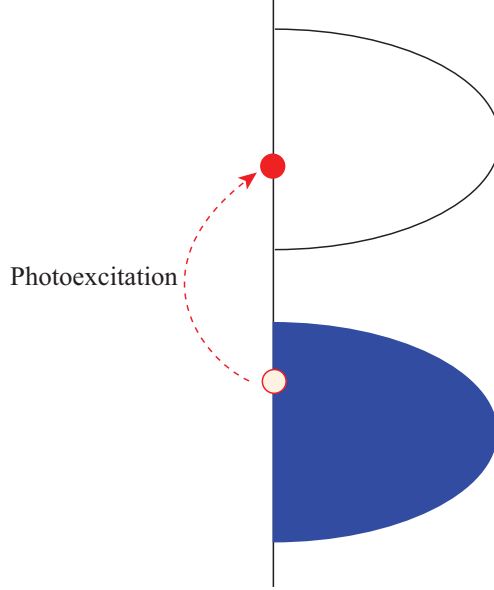


Figure 1.1: The schematic of photoexcitations.

(SDWs), bond order wave (BOWs), orbital-ordered systems, and so on.

K. Iwano discussed the precursor of photoinduced structural phase transitions in the coupled-chains system with the electron-lattice interaction, where an aggregation mechanism of photoinduced local CDW antodomains contributes to driving a global phase transition.^{2,3} S. Ishihara's group studied the photoinduced photodynamics in spin-charge coupled system within the double-exchange model. Photons induce the charge transfers of itinerant electrons, leading to the fluctuation of charge order waves. Through the Hund's coupling between the conduction electron and the localized spin, both charge orders and antiferromagnetic correlation can be collapsed by photoirradiation.⁵ S. Iwai reported the coherent control of charge and lattice dynamics in a photoinduced Neutral-to-Ionic transition of the charge-transfer compound, tetrathiafulvalene-*p*-chloranil (TTF-CA). By changing the interval of the two laser pulse, charge-lattice coupled oscillation could in phase be enhanced.⁶ T. Tohnyama' group investigated the photoinduced nonequilibrium evolution of the half-filled one-dimensional extended Hubbard model, where near the phase boundary, a sustainable charge order enhancement is found by carefully tuning the laser frequency and strength.⁷ In some other cases, ultrashort pulses are used to manipulate the gap value of BCS superconductors.⁸ K. Yonemitsu studied the photoinduced phase transitions between a charge-density-wave (CDW) phase and a charge-

polarization (CP) phase in a one-dimensional halogen-bridged binuclear platinum complex $R_4[\text{Pt}_2(\text{pop})_4\text{I}]_n\text{H}_2\text{O}[\text{pop} = \text{P}_2\text{O}_5\text{H}_2^{2-}, R = (\text{C}_2\text{H}_5)_2\text{NH}_2]$.⁹ Owing to that the lower energy charge-transfer processes occur only within a binuclear unit in the CP phase, the photoinduced transition takes place easily from the CDW phase to the CP phase, but the reverse conversion is hardly realized, so to say, phase transition behaves as an irreversible process. The direction of photoinduced phase transitions, whether they are reversible or not, stimulate us a great interest.

1.2 Introduction of polyacene, paracyanogen and boron-nitride acene

1.2.1 polyacene

As early as in 1992, S. Koshihara and Y. Tokura reported the photochromism in polydiacetylenes, where phase transitions between two different bond structures of a single crystals are induced by a single-shot-pulse irradiation.¹⁰ The intensity threshold of triggering the phase transition is quite low: Only one absorbed photon per 500 repeat units of the polymer is sufficient to induce the global phase transition. This high efficiency is believed due to cooperative interaction between the locally photoconverted domains. However, this photoinduced phase transition is strongly affected by the temperature. In such circumstances, we demonstrate a distinct photocontrol over a series of other polymers, especially focusing on the direction of phase transitions between their different isomers.

Polyacene (PA), which is nothing but two coupled polyacetylene chains with alternative inter-chain couplings (Fig. 1.1), has already been intensive investigated for more than a half century. We first introduce its bonding properties. Fig. 1.3(a) shows how two carbon atoms form the π -bond between them. 2s and 2p orbitals are almost of the same energy, which leads to the sp^2 hybridization between them and forms a triangle planar bond configuration. p_z orbital is left unaffected and is perpendicular to the triangle planar. The sp^2 orbitals approach to each other head to head and form the σ bond, while

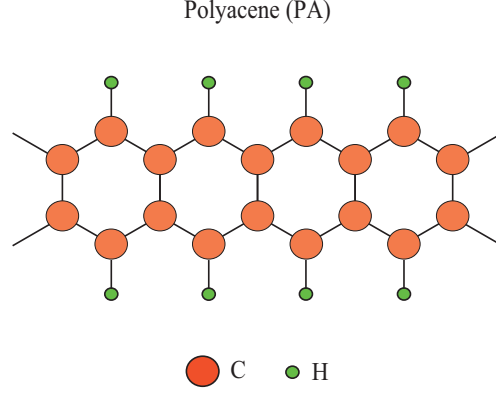


Figure 1.2: The illustration of polyacene.

the unhybridized p_z orbitals approach to each other in sideways, which forms the π bond. σ bonds are relatively strong and stable which form the skeleton of the material, while π bond is less efficient and delocalized. We learn from Fig. 1.3 (b) that, each carbon provides one π electron, then the system is a half-filling system.

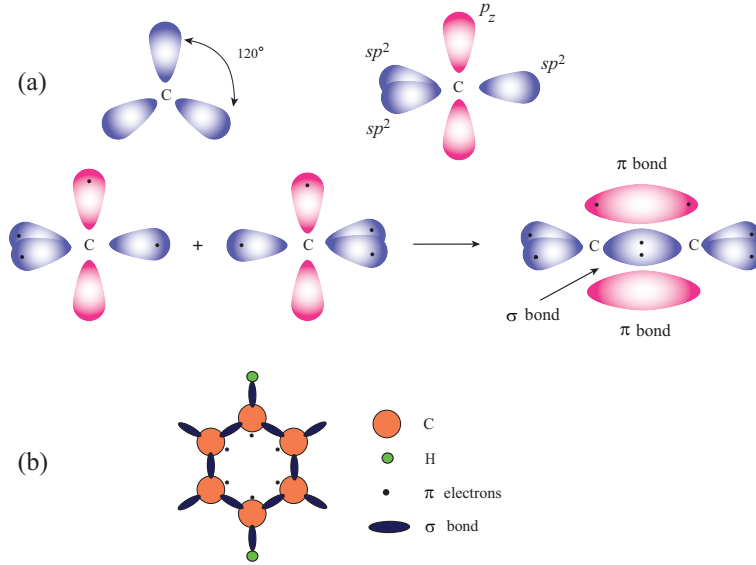


Figure 1.3: (a) sp_2 hybridization and π -bonds between two carbons; (b) bonding properties of polyacene, where one repeated unit is shown.

One remarkable distinguish between polyacene and the one chain system (for instance, polyacetylene) is that, the Peierls instability in polyacene is a conditional one.²⁰ This means a finite electron-lattice coupling is necessary to stabilize the bond-order-wave (BOW) states. If the strength of electron-phonon coupling and the Coulomb interac-

tion are both weak, the aromatic (AM) configuration of regular bond length should be stabilized. If the strength of electron-phonon coupling is sufficiently strong, there are two possible Peierls-distorted structure may be stabilized: double bonds in a *cis* pattern and those in a *trans* pattern, which read as in-phase (IP) and out-of-phase (OP) BOW respectively hereafter. There have been a long time controversy on whether the IP BOW or OP BOW is more stable.^{21–30} In the Su-Schrieffer-Heeger (SSH) model³¹ which has no any Coulomb correlations, the IP BOW and OP BOW have exactly the same energy. They are degenerate unless we take account of the electron itinerancy beyond the nearest-neighbor hopping³² and/or the electronic correlation beyond the Hartree-Fock (HF) scheme. Thus the *cis* and *trans* patterned lattice configuration may coexist in the real linear polybenzenoid oligomers.

Although it is very hard for us to energetically distinguish IP BOW and OP BOW of polyacene, their optical-conductivity spectra can do.²⁷ The *cis* and *trans* distorted configurations still have the degenerate perpendicular polarized optical spectroscopy, but the parallel polarized optical spectroscopy are quite distinct. This finding stimulate a renewed interest of optical manipulation of its isomers rather than energetically ranking them. Furthermore, photoinduced phase transitions between the two degenerate structures were also investigated in a first step,³⁰ and an interesting conclusion is achieved: the *trans* configuration is well convertible into the *cis* one, whereas the reverse conversion is much less feasible. However, the exact origin of such a one-way switching is not well answered yet. Thus motivated, we believe that more other cases need to be discussed, to obtain a thorough knowledge of the exact origin of this irreversible photoinduced phase transition.

1.2.2 paracyanogen

Paracyanogen (PCN) is another compound which is geometrically close to polyacene. It is nothing but replacing polyacene’s most outer carbons into nitride atoms (Fig. 1.4). Paracyanogen was first discovered by Guy Lussac,³³ and in the following few decades, much effort were contributed to achieve a better understanding of its chemical and physical properties.^{34–37} We briefly discuss the chemical bonding properties of paracyanogen in

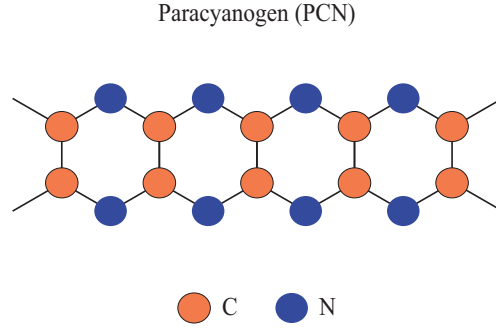


Figure 1.4: Illustration of paracyanogen.

Fig. 1.5. Between nitride and carbon, the σ - and π - bond are formed in the similar way through the sp^2 hybridization. For the liner polybenzenoid structure, there is a dangling lone pair of electrons on one σ - bond of nitride, beside which, each nitride or carbon provide one p_z -orbital electron. The whole system is also a half-filling π electron system.

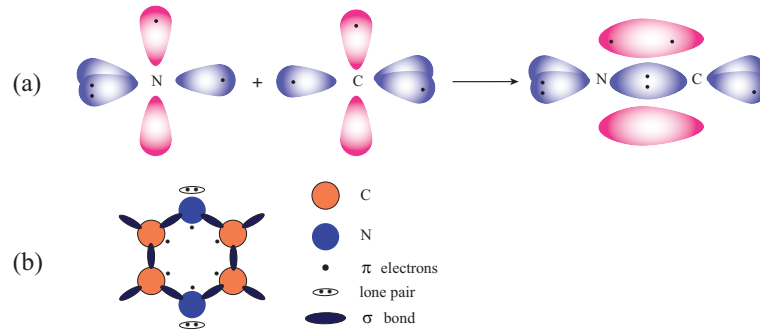


Figure 1.5: (a) sp^2 hybridization and π -bonds between nitride and carbon; (b) bonding properties of paracyanogen, where one repeated unit is shown.

Paracyanogen is generally believed to have the same electronic properties as polyacene in every aspect. It also has the *cis* (IP BOW) and *trans* (OP BOW) Peierls-distorted bond configurations. However, since the nitride atoms sit on the different sublattice of the honeycomb lattice, there may be some new phenomenon especially when we consider the polarized optical spectroscopy. The situation of photoinduced phase transitions between the two distorted states, is reversible or not, also stimulate our great interest.

1.2.3 BN-acene

Another heterocyclic aromatic compound is boron-nitride acene, which we abbreviate as BN-acene hereafter, also has the polybenzenoid structure (Fig. 1.6). Experimentally, BN-acene can be obtained by cutting a hexagonal BN sheet or unzipping a BN nanotube.³⁸ BN sheet and nanotube have already been intensively investigated about its chemical and electronic properties,^{39–43} and they are usually believed to be inorganic materials.³⁹

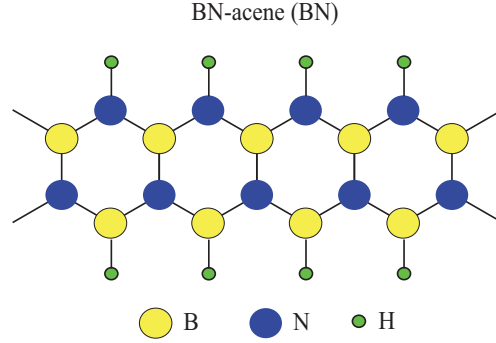


Figure 1.6: Illustration of boron-nitride acene.

The way of boron and nitride bonding to each other is shown in Fig. 1.7(a). We notice that nitride provide two p_z orbital electrons while boron provide nothing. Since nitride has a higher electron affinity than boron, the bond between nitride and boron has significant ionic properties. Fig. 1.7(b) demonstrates the bonding properties and itinerant electrons distributions of BN-acene, where it is also a half-filling π -electron system.

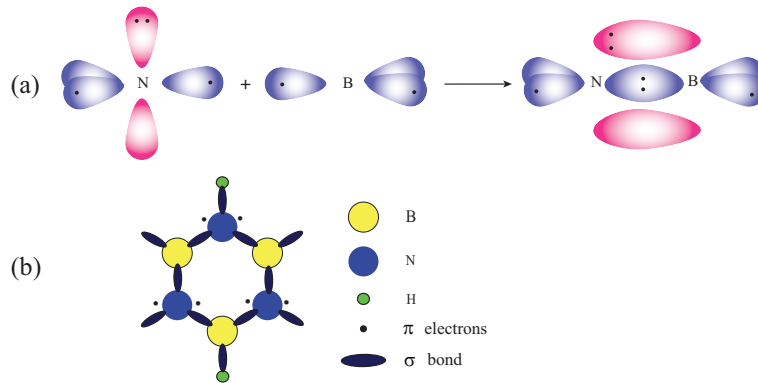


Figure 1.7: (a) sp^2 hybridization and π -bonds between nitride and carbon; (b) bonding properties of BN-acene, where one repeated unit is shown.

The role of electron-phonon coupling was also frequently discussed in many cases and sometimes was believed to play an important role.^{44–47} In our work, we take the SSH type electron-phonon coupling into account. Actually, we will show that it also has a conditional Peierls instability. When the electron-phonon coupling strength is sufficiently strong, two degenerate Peierls-distorted structure also exist. What we are interested is the photoinduced phase transitions between the two Peierls-distorted states among polyacene, paracyanogen and BN-acene. The schematic of their distorted structures are summarized in Fig. 1.8. By making a comparison of the photodynamics among them three, we hope some general knowledge of photoinduced phase transitions in such kind of polybenzenoid structure materials will be revealed.

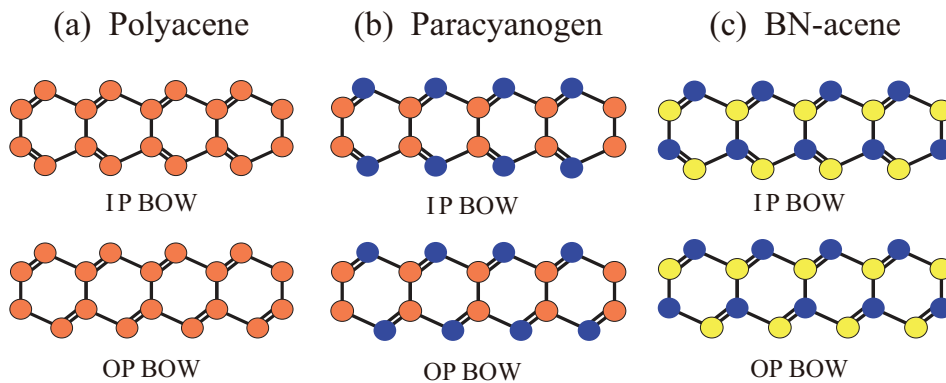


Figure 1.8: The in-phase (IP) and out-of-phase (OP) bond-order-wave (BOW) configurations of (a) polyacene (b) paracyanogen and (c) BN-acene.

Chapter 2

Ground state properties

2.1 Model Hamiltonian

We use an extended Peierls-Hubbard (EPH) Hamiltonian to describe all the three compounds,⁴⁸

$$\begin{aligned}
\mathcal{H} = & \sum_{l=1}^2 \sum_{m=1}^{2N} \sum_{s=\pm} \varepsilon_{l:m} n_{l:m,s} + \sum_{l=1}^2 \sum_{m=1}^{2N} \left(\frac{K}{2} r_{l:m}^2 + \frac{M}{2} \dot{u}_{l:m}^2 \right) \\
& - \sum_{l=1}^2 \sum_{m=1}^{2N} \sum_{s=\pm} \left[(t_{\parallel} - \alpha r_{l:m}) c_{l:m,s}^{\dagger} c_{l:m+1,s} + \text{H.c.} \right] \\
& - t_{\perp} \sum_{n=1}^N \sum_{s=\pm} (c_{1:2n-1,s}^{\dagger} c_{2:2n-1,s} + \text{H.c.}) \\
& + U \sum_{l=1}^2 \sum_{m=1}^{2N} \left(n_{l:m,+} - \frac{1}{2} \right) \left(n_{l:m,-} - \frac{1}{2} \right) \\
& + V_{\parallel} \sum_{l=1}^2 \sum_{m=1}^{2N} \sum_{s,s'=\pm} \left(n_{l:m,s} - \frac{1}{2} \right) \left(n_{l:m+1,s} - \frac{1}{2} \right) \\
& + V_{\perp} \sum_{n=1}^N \sum_{s,s'=\pm} \left(n_{1:2n-1,s} - \frac{1}{2} \right) \left(n_{2:2n-1,s} - \frac{1}{2} \right), \tag{2.1}
\end{aligned}$$

where $\varepsilon_{l:m}$ represents the π -electron orbital energy at site m th site of leg l . Its value depends on what atom appears on site ($l : m$). We set the orbital energy of boron, carbon and nitride to be $0.2 t_{\parallel}$, 0 and $-0.2 t_{\parallel}$ respectively. $c_{l:m,s}^{\dagger}$ ($c_{l:m,s}$) creates (annihilates) a π

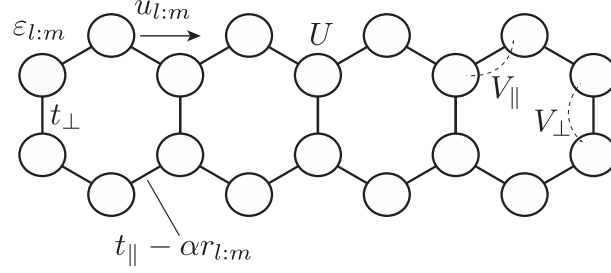


Figure 2.1: Schematic diagram of EPH model.

electron of spin $s = \uparrow, \downarrow \equiv \pm$ on site $(l : m)$. $r_{l:m} \equiv u_{l:m+1} - u_{l:m}$ signifies bond distortions caused by the m th and $m + 1$ th atoms on the leg l . We assume the rung ($\perp$) bond length is fixed as $a_{\perp} = 1.5 \text{ \AA}$, which is longer than the average parallel ($\parallel$) bond length $a_{\parallel} = 1.4 \text{ \AA}$.^{49,50} We assign a standard value, 2.4 eV ,^{26,28,51,52} for the average intra chain transfer integral $t_{\parallel}$, while the inter chain hopping integral is set as $t_{\perp} = 0.864 t_{\parallel}$.^{53,54} The σ -bond elastic constant K is assumed to be $15.5 \text{ eV/\AA}^2$.^{29,55,56} The electron-lattice coupling α is set for $4.1 \text{ eV/\AA}$ for polyacene and paracyanogen, while $4.6 \text{ eV/\AA}$ for boron nitride. The mass distinction among boron, carbon and nitride is ignored by setting them equally to be $1350 \text{ eV} \cdot \text{fs}^2/\text{\AA}^2$.^{54,57} The Coulomb interaction, ranging over neighboring sites, are modeled in $V_{\parallel(\perp)} = U/\kappa \sqrt{1 + 0.6117 a_{\parallel(\perp)}^2}$.⁵⁸ κ reads as a dielectric parameter with an intermediate value of 1.5. System sizes are set for $N=64$, which is long enough for studying the evolution of nonlinear excitations. Periodical boundary condition is applied through our calculation. The schematic diagram of the above Hamiltonian is shown in Fig. 2.1.

2.2 Ground state properties of polyacene

2.2.1 Phase diagram

Fig. 2.2 (a) shows the ground state phase diagrams of polyacene at sufficient low temperature $T = 0.005 t_{\parallel}$ as function of the on-site Coulomb interaction U and the electron-phonon coupling lattice α . There are phases of paramagnetic phase (PM), anti-ferromagnetic Mott-insulator phase (AF MI), charge-density-order phase (CDW), and in phase (IP) or

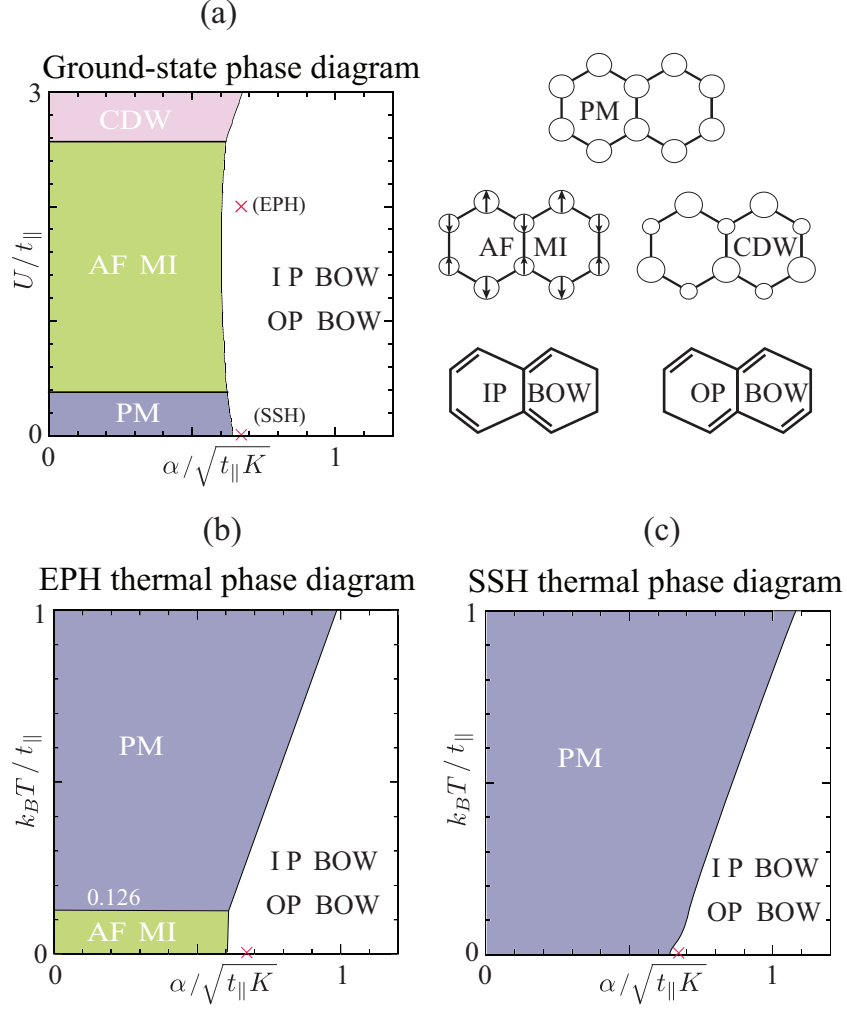


Figure 2.2: (a) Ground state phase diagram on the α - U plain and (b) thermal phase diagram within EPH model and (c) thermal phase diagram within SSH model of polyacene.

out-of-phase (OP) bond-order-wave (BOW) phase appear in the diagram. By increasing Coulomb interaction U , the metallic PM phase, is converted into the AF MI phase, accompanying with a second-order quantum phase transition. This phase transition strongly depends on the value of the dielectric parameter κ . In the $\kappa = 1$ case, namely, the bare correlation case, the PM phase can only be converted into CDW phase. While $\kappa = 2$, namely, the fully screened case, the Mott-insulator is fully stabilized in the most large U region. Here we use an intermediate value of $\kappa = 1.5$, then both AF MI and CDW phases are available.

On the other hand, by increasing the coupling strength α , the bond-order-wave phase

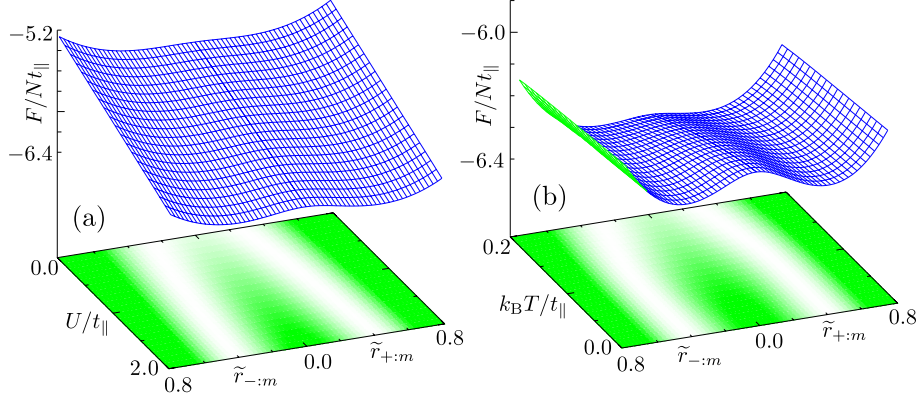


Figure 2.3: 3-D plot of free energy surface of IP BOW and OP BOW state in polyacene: (a) as functions of the Coulomb interaction and (b) as functions of the temperature.

is indeed stabilized, which just originates from the so-called conditional-Peierls instability. Two possible lattice-distorted structures, IP BOW and OP BOW, are always degenerate in energies.

The red crosses point out two parameters we will use later. The $U = 2$ point corresponds to the extended-Peierls-Hubbard (EPH) model, while the $U = 0$ point corresponds to the Su-Schrieffer-Hegger (SSH) model. In both two cases, we show the thermal phase diagrams of polyacene in Fig. 2.2 (b) and Fig. 2.2 (c). As the PM phase has relative higher entropy than BOW one, at high temperature, it gains much more free energy. With the same coupling strength the $\alpha = 4.1\text{eV}/\text{\AA}$, increasing temperature will melt down the BOW itself and drive the system converted into the PM phase.

We want to further clarify that by adjusting the Coulomb interactions and the temperature, how does the barrier between IP BOW and OP BOW changes. Fig. 2.3 (a) demonstrate the change of the barrier with varying Coulomb interactions. It is shown that decreasing the Coulomb interaction U will suppress the barrier. At the SSH level ($U = 0$), the strongly reduced barrier makes both IP BOW and OP BOW less stable. They are quite easy to fluctuate out their local minimum positions. At low temperature region, there is a remarkable barrier between IP BOW ($\tilde{r}_{+m}$) and OP BOW ($\tilde{r}_{-m}$) phases. With increasing the temperature, the barrier tends to shrink, while the depth of the two wells keep exactly the same between each other. At sufficient high temperature region,

the barrier almost disappear and the BOW phases are transited into the PM phase.

2.2.2 Optical conductivity

We use the parameter $U = 2t_{\parallel}$ within the EPH model to continue our discussion, since the Coulomb interaction is already believed to play an important role in describing the organic systems. Meanwhile, considering that in the SSH model, IP BOW and OP BOW have very weak lattice distortions and there is a very low barrier separating them. The Coulomb interaction is much favorable to obtain fully stabilized IP BOW and OP BOW phases.

Fig. 2.4 demonstrates the dispersion relations of IP BOW and OP BOW states of polyacene in the EPH model. Because there are four carbons in each repeated unit cell, they are molded into two valance (solid lines) and two conduction bands (dotted lines) fulfilling the electro-hole symmetry breaking. We notice that, IP BOW and OP BOW have exactly the same dispersion relations. The gap value is about $0.94t_{\parallel} = 2.25\text{eV}$. Both the lattice distortion and the Coulomb interaction contribute to the opening of this large gap. In the SSH model, the gap value is relatively lower, which is $0.24t_{\parallel} = 0.57\text{eV}$ only.

Considering that a charge-transfer excitation costs energy of eV order, we evaluate the real part of the optical conductivity as:

$$\sigma(\omega) = \frac{\pi}{\omega} \sum_i |\langle E_i | \mathcal{J} | E_0 \rangle|^2 \delta(E_i - E_0 - \hbar\omega). \quad (2.2)$$

$\mathcal{J}$ signifies the current operator, which is defined in the parallel ($\parallel$) and the perpendicular ($\perp$) direction, respectively, as

$$\mathcal{J}_{\parallel} = \frac{\sqrt{3}iea_{\parallel}}{2\hbar} \sum_{l,m,s} [(t_{\parallel} - \alpha r_{l:m}) c_{l:m,s}^{\dagger} c_{l:m+1,s} - \text{H.c.}], \quad (2.3)$$

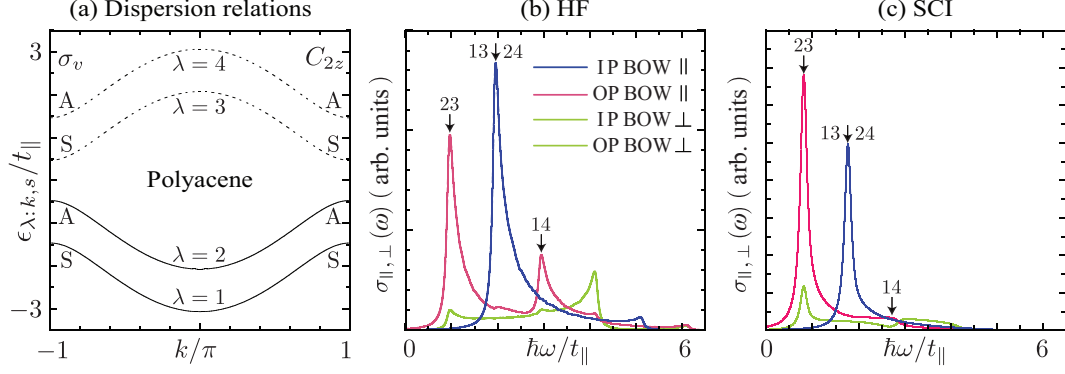


Figure 2.4: (a) Dispersion relations of polyacene in the EPH model with $U = 2t_{||}$; (b) polarized optical conductivity spectrum of polyacene calculated in the Hartree-Fock (HF) scheme; (c) polarized optical conductivity spectrum calculated in the single-excitation configuration interaction (SCI) scheme. Vertical black arrows indicate the peak positions of optical spectra. The corresponding inter-band transitions are also labeled.

$$\begin{aligned} \mathcal{J}_{\perp} = & \frac{iea_{||}}{2\hbar} \sum_{l,m,s} (-1)^l [(-1)^{m+1} (t_{||} - \alpha r_{l:m}) c_{l:m,s}^{\dagger} c_{l:m+1,s} \\ & - \text{H.c.}] + \frac{iea_{\perp}}{\hbar} \sum_{m,s} \delta_{m,2n-1} t_{\perp} (c_{1:m,s}^{\dagger} c_{2:m,s} - \text{H.c.}), \end{aligned} \quad (2.4)$$

$|E_0\rangle$ is the ground state and defined as

$$|E_0\rangle = \prod_{\kappa=1}^{2N} c_{\kappa}^{\dagger} |0\rangle, \quad (2.5)$$

with $|0\rangle$ being the true electron vacuum and $c_{\mu s}^{\dagger}$ creating an electron in the κ th Hartree-Fock orbital with energy ϵ_{κ} . $|E_i\rangle$ denoting the wave vector of the i th-lying state with energy E_i and is calculated within and beyond the Hartree-Fock scheme, being generally defined as:

$$|E_i\rangle = \sum_{\kappa(k\mu s)=1}^{2N} \sum_{\kappa(k\nu s)=2N+1}^{4N} f(k\mu\nu s; i) c_{\kappa(k\nu s)}^{\dagger} c_{\kappa(k\mu s)} |E_0\rangle, \quad (2.6)$$

Every excited state of the Hartree-Fock type is a single Slater determinant, where $f_{k\mu\nu s; i} = \delta_{k\mu\nu s, i}$. Those of configuration-interaction (CI) types consist of resonating Slater

determinants, where $f_{\mu,\nu,s;i}$ satisfies

$$\sum_{\kappa(k\mu s)=1}^{2N} \sum_{\kappa(k\nu s)=2N+1}^{4N} \langle E_0 | c_{\kappa(k\mu' s)}^\dagger c_{\kappa(k\nu' s)} | E_0 \rangle \quad (2.7)$$

$$\mathcal{H} c_{\kappa(k\nu s)}^\dagger c_{\kappa(k\mu s)} | E_0 \rangle f_{k\mu\nu s;i} = E_i f_{k\mu\nu s;i} . \quad (2.8)$$

We notice that there is no correction to the ground state but only excited states are refined because no single-excitation configurations interact with the Hartree-Fock ground state. It is not the case when higher order correlation effect is involved, for instance, the single-double-excitation configuration interaction (SDCI) scheme, then the ground state energy is also corrected. The cost of SDCI ($\sim N^6$) is extremely larger than those of Hartree-Fock ($\sim N^3$) and SCI ($\sim N^4$). Here we will not carry out the SDCI calculations.

Fig. 2.4 (b) and (c) show the polarized optical conductivity spectra calculated in the Hartree-Fock and single-excitation configuration interaction scheme respectively. For the perpendicular (to the conjugation direction) polarized direction, IP BOW and OP BOW show degenerate optical-conductivity spectrum (green curves). 1-to-3 and 2-to-4 inter-band transitions almost make no contributions to the perpendicular polarized optical spectrum, but the 2-to-3 transitions, contribute much to form the significant absorption peaks. For the parallel polarized direction, optical conductivity spectra show striking distinction between IP BOW and OP BOW (blue curves for IP and red curves for OP BOW respectively). 2-to-3 and 1-to-4 inter-band transitions are optically forbidden for IP BOW but they can be allowed for OP BOW; 1-to-3 and 2-to-4 inter-band transitions are optically allowed for IP BOW but they are forbidden for OP BOW.

To understand this striking contrast of polarized optical conductivity spectra between IP BOW and OP BOW, we need to analyze the matrix element of dipole transitions $\langle E_i | \mathcal{J} | E_0 \rangle$ to be zero or not. it means we need to analyze both the parity of wave functions of each band and the current operator $\mathcal{J}$ under a symmetry operation simultaneously.

First we check the parities of wavefunctions under a symmetry operation.

We write the Hamiltonian Eq. 2.1 in a matrix form:

$$\mathcal{H} = \begin{bmatrix} \cdots & c_{n:1}^\dagger & c_{n:2}^\dagger & c_{n:3}^\dagger & c_{n:4}^\dagger & \cdots \end{bmatrix} [H] \begin{bmatrix} \vdots \\ c_{n:1} \\ c_{n:2} \\ c_{n:3} \\ c_{n:4} \\ \vdots \end{bmatrix}. \quad (2.9)$$

To diagonalize the Hamiltonian, we have two steps:

step 1. Fourier transformation:

$$\begin{bmatrix} \cdots & c_{n:1}^\dagger & c_{n:2}^\dagger & c_{n:3}^\dagger & c_{n:4}^\dagger & \cdots \end{bmatrix} [U] = \begin{bmatrix} \cdots & c_{k:1}^\dagger & c_{k:2}^\dagger & c_{k:3}^\dagger & c_{k:4}^\dagger & \cdots \end{bmatrix}. \quad (2.10)$$

step 2. Numerical diagonalization:

$$\begin{bmatrix} \cdots & c_{k:1}^\dagger & c_{k:2}^\dagger & c_{k:3}^\dagger & c_{k:4}^\dagger & \cdots \end{bmatrix} [V] = \begin{bmatrix} \cdots & c_{k:\lambda=1}^\dagger & c_{k:\lambda=2}^\dagger & c_{k:\lambda=3}^\dagger & c_{k:\lambda=4}^\dagger & \cdots \end{bmatrix}. \quad (2.11)$$

Here, $[H]$, $[U]$, $[V]$ are all $4N \times 4N$ size matrices, and $k = 2\pi \frac{\tilde{k}}{N}$ ($\tilde{k} = 0, 1, \dots, N-1$).

Summarize the above two steps in one formula:

$$\begin{bmatrix} \cdots & c_{k:\lambda=1}^\dagger & c_{k:\lambda=2}^\dagger & c_{k:\lambda=3}^\dagger & c_{k:\lambda=4}^\dagger & \cdots \end{bmatrix} = \begin{bmatrix} \cdots & c_{n:1}^\dagger & c_{n:2}^\dagger & c_{n:3}^\dagger & c_{n:4}^\dagger & \cdots \end{bmatrix} [U][V] \quad (2.12)$$

The Fourier transformation are defined as:

$$\begin{aligned} c_{k:1}^\dagger &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{-ikn} c_{n:1}^\dagger = \frac{1}{\sqrt{N}} (e^{-ik} c_{1:1}^\dagger + e^{-2ik} c_{2:1}^\dagger + e^{-3ik} c_{3:1}^\dagger + \cdots) \\ c_{k:2}^\dagger &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{-ik(n+\frac{1}{2})} c_{n:1}^\dagger = \frac{1}{\sqrt{N}} (-ie^{-ik} c_{1:2}^\dagger - ie^{-2ik} c_{2:2}^\dagger - ie^{-3ik} c_{3:2}^\dagger - \cdots) \\ c_{k:3}^\dagger &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{-ikn} c_{n:3}^\dagger = \frac{1}{\sqrt{N}} (e^{-ik} c_{1:3}^\dagger + e^{-2ik} c_{2:3}^\dagger + e^{-3ik} c_{3:3}^\dagger + \cdots) \\ c_{k:4}^\dagger &= \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{-ik(n+\frac{1}{2})} c_{n:4}^\dagger = \frac{1}{\sqrt{N}} (-ie^{-ik} c_{1:4}^\dagger - ie^{-2ik} c_{2:4}^\dagger - ie^{-3ik} c_{3:4}^\dagger - \cdots) \end{aligned} \quad (2.13)$$

The elements of $[U]$ matrix are shown below (where $k = -\pi$ case are well presented):

$$[U] = \frac{1}{\sqrt{N}} \begin{bmatrix} e^{i\pi} & 0 & 0 & 0 & \dots & e^{-ik} & 0 & 0 & 0 & \dots \\ 0 & ie^{i\pi} & 0 & 0 & \dots & 0 & e^{-\frac{3}{2}ik} & 0 & 0 & \dots \\ 0 & 0 & e^{i\pi} & 0 & \dots & 0 & 0 & e^{-ik} & 0 & \dots \\ 0 & 0 & 0 & ie^{i\pi} & \dots & 0 & 0 & 0 & e^{-\frac{3}{2}ik} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \dots \\ e^{i\pi n} & 0 & 0 & 0 & \dots & e^{-ikn} & 0 & 0 & 0 & \dots \\ 0 & ie^{i\pi n} & 0 & 0 & \dots & 0 & e^{-ik(n+\frac{1}{2})} & 0 & 0 & \dots \\ 0 & 0 & e^{i\pi n} & 0 & \dots & 0 & 0 & e^{-ikn} & 0 & \dots \\ 0 & 0 & 0 & ie^{i\pi n} & \dots & 0 & 0 & 0 & e^{-ik(n+\frac{1}{2})} & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \dots \end{bmatrix} \quad (2.14)$$

Matrix $[V]$ is a block diagonalized one, which is shown in Fig. 2.9

$$[V] = \begin{bmatrix} \begin{array}{|c|c|c|c|} \hline V_{11} & V_{21} & V_{31} & V_{41} \\ \hline V_{12} & V_{22} & V_{32} & V_{42} \\ \hline V_{13} & V_{23} & V_{33} & V_{43} \\ \hline V_{14} & V_{24} & V_{34} & V_{44} \\ \hline \end{array} & & & \\ & \begin{array}{c} k = -\pi \end{array} & \ddots & \\ & & \begin{array}{|c|} \hline k = -\pi + \frac{2n\pi}{N} \\ \hline \end{array} & \\ & & & \ddots & \\ & & & & \begin{array}{|c|} \hline k = \pi - \frac{2\pi}{N} \\ \hline \end{array} \end{bmatrix}$$

Figure 2.5: Illustration of block diagonalized matrix V .

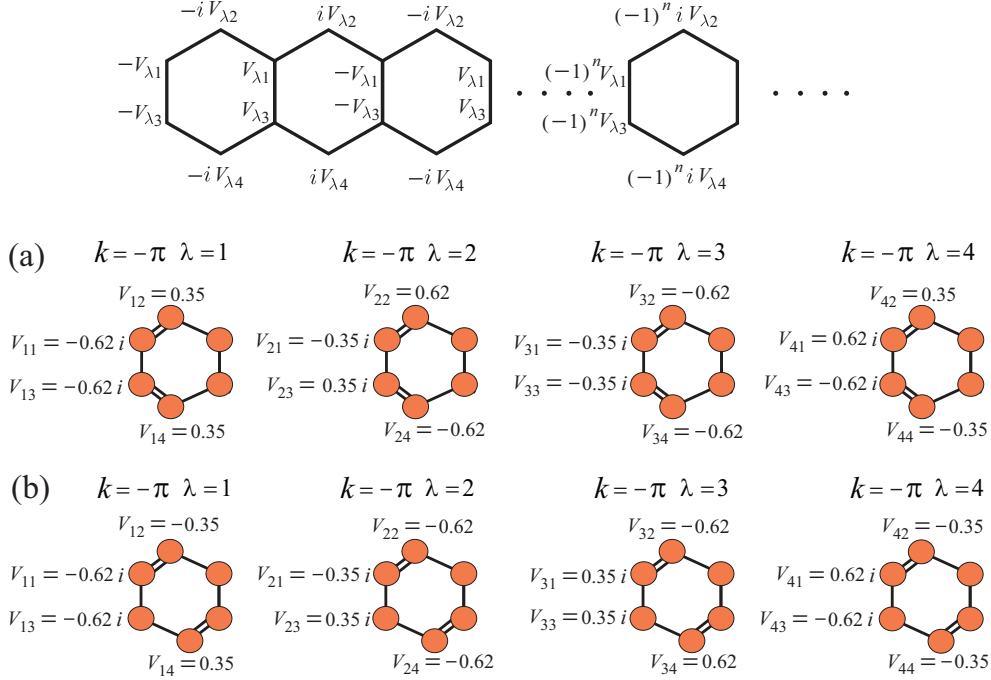


Figure 2.6: Illustration of mixing coefficients of wave functions at $k = -\pi$ expanded in the real space, where λ counts the band number; the detailed value of V in both IP BOW (a) and OP BOW (b) configurations are also shown.

The matrix $[W] = [UV]$ are

$$\begin{aligned}
 [W]_{k=-\pi} &= \begin{bmatrix} e^{i\pi} V_{11} & e^{i\pi} V_{21} & e^{i\pi} V_{31} & e^{i\pi} V_{41} & \cdots & \cdots \\ ie^{i\pi} V_{12} & ie^{i\pi} V_{22} & ie^{i\pi} V_{32} & ie^{i\pi} V_{42} & \cdots & \cdots \\ e^{i\pi} V_{13} & e^{i\pi} V_{23} & e^{i\pi} V_{33} & e^{i\pi} V_{43} & \cdots & \cdots \\ ie^{i\pi} V_{14} & ie^{i\pi} V_{24} & ie^{i\pi} V_{34} & ie^{i\pi} V_{44} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \end{bmatrix} \\
 [UV]_{k=-\pi} &= \begin{bmatrix} e^{i\pi n} V_{11} & e^{i\pi n} V_{21} & ie^{i\pi n} V_{31} & e^{i\pi n} V_{41} & \cdots & \cdots \\ ie^{i\pi n} V_{12} & ie^{i\pi n} V_{22} & ie^{i\pi n} V_{32} & ie^{i\pi n} V_{42} & \cdots & \cdots \\ e^{i\pi n} V_{13} & e^{i\pi n} V_{23} & e^{i\pi n} V_{33} & e^{i\pi n} V_{43} & \cdots & \cdots \\ ie^{i\pi n} V_{14} & ie^{i\pi n} V_{24} & ie^{i\pi n} V_{34} & ie^{i\pi n} V_{44} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \ddots \end{bmatrix}
 \end{aligned} \tag{2.15}$$

We further show the mixing coefficients of wave functions at $k = -\pi$ in the real space as well as the bare value of V in Fig. 2.6. Substitute the mixing coefficients of wave functions at $k = -\pi$ into Eq. 2.13, we get the final mixing coefficients in the real space

(Fig.2.7). The left four sketches are of four bands of IP BOW, which have the σ_v symmetry, while the right four are of four bands of OP BOW, which have the C_{2z} rotation invariance. From down to top, the energy bands count from $\lambda = 1$ to $\lambda = 4$. White and gray balls represent the wave functions of different sign. We find that for the IP BOW case, the odd-numbered bands consist of σ_v -symmetric (S) molecular orbitals, while the even-numbered bands consist of σ_v -antisymmetric (A) molecular orbitals. Similarly, for the OP BOW case, the odd-numbered bands consist of C_{2z} -symmetric (S) molecular orbitals, while the even-numbered bands consist of C_{2z} -antisymmetric (A) molecular orbitals.

Then we proceed to discuss the parity of the current operator under a symmetry operation. The parallel-polarized current operator $\mathcal{J}_{\parallel}$ of IP BOW under the mirror (σ_v) operation is written in:

$$\begin{aligned}
& \sigma_v \cdot \mathcal{J}_{\parallel} \\
&= \sigma_v \cdot \sum_{n,s} \left[\frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{1:2n-1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n-1,s}) \right. \\
&\quad + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n+1,s} - c_{1:2n+1,s}^\dagger c_{1:2n,s}) \\
&\quad + \frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{2:2n-1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n-1,s}) \\
&\quad \left. + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n+1,s} - c_{2:2n+1,s}^\dagger c_{2:2n,s}) \right] \\
&= \sum_{n,s} \left[\frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{2:2n-1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n-1,s}) \right. \\
&\quad + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n+1,s} - c_{2:2n+1,s}^\dagger c_{2:2n,s}) \\
&\quad + \frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{1:2n-1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n-1,s}) \\
&\quad \left. + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n+1,s} - c_{1:2n+1,s}^\dagger c_{1:2n,s}) \right] \\
&= \mathcal{J}_{\parallel}, \tag{2.16}
\end{aligned}$$

which is obviously an even function. The perpendicular polarized current operator $\mathcal{J}_{\perp}$ under the mirror (σ_v) operation is:

$$\begin{aligned}
& \sigma_v \cdot \mathcal{J}_\perp \\
&= \sigma_v \cdot \sum_{n,s} \left[\frac{(t_0 - \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n-1,s} - c_{1:2n-1,s}^\dagger c_{1:2n,s}) \right. \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n+1,s} - c_{1:2n+1,s}^\dagger c_{1:2n,s}) \\
&\quad + (t_\perp) (c_{1:2n-1,s}^\dagger c_{2:2n-1,s} - c_{2:2n-1,s}^\dagger c_{1:2n-1,s}) \\
&\quad + \frac{(t_0 - \alpha r_0)}{2} (c_{2:2n-1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n-1,s}) \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{2:2n+1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n+1,s}) \Big] \\
&= \sum_{n,s} \left[\frac{(t_0 - \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n-1,s} - c_{2:2n-1,s}^\dagger c_{2:2n,s}) \right. \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n+1,s} - c_{2:2n+1,s}^\dagger c_{2:2n,s}) \\
&\quad + (t_\perp) (c_{2:2n-1,s}^\dagger c_{1:2n-1,s} - c_{1:2n-1,s}^\dagger c_{2:2n-1,s}) \\
&\quad + \frac{(t_0 - \alpha r_0)}{2} (c_{1:2n-1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n-1,s}) \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{1:2n+1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n+1,s}) \Big] \\
&= -\mathcal{J}_\perp, \tag{2.17}
\end{aligned}$$

which is an odd function. OP BOW holds the C_{2z} symmetry, for the parallel current operator $\mathcal{J}_\parallel$, we have

$$\begin{aligned}
& C_{2z} \cdot \mathcal{J}_{\parallel} \\
&= C_{2z} \cdot \sum_{n,s} \left[\frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{1:2n-1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n-1,s}) \right. \\
&\quad + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n+1,s} - c_{1:2n+1,s}^\dagger c_{1:2n,s}) \\
&\quad + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{2:2n-1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n-1,s}) \\
&\quad \left. + \frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n+1,s} - c_{2:2n+1,s}^\dagger c_{2:2n,s}) \right] \\
&= \sum_{n,s} \left[\frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{2:2n+1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n+1,s}) \right. \\
&\quad + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n-1,s} - c_{2:2n-1,s}^\dagger c_{2:2n,s}) \\
&\quad + \frac{\sqrt{3}(t_0 + \alpha r_0)}{2} (c_{1:2n+1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n+1,s}) \\
&\quad \left. + \frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n-1,s} - c_{1:2n-1,s}^\dagger c_{1:2n,s}) \right] \\
&= -\mathcal{J}_{\parallel}, \tag{2.18}
\end{aligned}$$

which is an odd function. For the perpendicular current operator under the C_{2z} rotation:

$$\begin{aligned}
& C_{2z} \cdot \mathcal{J}_{\perp} \\
&= C_{2z} \cdot \sum_{n,s} \left[\frac{\sqrt{3}(t_0 - \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n-1,s} - c_{1:2n-1,s}^\dagger c_{1:2n,s}) \right. \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{1:2n,s}^\dagger c_{1:2n+1,s} - c_{1:2n+1,s}^\dagger c_{1:2n,s}) \\
&\quad + (t_{\perp}) (c_{1:2n-1,s}^\dagger c_{2:2n-1,s} - c_{2:2n-1,s}^\dagger c_{1:2n-1,s}) \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{2:2n-1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n-1,s}) \\
&\quad \left. + \frac{(t_0 - \alpha r_0)}{2} (c_{2:2n+1,s}^\dagger c_{2:2n,s} - c_{2:2n,s}^\dagger c_{2:2n+1,s}) \right]
\end{aligned}$$

$$\begin{aligned}
&= \sum_{n,s} \left[\frac{(t_0 - \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n+1,s} - c_{2:2n+1,s}^\dagger c_{2:2n,s}) \right. \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{2:2n,s}^\dagger c_{2:2n-1,s} - c_{2:2n-1,s}^\dagger c_{2:2n,s}) \\
&\quad + (t_\perp) (c_{2:2n-1,s}^\dagger c_{1:2n-1,s} - c_{1:2n-1,s}^\dagger c_{2:2n-1,s}) \\
&\quad + \frac{(t_0 + \alpha r_0)}{2} (c_{1:2n+1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n+1,s}) \\
&\quad \left. + \frac{(t_0 - \alpha r_0)}{2} (c_{1:2n-1,s}^\dagger c_{1:2n,s} - c_{1:2n,s}^\dagger c_{1:2n-1,s}) \right] \\
&= -\mathcal{J}_\perp,
\end{aligned} \tag{2.19}$$

which is an odd function. The parity properties of current operator in each case are summarized in Table 2.1.

Table 2.1: Parity of current operator of IP BOW and OP BOW of polyacene

	σ_v	C_{2z}
$\mathcal{J}_\parallel$	even	odd
$\mathcal{J}_\perp$	odd	odd

For the case that the current operator is an even function, judging from the dipole transition $\langle Ex | \mathcal{J} | E_0 \rangle$ ($|Ex\rangle$), only transitions between bands of same symmetry are allowed. On the other hand, when the current operator is an odd function, only transitions between bands of different symmetry are allowed. That is why in the parallel-polarized optical conductivity spectrum, 2-to-3 and 1-to-4 inter-band transitions are optically forbidden in IP BOW but they can be allowed in OP BOW; 1-to-3 and 2-to-4 inter-band excitations are allowed in IP BOW but they are forbidden in OP BOW.

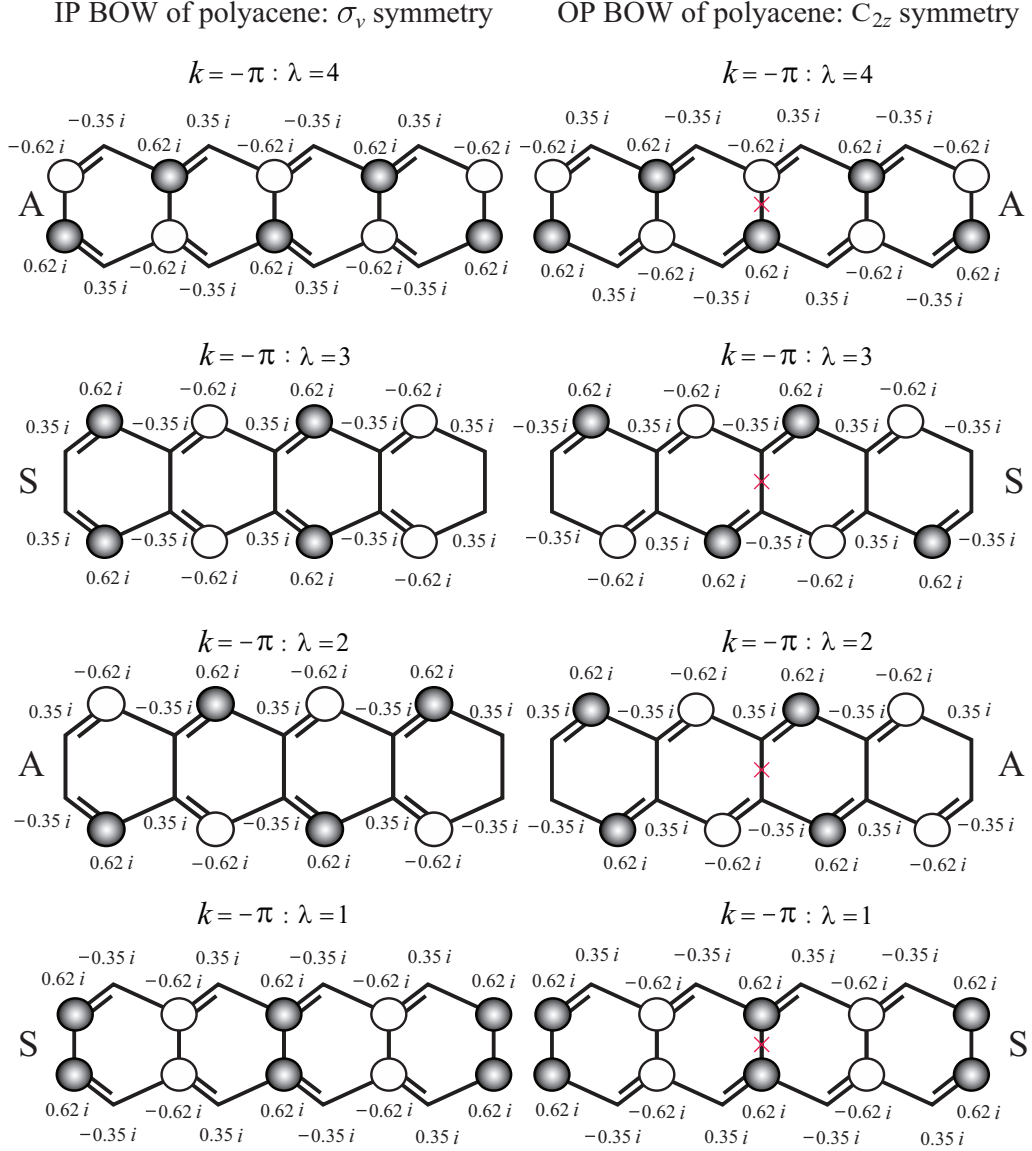


Figure 2.7: The illustration of symmetry properties of IP BOW and OP BOW of polyacene (the complex numbers are the mixing coefficients at $k = -\pi$) .

2.3 Ground state properties of paracyanogen

2.3.1 Phase diagram

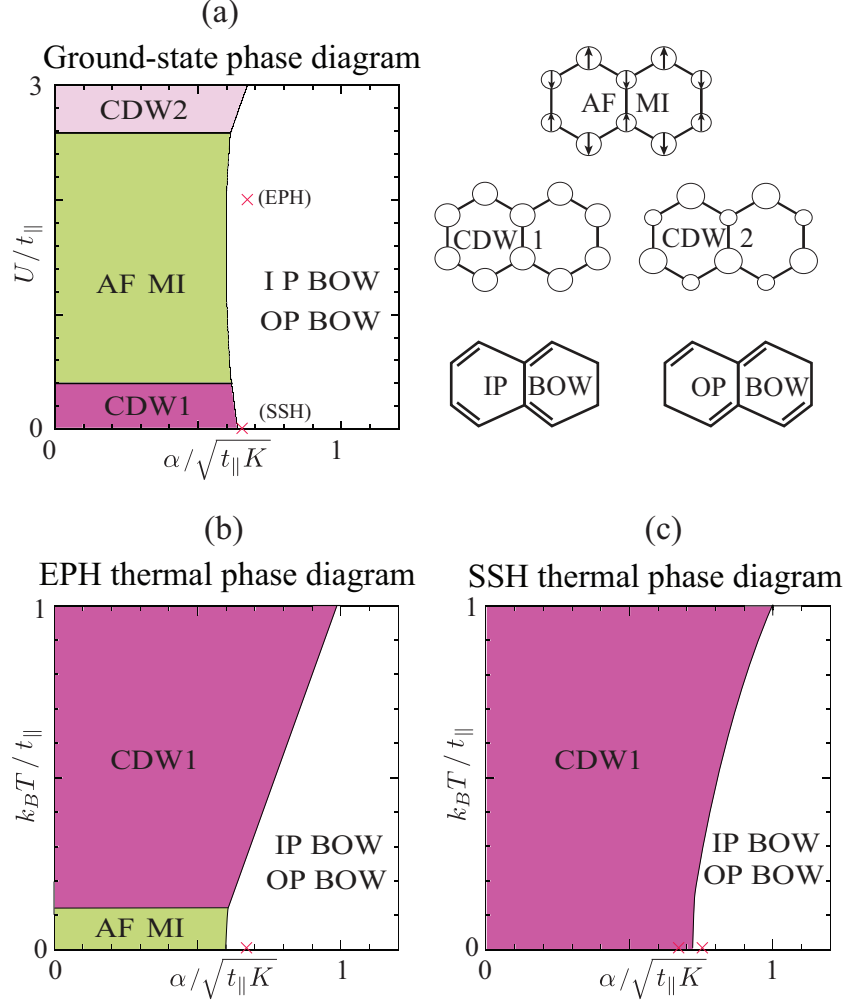


Figure 2.8: (a) Ground state phase diagram on the α - U plain and (b) thermal phase diagram within the EPH model and (c) thermal phase diagram within the SSH model of paracyanogen.

We show the ground-state phase diagrams of paracyanogen in Fig. 2.8. Because of the orbital-energy difference between carbon and nitride, the paramagnetism state is unavailable. Instead, the intrinsic charge-density-wave state (CDW1), which has an in-phase charge order between two legs, is stabilized when the electron-phonon coupling and the Coulomb interaction are both weak. A moderate strong Coulomb interaction

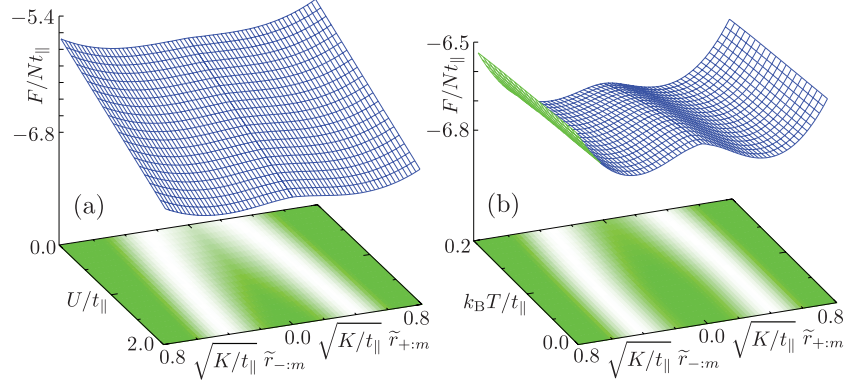


Figure 2.9: 3-D plot of free energy surface of IP BOW and OP BOW state in paracyanogen with (a) varying Coulomb interaction strength and (b) varying temperature.

drives stabilize the antiferromagnetic Mott-insulator. In the significant strong Coulomb interaction area, another type of charger-density-wave state (CDW2) is again stabilized. The CDW2 phase is caused by the inter-site Coulomb interaction V when the κ is 1.5, and it has the out-of-phase patterned charge order waves.

The same as polyacene, the Peierls instability of paracyanogen is also conditional. The IP BOW and OP BOW states remain energetically degenerate. The red crosses point out the parameters we used in the EPH and SSH model respectively. We learn from Fig. 2.8 (b) and (c) that, by increasing temperature, the BOW state shrinks into CDW state. But the threshold is higher than it in the polyacene case.

We show the 3-D plot of free energy surface of IP BOW and OP BOW with varying Coulomb interaction and temperature in Fig. 2.9. The Coulomb interaction contributes to the height of the barrier between the IP BOW and OP BOW of paracyanogen.

Varying temperature will also reduce this barrier height, but it is less effectively. At least even at room temperature, the barrier is still significant high to separate IP BOW and OP BOW. The importance point is that, both in polyacene and paracyanogen, the IP BOW and OP BOW states are always energetically degenerate.

2.3.2 Optical conductivity

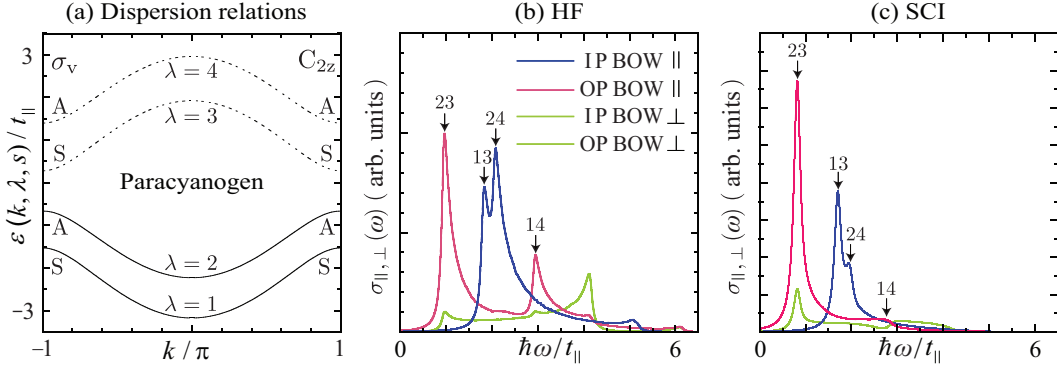


Figure 2.10: (a) Dispersion relations of IP BOW and OP BOW states of paracyanogen in the EPH model with $U = 2t_{||}$; (b) polarized optical conductivity spectra of paracyanogen, calculated in the Hartree-Fock (HF) scheme; (c) polarized optical conductivity spectra of paracyanogen, calculated in the single-excitation configuration interaction (SCI) scheme.

Fig. 2.10 presents the optical properties of IP BOW and OP BOW of paracyanogen.

We learn that, IP BOW and OP BOW still have degenerate dispersion relations.

However, from the location of the valence and conduction bands, we learn that the electron-hole (e-h) symmetry is broken. We later explain why the electron-hole symmetry breaks in paracyanogen in the Appendix.

Fundamentally, the optical-conductivity spectrum is the same with that in polyacene. It is natural because paracyanogen and polyacene share the same symmetry properties: σ_v symmetry of IP BOW while C_{2z} rotation invariance of OP BOW. Consequently, the energy bands of paracyanogen in IP BOW and OP BOW have the same parity with those in polyacene. The only difference comes from the electron-hole symmetry breaking. Peaks of parallel polarized optical spectrum in the IP BOW state, corresponding to 1-to-3 and 2-to-4 absorptions, are separated with each other and forms a split peak. Even we consider the correlation effect in the SCI scheme, this split peak is still visible. This split-peaked structure is one character to distinguish polyacene and paracyanogen.

2.4 Ground state of BN-acene

2.4.1 Phase diagram

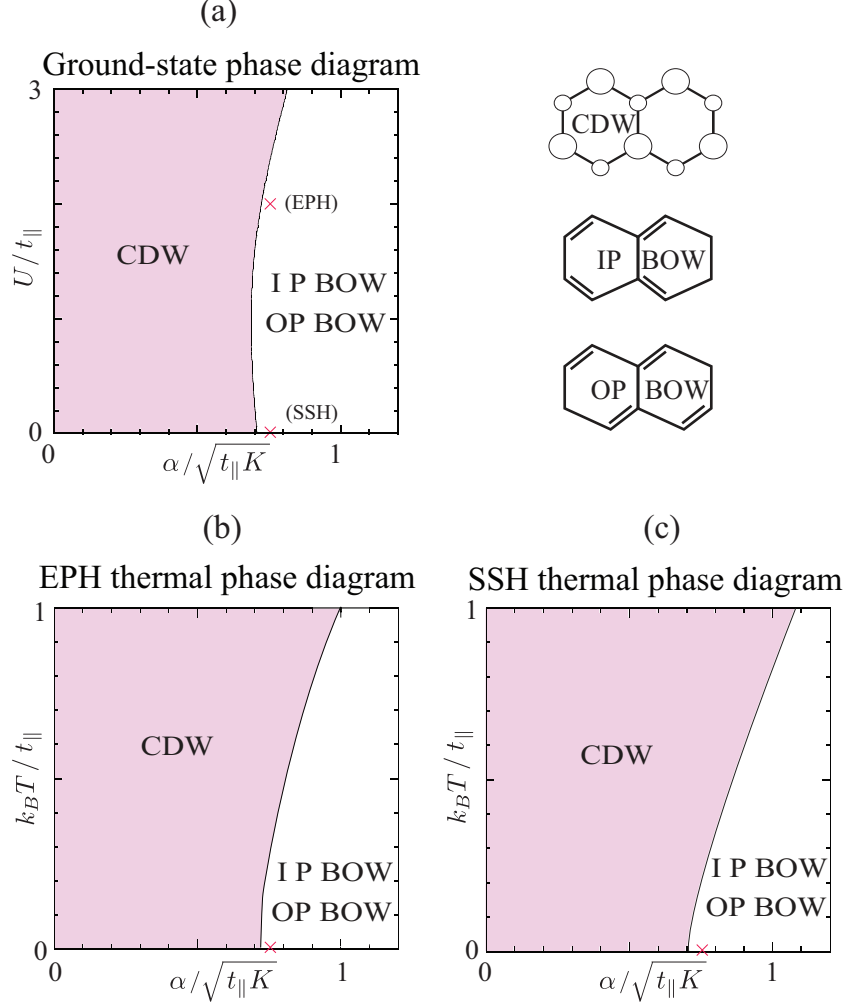


Figure 2.11: (a) Ground state phase diagram on the α - U plain and (b) thermal phase diagram within EPH model and (c) thermal phase diagram within SSH model of BN-acene.

Fig. 2.11 shows the phase diagrams of BN-acene. In subfigure (a), there are only two phases to be stabilized. Because the orbital-energy difference is very strong ($0.4t_{\parallel} = 0.96\text{eV}$) between boron and nitrid), the out-of-phase CDW phase covers a broad area in the low electron-lattice coupling region. The Peierls instability is still conditional. A finite electron-lattice coupling is necessary to form the bond order waves.

The two distorted patterns, IP BOW and OP BOW, remain energetically degenerate. The thermal phase diagrams in the EPH and SSH model are indicated in subfigure (b) and (c), respectively. Fundamentally the situation remains the same as in polyacene and paracyanogen: Increasing temperature tends to melt down the bond order waves, and room temperature is still sufficiently low to keep BN-acene to be stabilized in the bond-order-wave state. it is just the barrier height between IP BOW and OP BOW state of BN-acene is much higher than those in polyacene and paracyanogen.(Fig. 2.12).

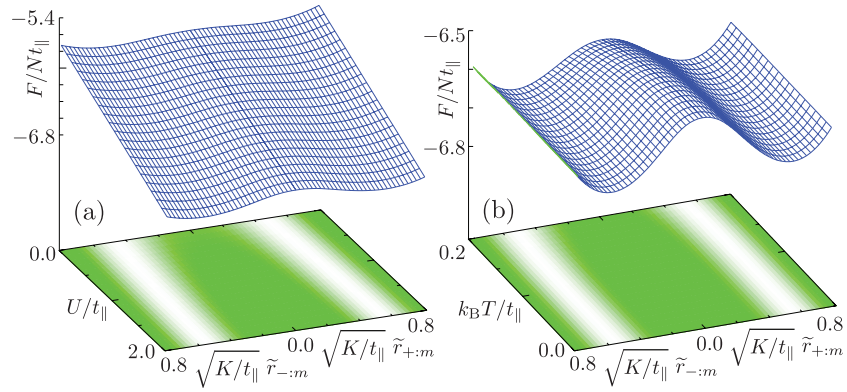


Figure 2.12: 3-D plot of the free energy surface of IP BOW and OP BOW state in BN-acene with (a) varying Coulomb interaction strength and (b) varying temperature.

2.4.2 Optical conductivity

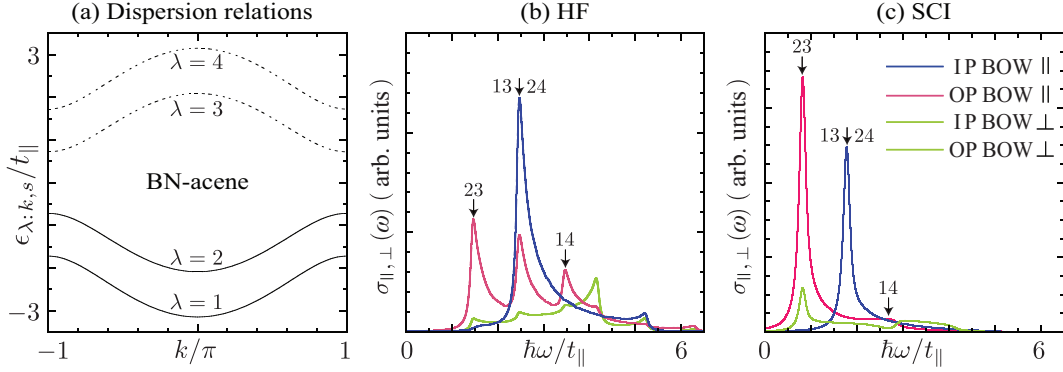


Figure 2.13: (a) Dispersion relations of BOW states of BN-acene in EPH model with $U = 2t_{||}$; (b) polarized optical conductivity spectra of BN-acene, calculated in Hartree-Fock (HF) scheme; (c) polarized optical conductivity spectra of BN-acene, calculated in single-excitation configuration interaction (SCI) scheme.

The optical properties of BN-acene are presented in Fig. 2.13. The Peierls gap is relatively larger than those of polyacene and paracyanogen. The electron-hole symmetry is preserved here. As there is no definite symmetry of IP BOW and OP BOW of BN-acene, the energy bands of them have no determined parity neither (Fig. 2.14). Therefore, all the absorption channels should be theoretically allowed. And indeed, we find that there is a triplet-peaked structure of parallel polarized spectra of OP BOW. For IP BOW, there is also a shoulder of spectrum corresponding to the 2-to-3 transitions. We have proved that, this shoulder would grow as energy difference between born and nitride increases.

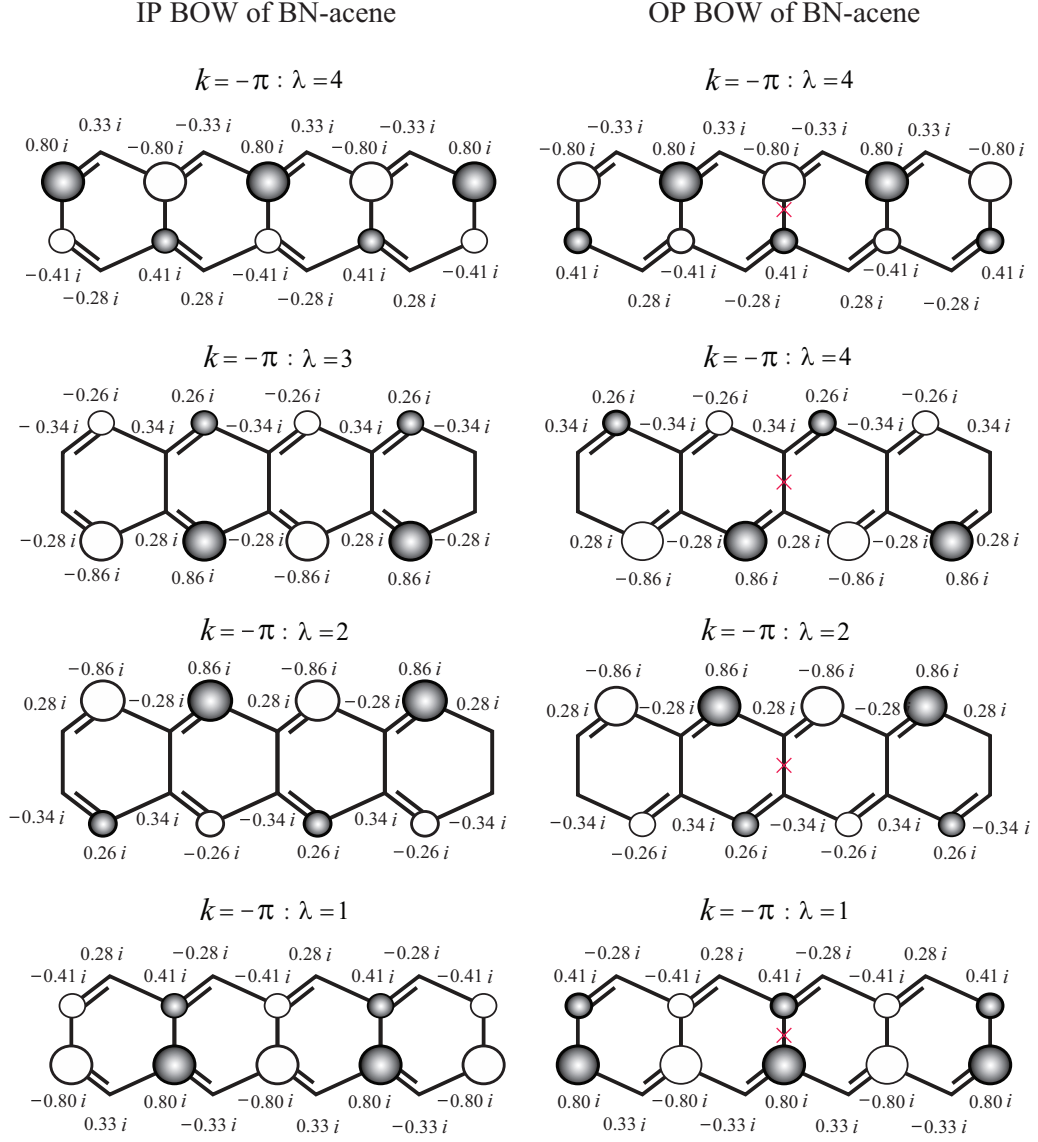


Figure 2.14: The illustration of symmetry properties of IP BOW and OP BOW of BN-acene (the mixing coefficients at $k = -\pi$) .

Chapter 3

Photoinduced phase transitions

3.1 Time dependent Hartree-Fock method

We proceed to study the photoinduced phase transitions in polyacene, paracyanogen and BN-acene. To simulate the effect of photons, we introduce a pulse of oscillating electric field as the Peierls phase into the transfer integral,^{4,5,59–62}

$$c_{i,s}^\dagger c_{j,s} \rightarrow e^{i(e/\hbar c)\mathbf{D}_{i,j}\cdot\mathbf{A}(t)} c_{i,s}^\dagger c_{j,s}, \quad (3.1)$$

with $\mathbf{D}_{i,j}$ the distance vector between site $i \equiv (l : m)$ and $j \equiv (l' : m')$, which can be set either parallel or perpendicular to the conjugation direction of polymer. $\mathbf{A}(t)$ is the vector potential and is given in a Gaussian function:

$$\mathbf{A}(t) = \mathbf{A}_0 \cos(\omega_0 t) \exp\left[-\frac{(t - t_c)^2}{2T^2}\right], \quad (3.2)$$

where $\mathbf{A}_0$, t_c and T denotes the amplitude, the center and the width of the pulse respectively. ω_0 is the frequency of the oscillating electric field. We set $t_c = 0$ through this thesis.

The process of time evolution is simulated by solving the Schrödinger equation

$$i\hbar\dot{\Psi}_s^\lambda(t) = \mathcal{H}_s^{\text{HF}}(t)\Psi_s^\lambda(t), \quad (3.3)$$

where spin- s sector of the Hamiltonian, $\mathcal{H}_s^{\text{HF}}$ and wave functions $\Psi_s^\lambda(t)$, are given by a square matrix and a column vector of degree $4N$. Discretizing the time variable as $t_j = j\Delta t$ ($j = 0, 1, 2, \dots$) with an interval much smaller than the optical-phonon time scale, say, $\Delta t = 10^{-3}\sqrt{M/K} \approx 0.01$ fs, we schematically integrate Eq. (3.3):

$$\Psi_s^\lambda(t_{j+1}) = \hat{T} \exp \left[-\frac{i}{\hbar} \int_{t_j}^{t_j+\Delta t} \mathcal{H}_s^{\text{HF}}(t) dt \right] \Psi_s^\lambda(t_j), \quad (3.4)$$

where $\hat{T}$ denotes the time ordering.

Employing a general decomposition theory of ordered exponentials,⁶³ we can carry out the time evolution of Eq. (3.4) by only numerically diagonalizing 8×8 matrices at every step,⁶⁴ which serves to accelerate the calculation.

Define the wave vectors as:

$$\begin{aligned} \Psi_s^\lambda(t) = & [\psi_{1:1,s}^\lambda(t), \psi_{1:2,s}^\lambda(t), \psi_{2:1,s}^\lambda(t), \psi_{2:2,s}^\lambda(t), \dots, \\ & \psi_{1:2n-1,s}^\lambda(t), \psi_{1:2n,s}^\lambda(t), \psi_{2:2n-1,s}^\lambda(t), \psi_{2:2n,s}^\lambda(t), \dots, \\ & \psi_{1:2N-1,s}^\lambda(t), \psi_{1:2N,s}^\lambda(t), \psi_{2:2N-1,s}^\lambda(t)]^T, \psi_{2:2N,s}^\lambda(t)]^T, \end{aligned} \quad (3.5)$$

and employ a unitary transformation:

$$U = \begin{bmatrix} 0 & I & 0 & \dots & 0 \\ 0 & 0 & I & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & 0 \\ 0 & \dots & 0 & 0 & I \\ I & 0 & \dots & 0 & 0 \end{bmatrix}, \quad (3.6)$$

where I denotes the unit matrix of degree 4, then the Hartree-Fock Hamiltonian can be expressed as

$$\begin{aligned} \mathcal{H}_s(t) = & \text{diag} [h_s^{(1)}(t), h_s^{(3)}(t), \dots, h_s^{(N-1)}(t)] \\ & + U^\dagger \text{diag} [h_s^{(2)}(t), h_s^{(4)}(t), \dots, h_s^{(N)}(t)] U. \end{aligned} \quad (3.7)$$

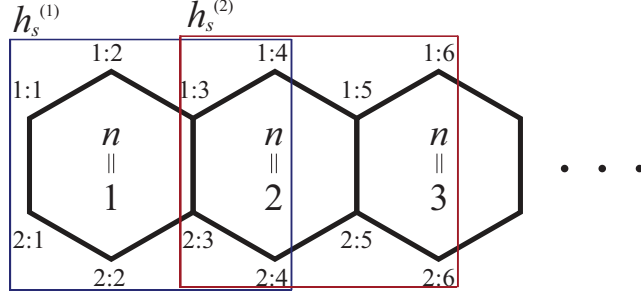


Figure 3.1: Illustration of Suzuki-Trotter decomposition.

$h_s^{(n)}$ are 8×8 matrices which read as:

$$2h_s^{(n)}(t) = \begin{bmatrix} \tilde{\rho}_{1:2n-1,s} & \tilde{t}_{1:2n-1,s}^{\parallel*} & \tilde{t}_{2n-1,s}^{\perp*} & 0 & 0 & 0 & 0 & 0 \\ \tilde{t}_{1:2n-1,s}^{\parallel} & \tilde{\rho}_{1:2n,s} & 0 & 0 & 2\tilde{t}_{1:2n,s}^{\parallel*} & 0 & 0 & 0 \\ \tilde{t}_{2n-1,s}^{\perp} & 0 & \tilde{\rho}_{2:2n-1,s} & \tilde{t}_{2:2n-1,s}^{\parallel*} & 0 & 0 & 0 & 0 \\ 0 & 0 & \tilde{t}_{2:2n-1,s}^{\parallel} & \tilde{\rho}_{2:2n,s} & 0 & 0 & 2\tilde{t}_{2:2n,s}^{\parallel*} & 0 \\ 0 & 2\tilde{t}_{1:2n,s}^{\parallel}(t) & 0 & 0 & \tilde{\rho}_{1:2n+1,s} & \tilde{t}_{1:2n+1,s}^{\parallel*} & \tilde{t}_{2n+1,s}^{\perp*} & 0 \\ 0 & 0 & 0 & 0 & \tilde{t}_{1:2n+1,s}^{\parallel} & \tilde{\rho}_{1:2n+2,s} & 0 & 0 \\ 0 & 0 & 0 & 2\tilde{t}_{2:2n,s}^{\parallel} & \tilde{t}_{2n+1,s}^{\perp} & 0 & \tilde{\rho}_{2:2n+1,s} & \tilde{t}_{2:2n+1,s}^{\parallel*} \\ 0 & 0 & 0 & 0 & 0 & 0 & \tilde{t}_{2:2n+1,s}^{\parallel} & \tilde{\rho}_{2:2n+2,s} \end{bmatrix}, \quad (3.8)$$

with

$$\begin{aligned} \tilde{\rho}_{l:m,s}(t) &= \varepsilon_{l:m} + U[d_{l:m,-s}(t) - \frac{1}{2}] + V_{\parallel}[d_{l:m-1}(t) \\ &\quad + d_{l:m+1}(t) - 2] + \delta_{m,2n-1}V_{\perp}[d_{3-l:m}(t) - 1], \\ \tilde{t}_{l:m,s}^{\parallel}(t) &= -[t_{\parallel} - \alpha r_{l:m}(t)] - V_{\parallel}p_{l:m,s}^{\parallel}(t), \\ \tilde{t}_{m,s}^{\perp}(t) &= -\delta_{m,2n-1}[t_{\perp} + V_{\perp}p_{m,s}^{\perp}(t)]. \end{aligned} \quad (3.9)$$

The on site electron densities and the bond electron densities are self-consistently

calculated through

$$\begin{aligned}
d_{l:m}(t) &= \sum_s d_{l:m,s}(t) = \sum_s \sum_{\lambda}' |\psi_{l:m,s}^{\lambda}(t)|^2, \\
p_{l:m}^{\parallel}(t) &= \sum_s p_{l:m,s}^{\parallel}(t) = \sum_s \sum_{\lambda}' \psi_{l:m,s}^{\lambda*}(t) \psi_{l:m+1,s}^{\lambda}(t), \\
p_m^{\perp}(t) &= \sum_s p_{m,s}^{\perp}(t) = \sum_s \sum_{\lambda}' \psi_{1:m,s}^{\lambda*}(t) \psi_{2:m,s}^{\lambda}(t),
\end{aligned} \tag{3.10}$$

with $\sum'$ denoting the summation over the initially occupied Hartree-Fock levels. We adopt the fractal decomposition up to the third order of Δt .

The dynamics of lattices are governed by Newton's equation of motion.

$$\begin{aligned}
M\ddot{u}_{l:m}(t) &= K[u_{l:m-1}(t) - 2u_{l:m}(t) + u_{l:m+1}(t)] \\
&\quad + 2\alpha \text{Re}[p_{l:m}^{\parallel}(t) - p_{l:m-1}^{\parallel}(t)] \equiv F_{l:m}(t),
\end{aligned} \tag{3.11}$$

and solvable stepwise:

$$\begin{aligned}
\dot{u}_{l:m}(t_{j+1}) &= \dot{u}_{l:m}(t_j) + \frac{F_{l:m}(t_j)}{M} \Delta t, \\
u_{l:m}(t_{j+1}) &= u_{l:m}(t_j) + \dot{u}_{l:m}(t_j) \Delta t.
\end{aligned} \tag{3.12}$$

The pure stationary initial ($t = t_0$) ground state of IP ($\sigma = 1$) BOW or OP ($\sigma = -1$) BOW is set for:

$$\sigma^l r_{l:m}(t_0) = -\sigma^l r_{l:m+1}(t_0), \quad \dot{r}_{l:m}(t_0) = 0. \tag{3.13}$$

We introduce the effective bond variables, $(\tilde{r}_{1:m} \pm \tilde{r}_{2:m})/2 \equiv \tilde{r}_{\pm:m}$, where the bare bond distortions $r_{l:m}$ are decomposed into their net ($\bar{r}_{l:m}$) and alternating ($\tilde{r}_{l:m}$) components as $\bar{r}_{l:m} = (2r_{l:m} + r_{l:m-1} + r_{l:m+1})/4$ and $\tilde{r}_{l:m} = (-1)^m(2r_{l:m} - r_{l:m-1} - r_{l:m+1})/4$. $\tilde{r}_{l:m}$ remaining constant with varying m reads as regular bond alternation on the l th chain, while a change of sign in them denotes a kink (domain wall) occurring. $\tilde{r}_{+:m}$ and $\tilde{r}_{-:m}$ work as order parameters to detect IP BOW and OP BOW configurations respectively. To quantitatively discuss how much the phase transitions are achieved, we define the converted fractions of phase transition as:

$$P_{\pm}(t) = \sum_{m=1}^{2N} \tilde{r}_{\pm:m}^2(t) / \sum_{m=1}^{2N} \tilde{r}_{ini:m}^2(t_0), \quad (3.14)$$

where *ini* is set for + (IP BOW) or – (OP BOW) which represents the state at t_0 .

$P_{\pm}(t)$ can be roughly taken as the possibility of finding IP BOW [$P_+(t)$] or OP BOW [$P_-(t)$] at time t . The numerator of $P_{\pm}(t)$ dose not work by it self, because the photoirradiating may also reduce the bond order waves themselves, which corresponds to a photoinduced reduction of the gap value. That is why we need to normalize it by $\sum_{m=1}^{2N} \tilde{r}_{ini:m}^2(t_0)$.

3.2 Photoinduced phase transitions in polyacene

We first study photoinduced phase transitions in polyacene with the initial state of IP BOW being photoexcited. Being reminded from the static optical-conductivity spectra of polyacene (Fig. 2.4), IP BOW can not absorb parallel polarized photons with the energy equal to gap value, but only higher energy excitations (electronic transition energy between bands 1-to-3 or 2-to-4) are allowed. However, high-energy absorption cases are not of interested here. Because absorbed high-energy photons are much easier to melt down the bond order wave itself, rather than induce a phase transition between two BOW states. For the perpendicular polarized photons, they can make contributions to the HOMO-to-LUMO electronic transitions against the IP BOW configuration of polyacene. Otherwise noted, all the photon energies $\hbar\omega$ are set for the gap value of the initial state.

Fig. 3.2 shows the dynamical process after IP BOW of polyacene is irradiated with the perpendicular polarized pulse of the frequency $\hbar\omega_0 = 0.94 t_{\parallel}$ (HOMO-to-LUMO excitation energy), the amplitude $\mathbf{A}_0 = 14.7 \times 10^{-2} \frac{\hbar c}{ea_{\parallel}}$ and the duration time $T = 5$ fs. Obviously, the evolution of $P_{\sigma/+}(\sigma = +\text{or}-)$ indicates that no phase transitions occur: the signals of IP BOW $P_{+/+}$ remains significant after 3 picoseconds, meanwhile OP BOW fractions $P_{+/-}$ keep zero. To understand what exactly happened during this process, we show the evolutions of effective bonds orders $\tilde{r}_{l:m}(l = 1 \text{ or } 2)$ and

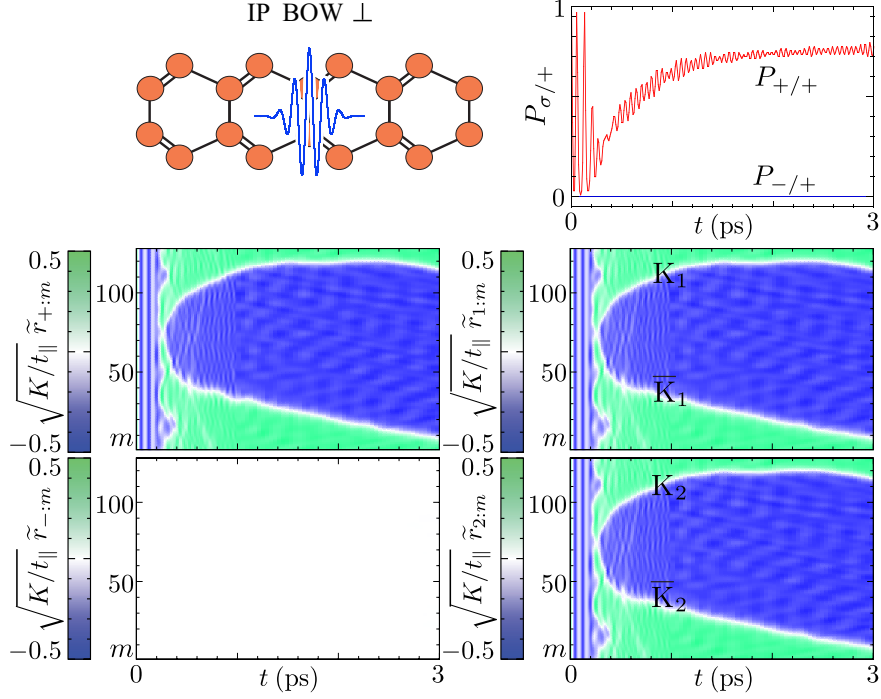


Figure 3.2: Photoinduced phase transitions of polyacene with the initial state IP BOW being irradiated with the perpendicular polarized light; the time-dependent phase-conversion fractions $P_{\sigma/+}$, the 3-D contour plot of bare bond variables $\tilde{r}_{l;m}$, and the phase detectors $\tilde{r}_{l;\pm}$ are shown simultaneously. K_l ($\bar{K}_l$) represents the kink (antikink) on chain l .

$\tilde{r}_{\sigma;m}(\sigma = +\text{or}-)$ simultaneously. We notice that, at the first stage, the absorbed photon energy induce a global oscillation of bond order waves: IP BOW background temporally slides into the metal phase, then converts to the $\bar{\text{IP}}$ BOW phase ($\tilde{r}_{l;+} < 0$), then oscillate back to the initial one. After about 0.4 picoseconds, such an oscillation is destroyed by the nucleation of a pair of kink and antikinks on each chain. The interesting point is that the forming of these kink pairs and the subsequent of motion of them are strictly in a harmony way between two chains. This phenomenon is very persistent, at least we checked that, increasing the intensity of incident light is hard to break such a harmony behavior. It is also the case that parallel polarized photons with higher energy (electronic transition energy between bands 1-to-3 and 2-to-4) are effectively absorbed, sometimes small dirty-phase of OP BOW islands occur here and there, but kink pairs

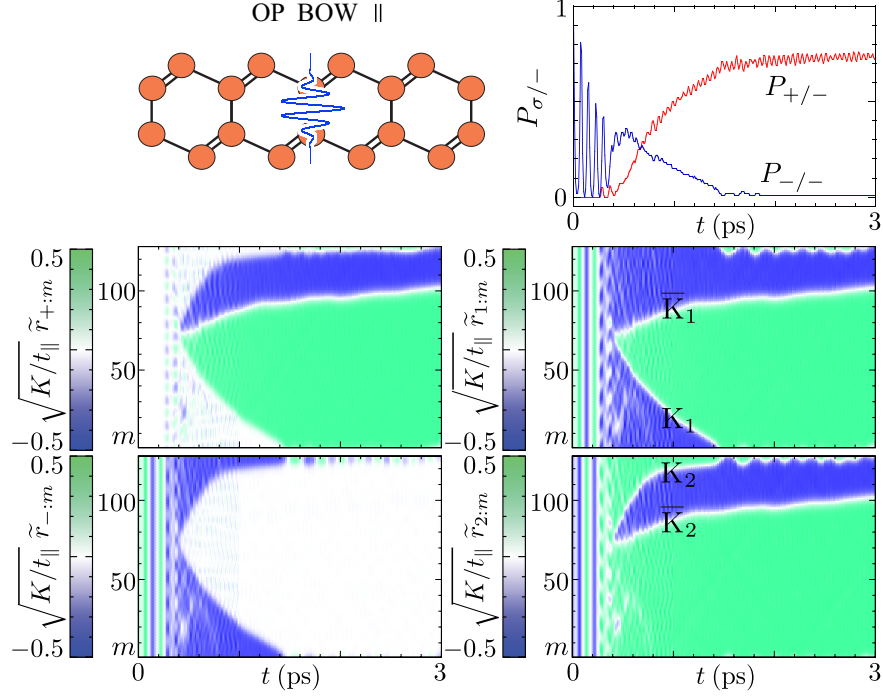


Figure 3.3: The same as Fig. 3.2, but the case of the initial state OP BOW of polyacene being irradiated with the parallel polarized light.

always keep in phase between two legs.

Next we discuss the reverse case, namely, the initial state is set for OP BOW. Since HOMO-to-LUMO transitions can be allowed in both parallel or perpendicular polarized photoirradiation for OP BOW background, we need to discuss both these two cases.

Fig. 3.9 indicates the evolution of bond variables after the initial OP BOW is photoexcited with the pulse of $\hbar\omega_0 = 0.94 t_{||}$, $\mathbf{A}_0 = 7.39 \times 10^{-2} \frac{\hbar c}{ea_{||}}$ and $T = 5$ fs. Judging from the time-dependent converted fractions $P_{\sigma/-}(t)$, the initial OP BOW is finally successfully converted into IP BOW phase. More details of this process are demonstrated: at the first stage, the global bond configuration oscillates, then after about 0.4 picoseconds, the nucleation by kink pairs happens on each leg. The formed antidomains between the new born kink and antikink pairs grow in the opposite direction between two legs, forming a pair of domain and antidomain.

Fig. 3.4 demonstrate the case that OP BOW is photoirradiated, with the perpendicular polarized pulse of $\hbar\omega_0 = 0.94 t_{||}$, $\mathbf{A}_0 = 14.7 \times 10^{-2} \frac{\hbar c}{ea_{||}}$ and $T = 5$ fs is used. Again, the

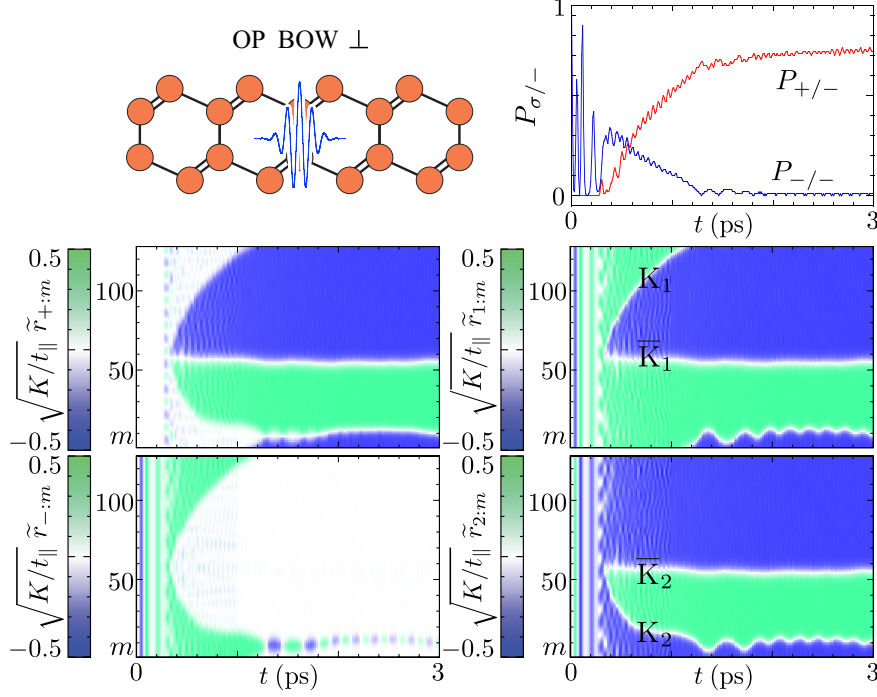


Figure 3.4: The same as Fig. 3.3, but using the perpendicular polarized incident light.

global OP-to-IP phase transition is successfully achieved. The dynamical process is qualitatively the same with that in Fig. 3.4.

To experimentally observe the photoinduced lattice evolution process, we calculate the time-resolved optical conductivity spectra in the cases IP BOW (Fig. 3.2) and OP BOW (Fig. 3.4) are irradiated with the perpendicular polarized light, which are shown in Fig. 3.5. After IP BOW is photo irradiated [subfigure (a)], the optical spectrum qualitatively keeps its initial structure. We focus on the transient optical conductivity spectrum at time $t = 3\text{ps}$. The main peak corresponds to the photoinduced inter-band transitions of 1-to-3 and 2-to-4, which just characters the IP BOW state. This is a proof that IP BOW is persistent against photoirradiation. Meanwhile, we notice that there are some small tips on the lower energy side of the main peak. We find that they originate from the photoinduced local defects' (kink-antikink pairs) additional contributions. We qualitatively show the energy band structure as well as the energy levels of local defects. There are two types of local states, one type is the usual intra gap state we are well known, the other type of local states hide deeply in the continuous bands. The

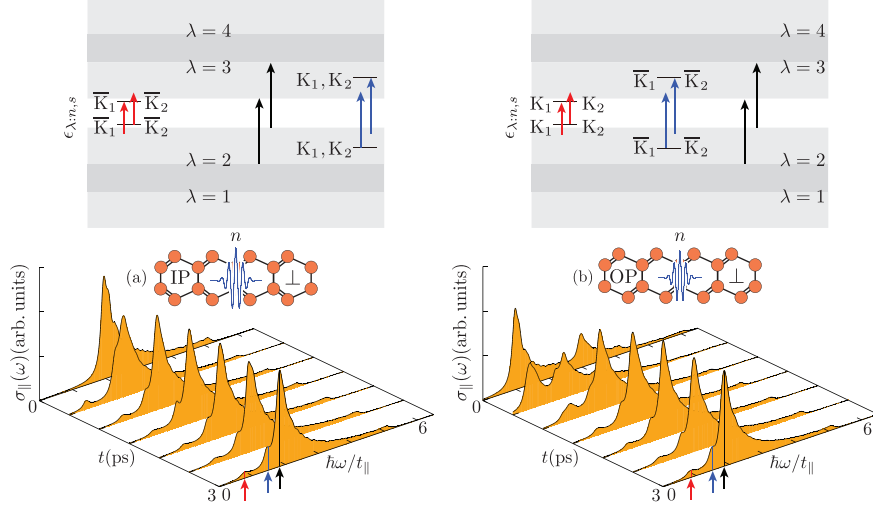


Figure 3.5: Time-resolved photoinduced optical conductivity spectra on the lattice dynamics demonstrated in Fig. 3.2 and Fig. 3.4. Notable absorption peaks at $t = 3$ ps are illustrated with their background energy structure, which consists of photoinduced levels of kinks ($\bar{K}_l$) and antikinks ($\bar{K}_l$), sitting around a certain unit n on chain l . The delocalized energy bands numbering from 1 to 4 are also shown.

transitions between these defect states and the extended state contribute to these tiny tips of optical conductivity. Fig. 3.6 demonstrates the local density of state (LDOS) around the kinks and antikinks positions at $t = 3$ ps on the lattice dynamics of Fig. 3.2 and Fig. 3.4 respectively. The sharp peaks originating from the divergence of LDOS, just indicates the locations of kinks and antikinks in the band structure explicitly.

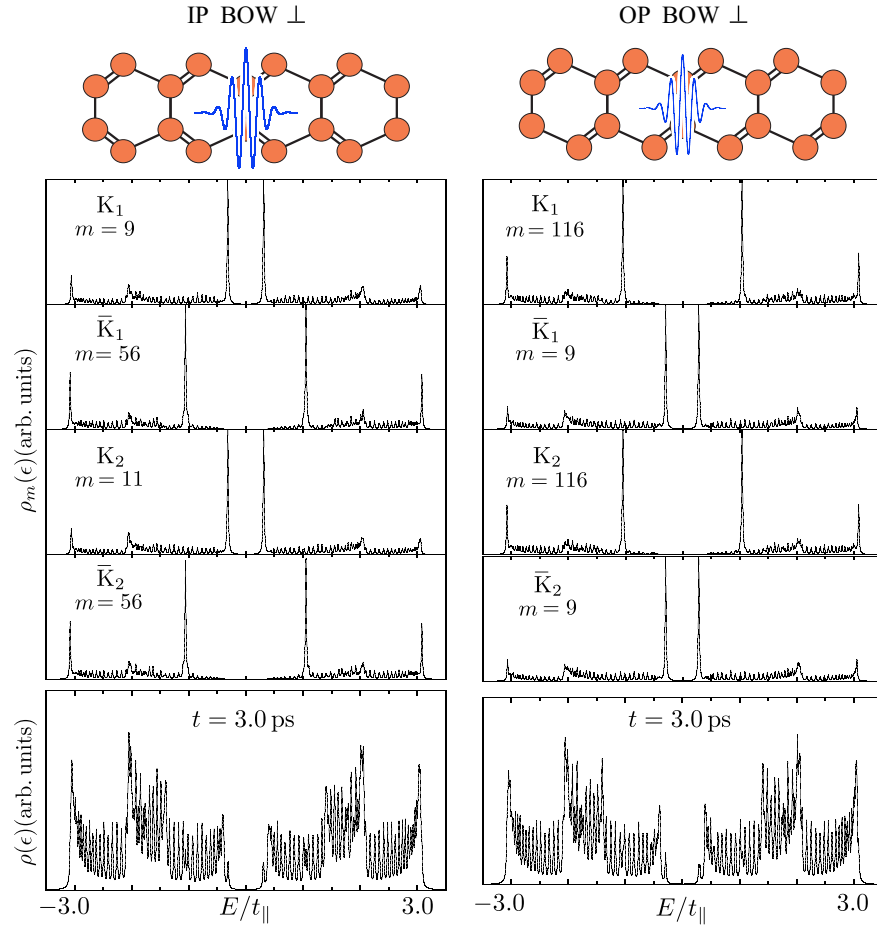


Figure 3.6: Local density of state around the kinks and antikinks at $t = 3\text{ps}$ on the lattice dynamics demonstrated in Fig. 3.2 and Fig. 3.4.

3.3 Photoinduced phase transition in paracyanogen

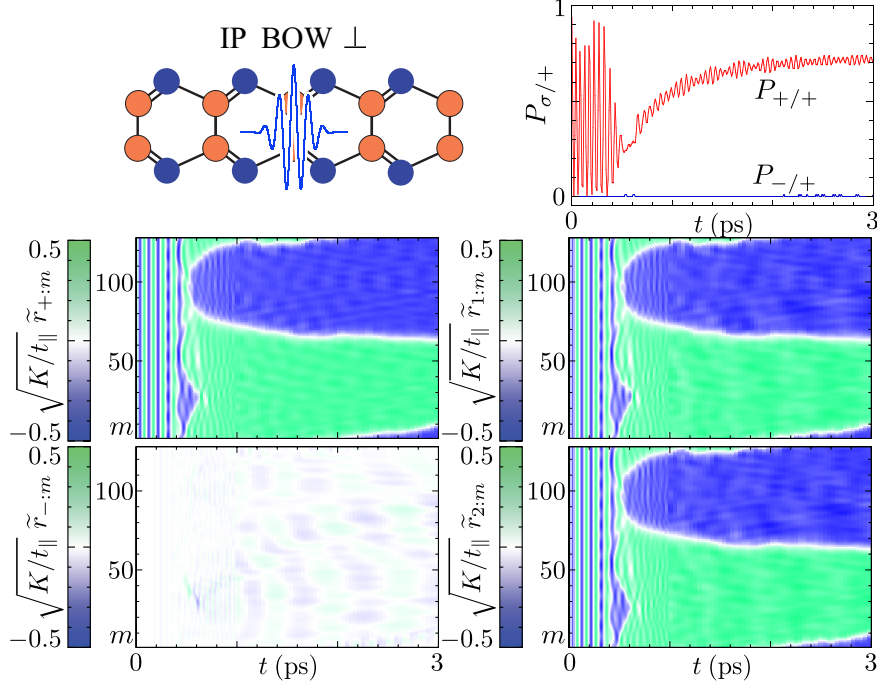


Figure 3.7: Photoinduced phase transitions of paracyanogen in case of the initial phase IP BOW being irradiated with the perpendicular polarized light; the converted fractions $P_{\sigma/+}$, the 3-D plot of effective bond variables $\tilde{r}_{l;m}$, and the phase detectors $\tilde{r}_{l;\pm}$ are shown respectively.

We proceed to study the photoinduced phase transitions in paracyanogen. Fig. 3.7 demonstrates the case that IP BOW of paracyanogen is photoirradiated with the perpendicular polarized pulse of $\hbar\omega_0 = 0.94t_{\parallel}$, $\mathbf{A}_0 = 13.8 \times 10^{-2} \frac{\hbar c}{ea_{\parallel}}$ and $T = 5$ fs. The resultant photoinduced lattice dynamics are similar with those in polyacene: the absorbed photons first spend on a rapid uniform oscillation of background, then the nucleation of kink-antikink pairs occur on each chain simultaneously. The motions of the resultant antidomains keep *in phase* within several picoseconds and no OP BOW domains are formed during this process.

Increasing the intensity of the incident light makes much more photons absorbed. In this case, there are indeed some OP BOW domain islands occasionally happen, but none of them proliferate to a global one. IP BOW of paracyanogen is so persistent

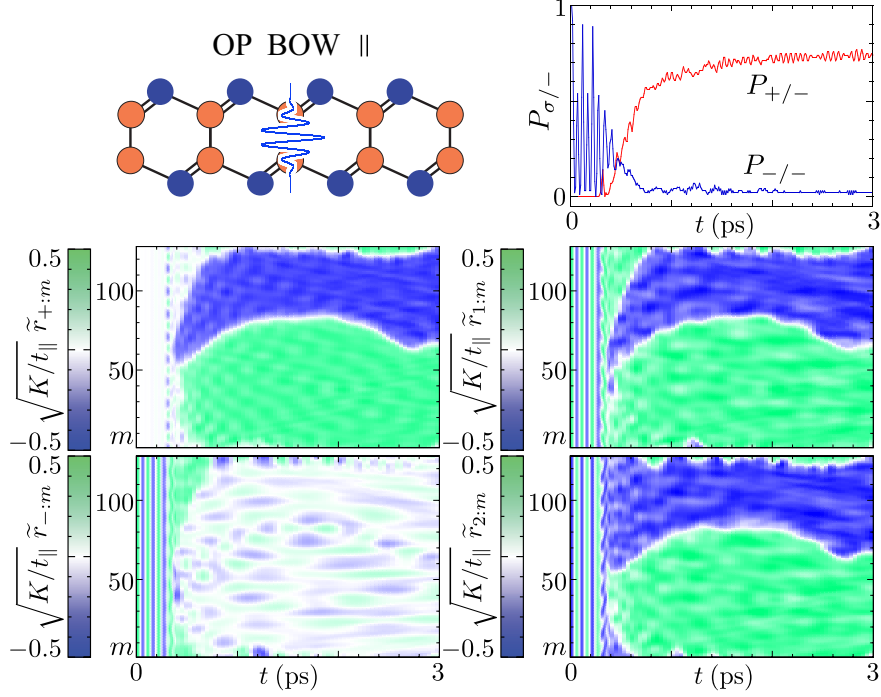


Figure 3.8: The same as Fig. 3.7, but the case that the initial state OP BOW is irradiated with the parallel polarized light.

against any kind of photons.

Fig. 3.8 gives an example that OP BOW of paracyanogen is irradiated with the parallel polarized pulse of $\hbar\omega_0 = 0.94 t_{\parallel}$, $\mathbf{A}_0 = 13.8 \times 10^{-2} \frac{\hbar c}{ea_{\parallel}}$ and $T = 5$ fs. Absorbed photons induce the lattice configuration to oscillate uniformly, then after about 400 femtoseconds, the kink-antikink pairs form on each chain, and the resultant antidomains leave each other fast. It is less than 200 femtoseconds, the whole system has already been converted into IP BOW phase. The achieved IP BOW fraction $P_{+/-}$ reaches about 0.8 after 3 picoseconds.

The polarized direction of the incident light has no qualitative effects on photoinduced phase transitions. Using the perpendicular polarized pulse with $\hbar\omega_0 = 0.94 t_{\parallel}$, $\mathbf{A}_0 = 7.6 \times 10^{-2} \frac{\hbar c}{ea_{\parallel}}$ and $T = 5$ fs, the OP-to-IP BOW phase transition is also achievable (Fig. 3.9). The resultant kink pairs move in a harmony way and keep in phase.

No matter the initial state is IP BOW or OP BOW phase, after photoexcitation, the resultant phases are IP BOW and $\overline{\text{IP}}$ BOW domain pairs. In Fig. 3.7 and Fig. 3.9,

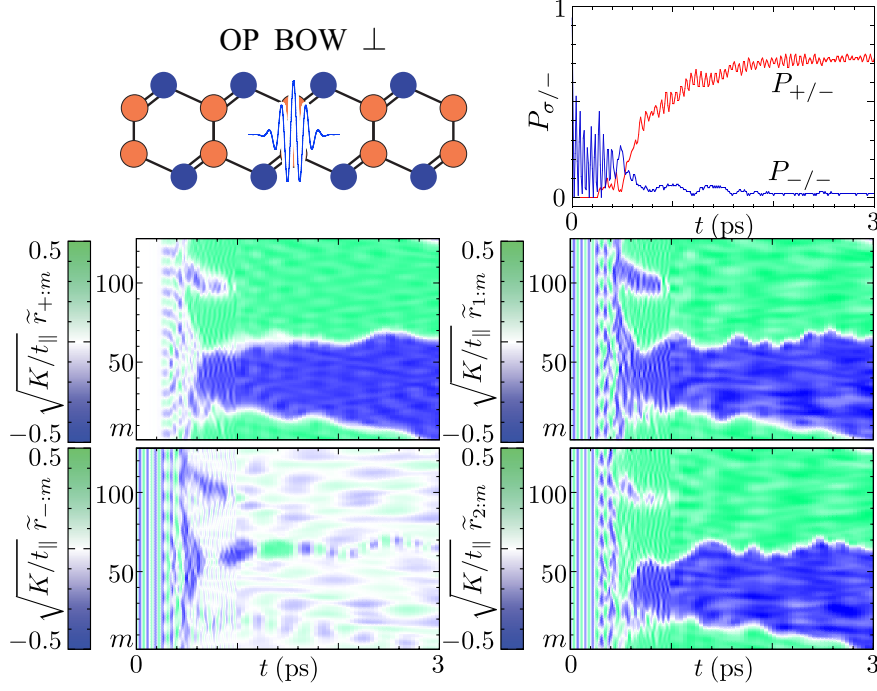


Figure 3.9: The same as Fig. 3.8, but the case that the initial state OP BOW is irradiated with the perpendicular polarized light.

there are same numbers of domain walls formed in each case. Their local densities of state (LDOS) corresponding to these domain walls are presented in Fig. 3.11. However, the electron-hole symmetry breaking makes the valance bands and conduction bands no more symmetry, which is also easily learned from the DOS spectrum, where the lower-energy local state levels are rather closer to the HOMO level, while the higher-energy ones separate well from the LUMO level.

Although in both compounds of polyacene and paracyanogen, the photoinduced final phase will be a pair of IP BOW and $\overline{\text{IP}}$ BOW domain pairs, there are still quantitatively difference of photodynamics between paracyanogen and polyacene. We find that in paracyanogen, it seems much easier for many tiny but visible dirty antidomains formed after the BOW configuration is photoirradiated. And tiny IP-to-OP BOW conversions are also sometimes visible. As we increase the intensity of incident light, these phenomenons become much more notable. We believe that these tiny differences originate from the electron-hole symmetry breaking in paracyanogen. We clarify that the solitons formed in the EPH model in paracyanogen convey net spin

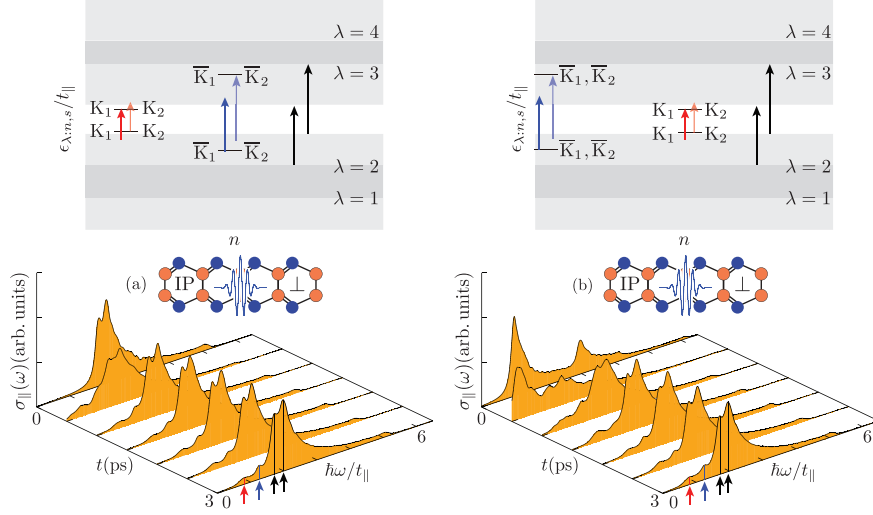


Figure 3.10: The Same as Fig. 3.5 but on the lattice dynamics demonstrated in Fig. 3.7 and 3.9.

density of opposite sign. This electron-hole symmetry breaking makes the forming of these spin-soliton pairs easier to gain energy. So to say, paracyanogen is easier to nucleate kinks upon photoirradiation than polyacene. When the intensity of the incident light is strong, there happens the multinuclear fluctuations, which induces more antidomain islands appearing. However, such a behavior is only significant in very strong photoirradiation cases, for that may break the bond order waves themselves. Thus, paracyanogen is also categorized as a directionally photoswitchable material. Fig. 3.10 gives the time-resolved optical conductivity on the lattice dynamics demonstrated in Fig. 3.7 and Fig. 3.9. In subfigure (a), the initial split main peak is persistent against photoexcitations, signifying that there is no phase transition occurring. In subfigure (b), the initial OP BOW state has the significant 2-to-3 and 1-to-4 absorption peaks. With the process of OP-to-IP BOW phase transition, the 2-to-3 and 1-to-4 absorption peaks shrink, while 1-to-3 and 2-to-4 peaks grow up. Since soliton pairs are formed during the dynamic process in both cases of (a) and (b), there can be found the corresponding tips (indicated by the red and blue arrows) on the background spectra. It is again due to the electron-hole symmetry breaking that, these tips are also split ones.

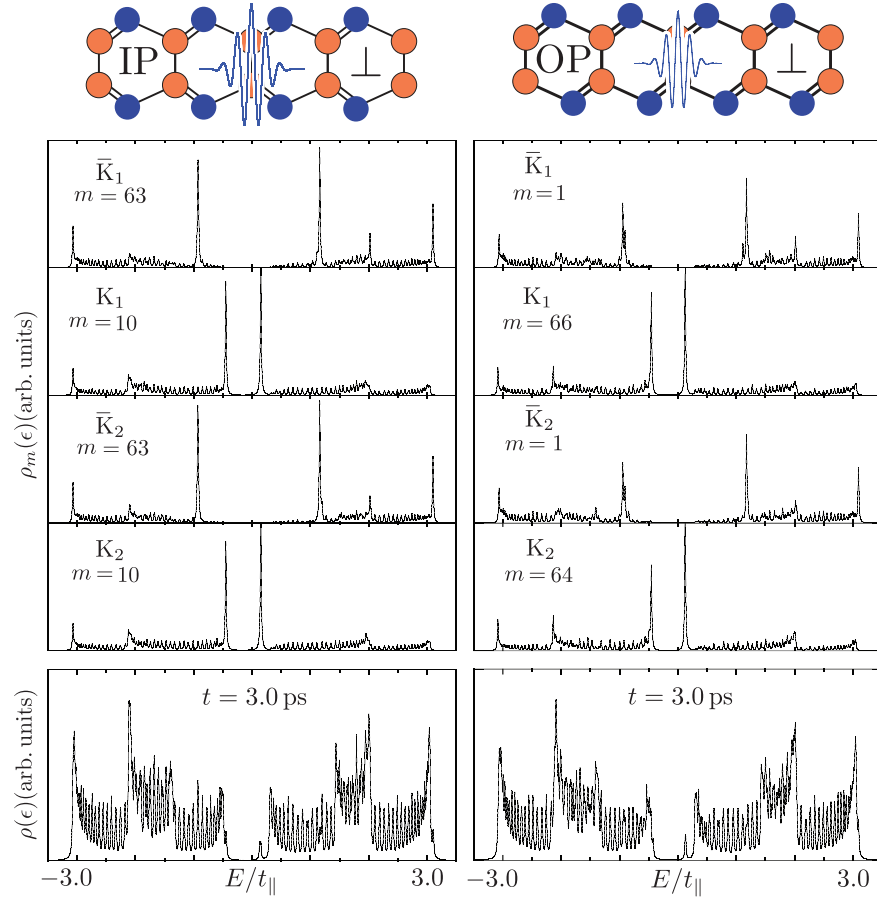


Figure 3.11: Local density of state around the kinks and antikinks at $t = 3\text{ps}$ on the lattice dynamics demonstrated in Fig. 3.7 and Fig. 3.9.

3.4 Photoinduced phase transitions in BN-acene

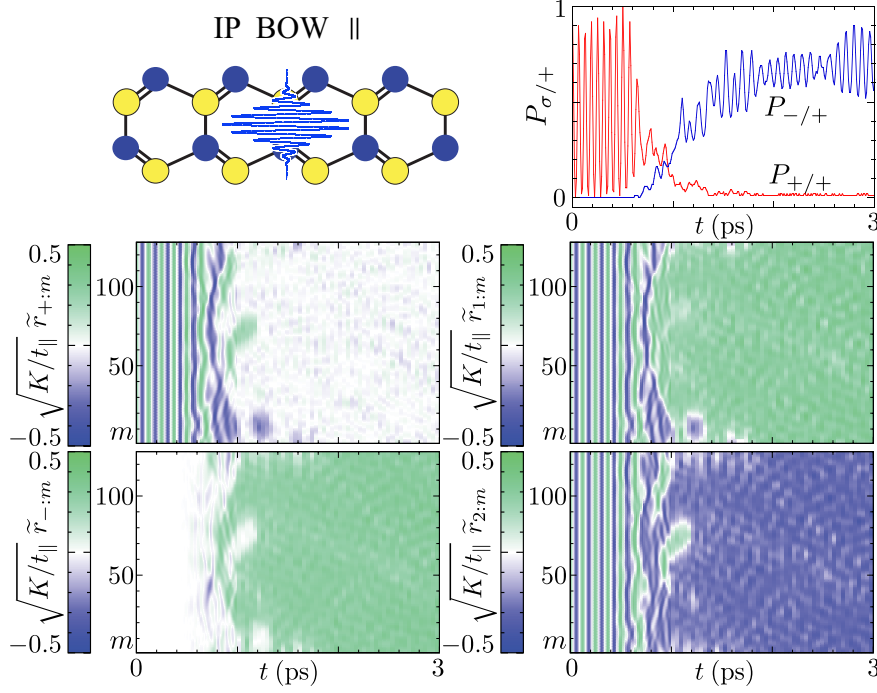


Figure 3.12: Photoinduced phase transitions in BN-acene with the initial phase IP BOW being irradiated with the parallel polarized light: the converted fractions $P_{\sigma/+}$, the 3-D plot of effective bond variables $\tilde{r}_{l:m}$, and phase detectors $\tilde{r}_{l:\pm}$ are shown simultaneously.

Being reminded that in BN-acene, no matter IP BOW or OP BOW, there is no definite symmetry. Thus all the possible photon absorption channels are theoretically allowed, no matter for the parallel or perpendicular polarized incident light. The low energy absorption channel (HOMO-to-LUMO) contributes to a shoulder to the optical conductivity spectrum of IP BOW. Fig. 3.12 shows an typical example that what happens when IP BOW is photoirradiated with the parallel polarized pulse of $\hbar\omega_0 = 1.3 t_{\parallel}$ (HOMO-to-LUMO excitation energy), $\mathbf{A}_0 = 10.7 \times 10^{-2} \frac{\hbar c}{ea_{\parallel}}$ and $T = 5$ fs. The first stage is no surprising again the uniform oscillation of the background lattice configuration. It is after about 400 femtoseconds, two chains lose their harmony and the OP BOW phase is achieved and ranges over the whole system. The IP-to-OP BOW phase transition is allowed in BN-acene. This scenario is striking contrast to the photodynamics in polyacene and paracyanogen, where photoinduced IP-to-OP BOW

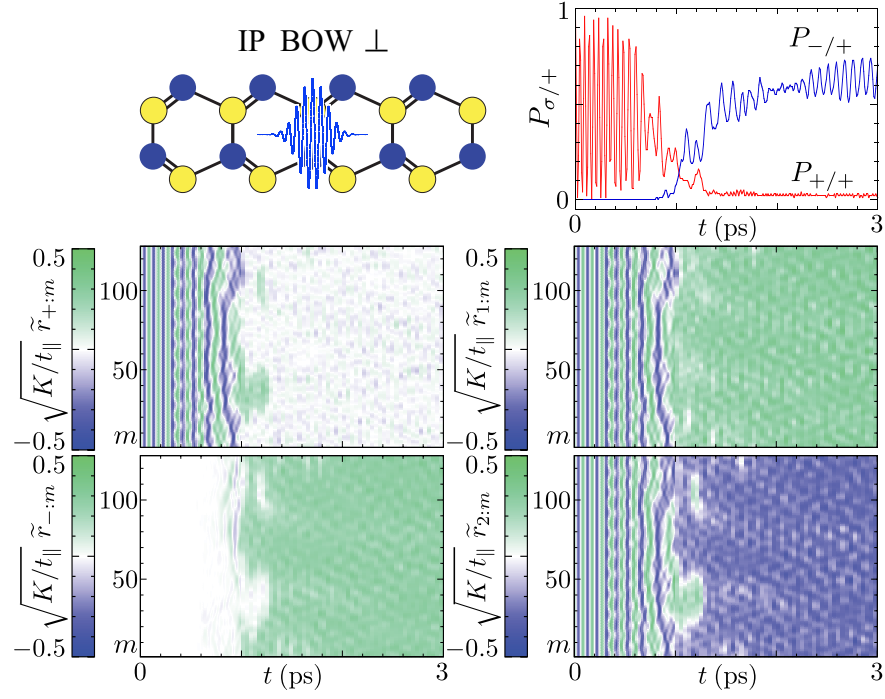


Figure 3.13: The same as Fig. 3.12, but the case of the initial state IP BOW being irradiated with the perpendicular polarized light.

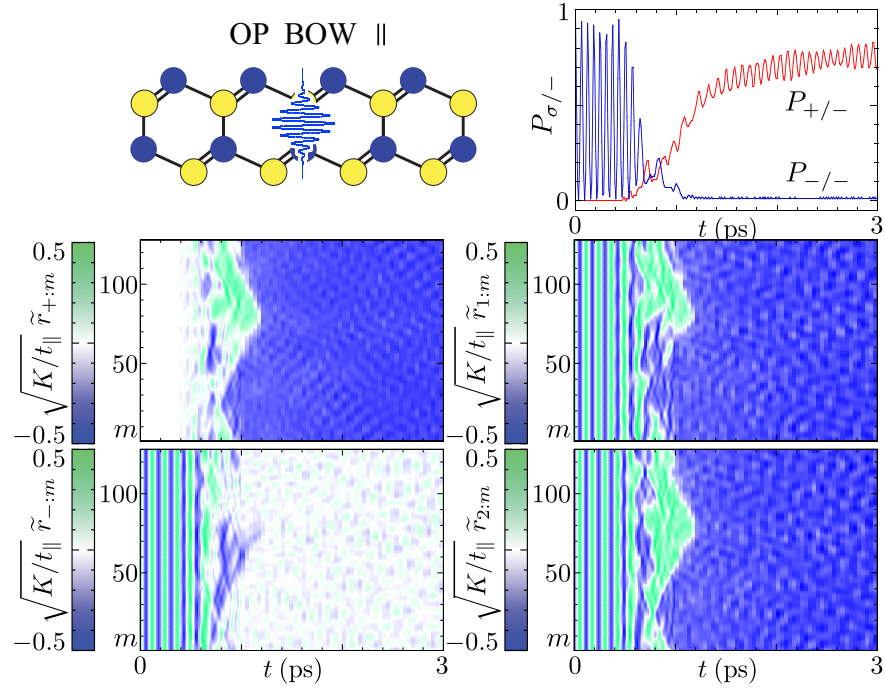


Figure 3.14: The same as Fig. 3.12, but the case of the initial state OP BOW being irradiated with the parallel polarized light.

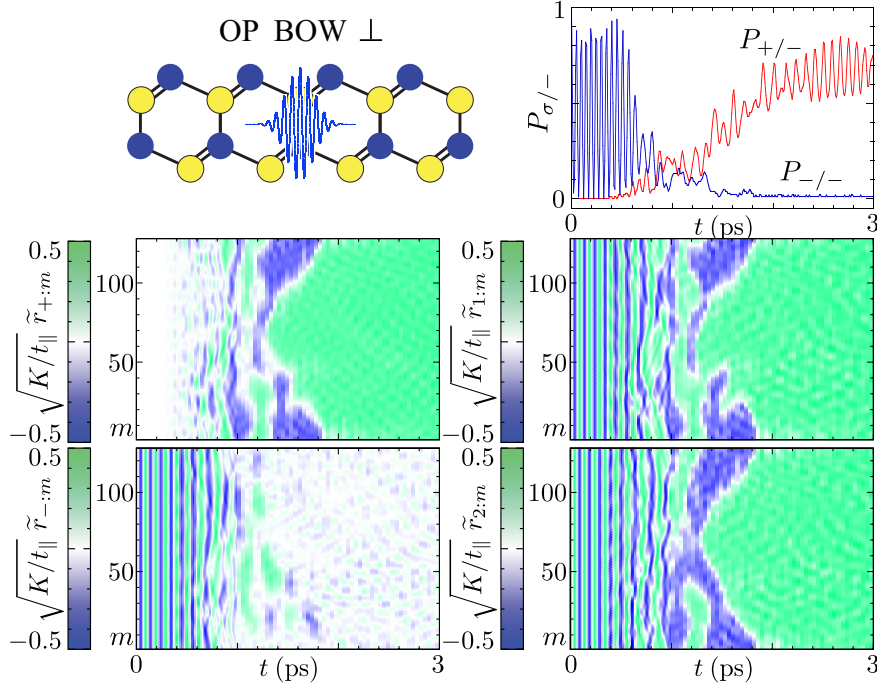


Figure 3.15: the same as Fig. 3.12, but case of the initial state OP BOW being irradiated with the perpendicular polarized light.

phase transitions are forbidden. We also notice that the photoinduced newborn OP BOW is a pure one without any domain walls formed.

We change the polarization of the incident light to be perpendicular direction, and show the results in Fig. 3.13. The scenario is qualitatively the same with the case of parallel polarized photoirradiation. The polarization direction of incident light has no effects on photoinduced phase transitions.

For the reverse conversion, namely, the OP-to-IP BOW phase transitions, they are still allowed just like in polyacene and paracyanogen. We again try the parallel and perpendicular polarized incident light respectively and present the results in Fig. 3.14 and Fig. 3.15. The incident puls are set for $\hbar\omega_0 = 1.3 t_{||}$, $T = 5$ fs, and

$\mathbf{A}_0 = 4.56 \times 10^{-2} \frac{\hbar c}{ea_{||}}$ for the parallel polarized one while $\mathbf{A}_0 = 9.6 \times 10^{-2} \frac{\hbar c}{ea_{||}}$ for the perpendicular polarized one respectively. The initial OP BOW can be globally

converted into the IP BOW phase, meanwhile without any kink-antikink pairs formed during the whole process.

Fig. 3.16 shows the time-resolved optical conductivities on the lattice dynamics

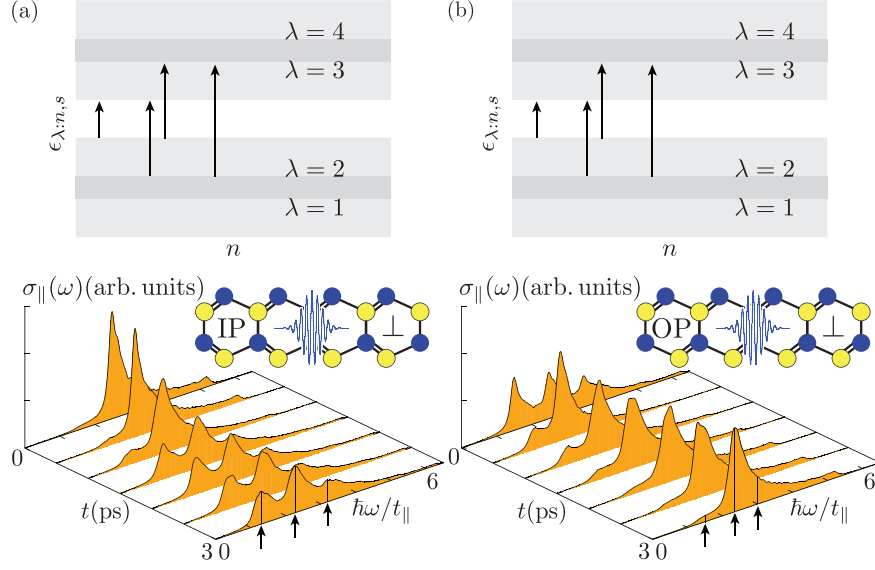


Figure 3.16: The same as Fig. 3.11 but on the lattice dynamics demonstrated in Fig. 3.13 and Fig. 3.15.

demonstrated in Fig. 3.13 and Fig. 3.15. In subfigure (a), the initial optical-conductivity spectrum has the significant peak corresponding to the 1-to-3 and 2-to-4 electronic transitions, which is nothing but the character of IP BOW phase. After photoirradiation, this main peak is to shrink, and the 2-to-3 and 1-to-3 absorption peaks grow up. The final achieved optical-conductivity spectrum is a triplet-peaked one, signifying that the final state is indeed the OP BOW. The scenario in subfigure (b) is just opposite, where the initial triplet-peaked spectrum finally turns into a single-peaked one, indicating the OP-to-IP BOW phase transition is achieved. We also notice that different with polyacene and paracyanogen, there are no small tips on the background of main spectra. This is reasonable since there are no kink-antikink pairs formed in the photoinduced phase transitions in BN-acene.

3.5 Why phase transitions are reversible or irreversible.

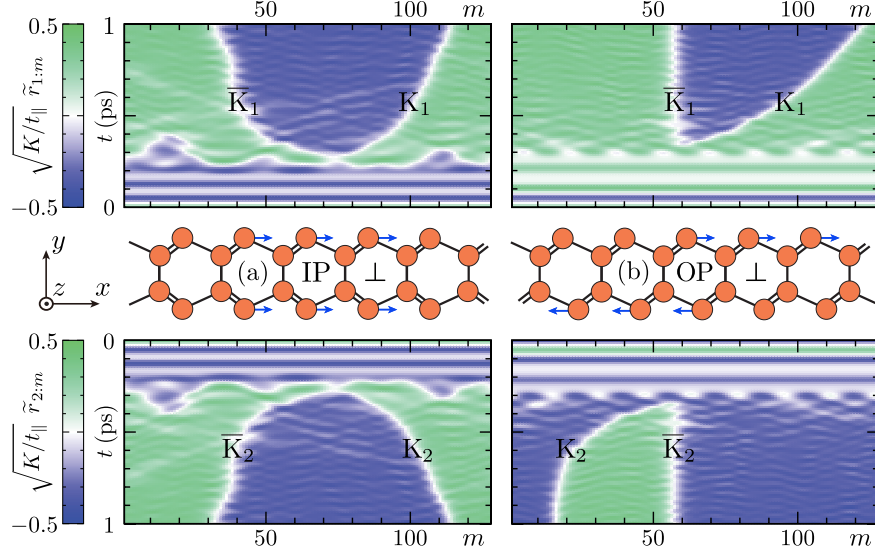


Figure 3.17: Spatial distribution of the bare bond variables $\tilde{r}_{1:m}$ and $\tilde{r}_{2:m}$ as functions of time t on the photoinduced dynamics presented in Fig. 3.2 and Fig. 3.4.

We have already systematically introduced the photoinduced phase transitions in polyacene, paracyanogen, and BN-acene. The most significant contrast among them is that the phase conversions in polyacene and paracyanogen are directional (irreversible) switchings, while they are bidirectional (reversible) conversions in BN-acene. Polyacene and paracyanogen have the same geometric properties, their IP BOW states have the mirror σ_v symmetry while OP BOW states have the C_{2z} rotation invariance. We propose that the symmetry deeply affect the photoinduced lattice fluctuations. In Fig. 3.17, we demonstrate the bare bond variables $\tilde{r}_{1:m}$ and $\tilde{r}_{2:m}$ as functions of time t when (a) IP BOW and (b) OP BOW of polyacene are irradiated with the perpendicular polarized light. For convenience of understanding our point, the qualitative sketches of the lattice fluctuations are also given. As shown, an antdomain is nucleated on each bond ordered chain at almost the same moment and the same space site, but the following motions of domain walls totally depend on the symmetry of their initial states. For the IP BOW initial state, the antdomains grow in harmony way, it seems

the system is very reluctant to destroy the mirror symmetry. However, for the OP BOW initial state, the pair of antodomains grow in the opposite direction. Since we use the periodical boundary conditions in the calculation, the initial C_{2z} symmetry is a global one. The photoinduced local antodomains destroy this global character, and make the system has no longer any long range orders. However, even in this case, the system still tends to preserve the C_{2z} symmetry, at least in a local way. And indeed we can see, the new formed antodomains on two legs keep a C_{2z} symmetry when they are growing. We also notice that, the two antodomains are not perfectly be C_{2z} rotated to each other. This is just because of the multiple excitation effects. We tried the dynamical calculations by changing the occupancy of Hartree-Fock levels with only one electron being pumped, then the motion of two resultant antodomains would show a perfect C_{2z} symmetry.

APPENDIX : The electron-hole symmetry breaking in paracyanogen

There is the split-peaked structure of parallel-polarized optical conductivity in IP BOW of paracyanogen. It originates from the electron-hole symmetry breaking. To analytically understand this electron hole symmetry breaking, we adopt the SSH model of IP BOW in the momentum space.

The Fourier transformations are:

$$\begin{aligned} c_{l:2n-1,s}^\dagger &= \frac{1}{\sqrt{N}} \sum_k e^{\frac{-ik(2n-1)}{2}} c_{l:1,k,s}^\dagger, \\ c_{l:2n,s}^\dagger &= \frac{1}{\sqrt{N}} \sum_k e^{\frac{-ik(2n)}{2}} c_{l:2,k,s}^\dagger, \end{aligned} \quad (3.15)$$

where index $(l : 1)$ $[(l : 2)]$ indicates the sublattice consisted of odd (even)-number sites on chain l .

$$\begin{aligned} H_{\text{SSH}} &= \sum_{k,s} (\varepsilon_{1:1} c_{1:1,k,s}^\dagger c_{1:1,k,s} + \varepsilon_{1:2} c_{1:2,k,s}^\dagger c_{1:2,k,s} + \varepsilon_{2:1} c_{2:1,k,s}^\dagger c_{2:1,k,s} + \varepsilon_{2:2} c_{2:2,k,s}^\dagger c_{2:2,k,s}) \\ &\quad - \sum_{k,s} (t_0 - \alpha r_0) (c_{1:1,k,s}^\dagger c_{1:2,k,s} e^{\frac{ik}{2}} + \text{H.c.}) - \sum_{k,s} (t_0 + \alpha r_0) (c_{1:2,k,s}^\dagger c_{1:1,k,s} e^{\frac{ik}{2}} + \text{H.c.}) \\ &\quad - \sum_{k,s} (t_0 - \alpha r_0) (c_{2:1,k,s}^\dagger c_{2:2,k,s} e^{\frac{ik}{2}} + \text{H.c.}) - \sum_{k,s} (t_0 + \alpha r_0) (c_{2:2,k,s}^\dagger c_{2:1,k,s} e^{\frac{ik}{2}} + \text{H.c.}) \\ &\quad - \sum_{k,s} t_\perp (c_{1:1,k,s}^\dagger c_{2:1,k,s} + \text{H.c.}) \end{aligned} \quad (3.16)$$

where r_0 denotes the ground-state bond distortion.

The k -dependence Hamiltonian can be written in:

$$H_{\text{SSH}}(k) = \begin{bmatrix} \varepsilon_{1:1} & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} & -t_{\perp} & 0 \\ -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & \varepsilon_{1:2} & 0 & 0 \\ -t_{\perp} & 0 & \varepsilon_{2:1} & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} \\ 0 & 0 & -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & \varepsilon_{2:2} \end{bmatrix}. \quad (3.17)$$

For polyacene (PA) case, we set the orbital energy as:

$$\varepsilon_{1:1} = \varepsilon_{1:2} = \varepsilon_{2:1} = \varepsilon_{2:2} = 0, \quad (3.18)$$

Then the k -dependence Hamiltonian of polyacene is written in:

$$H_{\text{SSH}}^{\text{PA}}(k) = \begin{bmatrix} 0 & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} & -t_{\perp} & 0 \\ -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & 0 & 0 & 0 \\ -t_{\perp} & 0 & 0 & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} \\ 0 & 0 & -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & 0 \end{bmatrix}. \quad (3.19)$$

Then we have the dispersion relations [bands number from 1 (lowest band) to 4 (highest band)] as

$$\begin{aligned}
\epsilon_1^{\text{PA}}(k) &= \frac{-\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2} - t_\perp}{2}, \\
\epsilon_2^{\text{PA}}(k) &= \frac{-\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2} + t_\perp}{2}, \\
\epsilon_3^{\text{PA}}(k) &= \frac{\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2} - t_\perp}{2}, \\
\epsilon_4^{\text{PA}}(k) &= \frac{\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2} + t_\perp}{2}.
\end{aligned} \tag{3.20}$$

We notice that

$$\begin{aligned}
\epsilon_1^{\text{PA}}(k) &= -\epsilon_4^{\text{PA}}(k), \\
\epsilon_2^{\text{PA}}(k) &= -\epsilon_3^{\text{PA}}(k),
\end{aligned} \tag{3.21}$$

which just means electron-hole symmetry is preserved.

For paracyanogen case (PC), we set $\varepsilon_{1:1} = \varepsilon_{2:1} = \varepsilon_0/2$, $\varepsilon_{1:2} = \varepsilon_{2:2} = -\varepsilon_0/2$, the k -dependence Hamiltonian is written as

$$H_{\text{SSH}}^{\text{PC}}(k) = \begin{bmatrix} \frac{\varepsilon_0}{2} & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} & -t_\perp & 0 \\ -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & -\frac{\varepsilon_0}{2} & 0 & 0 \\ -t_\perp & 0 & \frac{\varepsilon_0}{2} & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} \\ 0 & 0 & -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & -\frac{\varepsilon_0}{2} \end{bmatrix} \tag{3.22}$$

Then we have the dispersion relations as

$$\begin{aligned}
\epsilon_1^{\text{PC}}(k) &= \frac{-\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2 - 2t_\perp\varepsilon_0 + \varepsilon_0^2} - t_\perp}{2}, \\
\epsilon_2^{\text{PC}}(k) &= \frac{-\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2 + 2t_\perp\varepsilon_0 + \varepsilon_0^2} + t_\perp}{2}, \\
\epsilon_3^{\text{PC}}(k) &= \frac{\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2 - 2t_\perp\varepsilon_0 + \varepsilon_0^2} - t_\perp}{2}, \\
\epsilon_4^{\text{PC}}(k) &= \frac{\sqrt{16t_0^2\cos^2\frac{k}{2} + 16\alpha^2r_0^2\sin^2\frac{k}{2} + t_\perp^2 + 2t_\perp\varepsilon_0 + \varepsilon_0^2} + t_\perp}{2}.
\end{aligned} \tag{3.23}$$

Notice that in the above equations, electron-hole symmetry has already broken:

$$\begin{aligned}
\epsilon_1^{\text{PC}}(k) &\neq -\epsilon_4^{\text{PC}}(k), \\
\epsilon_2^{\text{PC}}(k) &\neq -\epsilon_3^{\text{PC}}(k).
\end{aligned} \tag{3.24}$$

There is a term $(-2t_\perp\varepsilon_0)$ appears in the square root. Both the interchain hopping term $t_\perp$ and the orbital-energy difference ε_0 contribute to the electron-hole symmetry breaking.

For the BN-acene (BN) case, we set $\varepsilon_{1:1} = \varepsilon_{2:2} = \varepsilon_0$, $\varepsilon_{1:2} = \varepsilon_{2:1} = -\varepsilon_0$, and the k -dependence Hamiltonian is written in

$$H_{\text{SSH}}^{\text{BN}}(k) = \begin{bmatrix} \varepsilon_0 & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} & -t_\perp & 0 \\ -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & -\varepsilon_0 & 0 & 0 \\ -t_\perp & 0 & -\varepsilon_0 & -2t_0\cos\frac{k}{2} + 2i\alpha r_0\sin\frac{k}{2} \\ 0 & 0 & -2t_0\cos\frac{k}{2} - 2i\alpha r_0\sin\frac{k}{2} & \varepsilon_0 \end{bmatrix}. \tag{3.25}$$

Then we have the dispersion relations as

$$\begin{aligned}
\epsilon_1^{\text{BN}}(k) &= \frac{-\sqrt{t_\perp \sqrt{16t_0^2 \cos^2 \frac{k}{2} + 16\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2} + 8t_0^2 \cos^2 \frac{k}{2} + 8\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2 + 2\varepsilon_0^2}}{\sqrt{2}}, \\
\epsilon_2^{\text{BN}}(k) &= \frac{-\sqrt{-t_\perp \sqrt{16t_0^2 \cos^2 \frac{k}{2} + 16\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2} + 8t_0^2 \cos^2 \frac{k}{2} + 8\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2 + 2\varepsilon_0^2}}{\sqrt{2}}, \\
\epsilon_3^{\text{BN}}(k) &= \frac{\sqrt{-t_\perp \sqrt{16t_0^2 \cos^2 \frac{k}{2} + 16\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2} + 8t_0^2 \cos^2 \frac{k}{2} + 8\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2 + 2\varepsilon_0^2}}{\sqrt{2}}, \\
\epsilon_4^{\text{BN}}(k) &= \frac{\sqrt{t_\perp \sqrt{16t_0^2 \cos^2 \frac{k}{2} + 16\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2} + 8t_0^2 \cos^2 \frac{k}{2} + 8\alpha^2 r_0^2 \sin^2 \frac{k}{2} + t_\perp^2 + 2\varepsilon_0^2}}{\sqrt{2}} \quad (3.26)
\end{aligned}$$

,

$$(3.27)$$

Then we have the dispersion relations:

$$\begin{aligned}
\epsilon_1^{\text{BN}}(k) &= -\epsilon_4^{\text{BN}}(k) \\
\epsilon_2^{\text{BN}}(k) &= -\epsilon_3^{\text{BN}}(k), \quad (3.28)
\end{aligned}$$

which means electron-hole symmetry is preserved in BN-acene.

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