Model calculation of the band energy gap for poly(p-phenylenevinylene)

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Abstract
The direct band gap of the conjugated polymer poly(p-phenylenevinylene) (PPV) is calculated in an effective single-band model by means of a renormalization scheme. This model provides a simple computational method for obtaining the band gap of a many-band conjugated π-electron system of long polymers. The calculation shows that, for the existing data for PPV, the present renormalization scheme works well and its results as regards the band energy gap are comparable to those obtained by other approaches including *ab initio* calculation.

1. Introduction

The successful demonstration of a PPV-based light-emitting diode [1, 2] has created a great deal of interest in studying the luminescence mechanism of this material, and its derivatives of various kinds, both theoretically and experimentally. Such luminescence in PPV materials mainly arises from recombination of a B_u-state electron–hole pair in the excitonic spectra. In determining the excitonic spectra for quasi-one-dimensional π-conjugated polymer systems such as PPV, it is important to know the band energy gap or the threshold state nB_u of the continuous spectra of the conduction band, but these become difficult to determine when an electron is excited from the conduction band to the valence band due to the multi-π-band character of PPV. This difficulty is caused by the combined effects of the electron–lattice interaction, the lattice relaxation, the polarizing effects, and the electronic correlation effects. The difficulty in determining the band energy gap or nB_u then causes the exact positions of excitons in the spectra [3] to be ambiguous. According to the Coulomb model of the exciton [4], the threshold state nB_u is consistent with the Hartree–Fock (HF) band energy gap [3, 4]. Thus, the correct determination of the band energy gap for materials such as PPV becomes

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an important task in determining the excitonic positions and the exciton binding energy. At present, the band energy gap for PPV can be calculated using the GW-approximation in an *ab initio* approach [5], which includes the electron exchange and the correlation effects while overcoming the shortcomings of empirical methods. However, using *ab initio* calculations can impose a heavy computational burden when looking at a many-band system with large unit cells. Therefore, in this paper we propose a simple approach for arriving at a reasonable value of the band energy gap for PPV.

It is known that among the π-conjugated polymers, polyene (PE) is the simplest polymer—just a chain of alternating single and double bonds—and polyacetylene (PA) is, except that it has two different configurations—the *trans*-configuration and the *cis*-configuration—also simple, being composed of alternating single and double bonds. They are both single-π-band systems and each has two sites in its unit cell. Thus, they have been widely and successfully described using the Su–Schrieffer–Heeger (SSH) Hamiltonian or an extended SSH Hamiltonian [6]. The PPV polymer, however, is more complex, being composed of alternating phenylene units and vinylene units. In every phenylene unit, there are two single bonds and a benzene ring. The multi-band electronic structure character of PPV results from the benzene rings. There are four main energy bands in each of the valence and conduction bands [7, 8]. The existing method which works for PE or PA cannot be directly applied to the PPV polymer due to this multi-band nature. For PPV polymers some previous authors have used an effective hopping parameter, considering a larger phenylene unit to describe the system. But this parameter was adjusted empirically [9] and was not connected with the basic electronic structure related to the optical absorption, which can be directly measured in experiments.

In PPV polymer and its derivatives, the fundamental optical absorption is mainly due to the transition from the top level of the four valence bands (the HOMO: highest occupied molecular orbital) to the bottom level of the four conduction bands (the LUMO: lowest unoccupied molecular orbital). The band energy gap is just determined by these two levels. Other branch bands are not so important in the optical excitation, and thus can be neglected in determining the band energy gap. We consider this basic fact enlightening; it gave us the central idea of setting up a simple approach. We may regard those two levels between which the main optical transition occurs as arising from an equivalent system which has single-band character. To complete this idea, the renormalization approach is the best candidate. Therefore, in the present paper a partial renormalization technique [10] is applied to the phenylene units to simplify the description of the PPV polymer to an effective 'dimerized' one, while keeping unchanged the electronic structure that the system possesses. Thus, an effective 'dimerized' PPV chain with an effective hopping parameter, t_{re}, and an effective interaction, Δt_{ee}^{re}, corresponding to the effective single bond plus the Hartree–Fock correction is proposed in terms of the original parameters.

The organization of the paper is as follows.

In section 2.1, our model is described. In section 2.2, a simple description of the renormalization procedure is given and the expressions for the effective hopping t_{re} and the effective site energy $\bar{\epsilon}$ are given. In section 2.3, a discussion of electron–electron interactions in the Hartree–Fock approximation for PPV and the effective electron–electron interaction correction, Δt_{ee}^{re}, are given, and an effective single-band model Hamiltonian is formulated.

In section 3, we show how to obtain the desired effective hopping parameter t_{re} and discuss its relation to the band energy gap and also the lowest unoccupied molecular orbital and the highest occupied molecular orbital. The numerical results are also given.

In section 4, we discuss our results, the validity of the present renormalization scheme, and the model Hamiltonian.

The final section gives our conclusions.

2. Model

2.1. Model Hamiltonian

We start from the following Hamiltonian for describing PPV: a sum of the single-electron term H_0 plus the electron–electron interaction term H_{e-e}:

$$H = H_0 + H_{e-e}. \tag{1}$$

Here

$$H_0 = H_d + H_b \tag{2}$$

where H_d refers to the vinylene double bonds and H_b to the phenylene units:

$$H_d = -\sum_{m,\sigma} t_v (C^\dagger_{2m,\sigma} C_{2m+1,\sigma} + C^\dagger_{2m+1,\sigma} C_{2m,\sigma}) \tag{3}$$

$$\begin{aligned}
H_b = &\sum_{m,\sigma} \epsilon_{2m-1} n_{2m-1,\sigma} + \sum_{m,s\sigma} \epsilon^b_s n_{2m-1,s,\sigma} + \sum_{m,\sigma} \epsilon_{2m} n_{2m,\sigma} \\
&- \sum_{m,\sigma} t_s (C^\dagger_{2m-1,\sigma} C_{2m-1,1,\sigma} + C^\dagger_{2m-1,1,\sigma} C_{2m-1,\sigma}) \\
&- \sum_{m,s,s'\sigma}^{s\neq s'} t_{ss'} (C^\dagger_{2m-1,s,\sigma} C_{2m-1,s',\sigma} + C^\dagger_{2m-1,s',\sigma} C_{2m-1,s,\sigma}) \\
&- \sum_{m,\sigma} t_s (C^\dagger_{2m-1,4,\sigma} C_{2m,\sigma} + C^\dagger_{2m,\sigma} C_{2m-1,4,\sigma})
\end{aligned} \tag{4}$$

and H_{e-e} is the electron–electron interaction term:

$$H_{e-e} = \sum_i U \rho_{i\uparrow} \rho_{i\downarrow} + \frac{1}{2} \sum_{ij}^{i\neq j} V_{ij} (n_i - 1)(n_j - 1). \tag{5}$$

Here $C^\dagger_{i\sigma}$ ($C_{i\sigma}$) are π-electron creation (annihilation) operators with spin σ at the site i, $n_i = \sum_\sigma n_{i\sigma}$, $n_{i\sigma} = C^\dagger_{i\sigma} C_{i\sigma}$, $\rho_{i\sigma} = n_{i\sigma} - 1/2$; $\sum_{s,s'}^{s\neq s'}$ runs over nearest-neighbour-site pairs on the benzene rings; ϵ_{2m} (ϵ_{2m-1}) is the site energy of a π-electron at a carbon-atom site of the vinylene unit and is identified with the parameter α in Hückel theory, and $\epsilon^b_{2m-1,s}$ is the site energy on the benzene ring. The $t_{ss'}$ ($s \neq s'$) are hopping integrals of π-electrons on the benzene ring. Here we only consider nearest-neighbour hopping between the carbon atoms. Then t_b denotes the nearest-neighbour hopping integral for the carbon atoms in the benzene ring, t_s denotes the hopping integral for π-electrons hopping between the benzene ring and the vinylene unit, and t_v the hopping integral on the vinylene double bond. The hopping integral is the resonance integral β in Hückel theory. Figure 1(a) illustrates the PPV geometry and the subscript notation. The hydrogen atom attached to every C atom has not been drawn in, and their effects on the system are assumed to be absorbed in the original parameters. In H_{e-e}, U is the on-site Coulomb interaction for the carbon atoms, and the long-range Coulomb interaction, V_{ij}, is given by the parametrized Ohno potential [11]:

$$V_{ij} = \frac{U}{\kappa \sqrt{1 + 0.6117 r_{ij}^2}} \tag{6}$$

where r_{ij} is the inter-atomic distance in Å. κ is the screening arising from the other surrounding chains and the polarization effects.
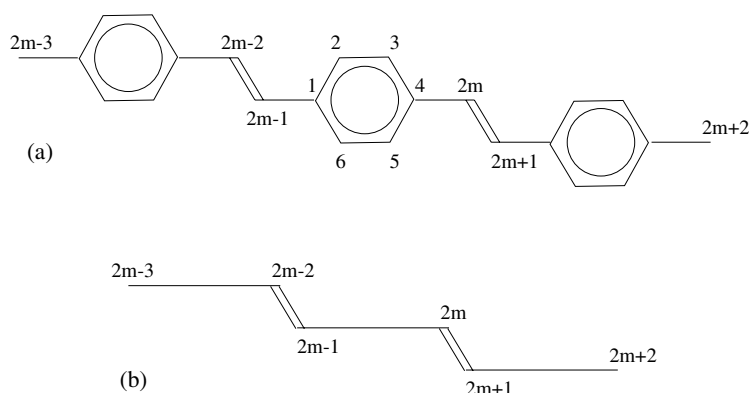
Figure 1. (a) PPV geometry; (b) reduced PPV.

The above electronic Hamiltonian (1) for PPV includes almost all information relevant to the optical excitation process. However, it is not possible to completely solve this many-body problem in an analytical manner like in solving for PE and PA. Thus we need a method for simplifying the structure of PPV but keeping its main electronic character unchanged, as mentioned in the introduction.

2.2. Structure renormalization of phenylene units

Each phenylene unit includes a benzene ring and two single bonds. An isolated benzene ring has six C-atom sites on which there are six localized π-electrons which themselves produce six energy states distributed symmetrically about zero energy: $b_{2g}(\alpha + 2\beta)$, $e_{2u}(\alpha + \beta)$ (doubly degenerate), $e_{1g}(\alpha - \beta)$ (doubly degenerate), and $a_{2u}(\alpha - 2\beta)$ [12], where α and β are Hückel parameters and are negative. Three of them are lower states and the other three are higher states. Thus, an isolated benzene ring supports four energy values. If each benzene ring can be viewed as an effective molecular 'site', then that site must allow the four orbitals in which the difference between the LUMO ($\alpha - \beta$) and the HOMO ($\alpha + \beta$) is just 2β.

It is known that in a π-conjugated system composed of many such benzene rings, like poly(*para*-phenylene) (PPP), the difference between the LUMO and the HOMO will be smaller than 2β and will decrease with increasing length and reach a converged value when the chain is rather long [13]. (The convergence occurs before the chain becomes infinite.) A similar process also occurs in PPV, where each PPV unit has eight carbon atoms.

In the energy band of PPV, the highest bonding energy band, denoted by π, and the lowest antibonding energy band, denoted by π^*, determine the band energy gap. The localized π-electrons on the benzene rings contribute energy bands that are lower (higher) than the highest bonding (lowest antibonding) energy bands. The π–π^* energy bands are thus due mainly to the delocalized π-electrons on the vinylene double bonds. As stated in the introduction, the aim of the renormalization is to model the π–π^* energy bands from the multi-band set of PPV.

In PPV, the benzene rings have relatively stable bond structure as compared to the vinylene units. The bond-length change mainly occurs on the vinylene double bond [8]. Thus, we may separate the phenylene unit from the PPV chain. This unit has the Hamiltonian H_b in (4). According to a renormalization study of the benzene ring [14], the phenylene unit can be reduced to two effective 'sites' and an effective hopping between these two 'sites' by means

of the following sets of equations:

$$t_{re} = \frac{t_s^2 \tau}{(E - \bar{\alpha})(E - \bar{\beta}) - \tau^2} \tag{7a}$$

$$\bar{\epsilon}_{2m-1} = \epsilon_{2m-1} + \frac{t_s^2}{E - \bar{\alpha} - (\tau^2/[E - \bar{\beta}])} \tag{7b}$$

$$\bar{\epsilon}_{2m} = \epsilon_{2m} + \frac{t_s^2}{E - \bar{\beta} - (\tau^2/[E - \bar{\alpha}])} \tag{7c}$$

and

$$\bar{\alpha} = \epsilon_{2m-1,1}^b + \frac{2t_b^2}{E - \epsilon_{2m-1,2}^b} + \frac{2(t_b^2/[E - \epsilon_{2m-1,2}^b])^2}{E - \epsilon_{2m-1,3}^b - (t_b^2/[E - \epsilon_{2m-1,2}^b])} \tag{8a}$$

$$\bar{\beta} = \epsilon_{2m-1,4}^b + \frac{2t_b^2}{E - \epsilon_{2m-1,3}^b} + \frac{2(t_b^2/[E - \epsilon_{2m-1,3}^b])^2}{E - \epsilon_{2m-1,2}^b - (t_b^2/[E - \epsilon_{2m-1,3}^b])} \tag{8b}$$

$$\tau = \frac{2t_b^3}{(E - \epsilon_{2m-1,2}^b)(E - \epsilon_{2m-1,3}^b) - t_b^2} \tag{8c}$$

where E is the energy of the system. In this way, H_b can be reduced to

$$\tilde{H}_b = \sum_{m,\sigma} \bar{\epsilon}_{2m-1} n_{2m-1,\sigma} + \sum_{m,\sigma} \bar{\epsilon}_{2m} n_{2m,\sigma} - \sum_{m,\sigma} t_{re}(C_{2m-1,\sigma}^\dagger C_{2m,\sigma} + C_{2m,\sigma}^\dagger C_{2m-1,\sigma}) \tag{9}$$

where t_{re}, $\bar{\epsilon}_{2m-1}$, and $\bar{\epsilon}_{2m}$ are the effective hopping parameter and the effective 'site' energies. Suppose t_v, the hopping integral on the vinylene double bond, is not changed when the phenylene unit is renormalized [15] (in fact it may be affected by the renormalization process but we ignore such change); we then arrive at an effective Hamiltonian

$$\tilde{H}_0 = H_d + \tilde{H}_b. \tag{10a}$$

That is,

$$\tilde{H}_0 = \sum_{m,\sigma} \bar{\epsilon}_{2m-1} n_{2m-1,\sigma} + \sum_{m,\sigma} \bar{\epsilon}_{2m} n_{2m,\sigma} - \sum_{m,\sigma} t_v(C_{2m,\sigma}^\dagger C_{2m+1,\sigma} + C_{2m+1,\sigma}^\dagger C_{2m,\sigma})$$
$$- \sum_{m,\sigma} t_{re}(C_{2m-1,\sigma}^\dagger C_{2m,\sigma} + C_{2m,\sigma}^\dagger C_{2m-1,\sigma}). \tag{10b}$$

$\tilde{H}_0$ looks like the single-band SSH Hamiltonian for polyacetylene and thus can be easily diagonalized.

For simplicity, we assume that all C atoms have identical site energies, denoted by a. Then, the renormalized site energies at all m sites, $\bar{\epsilon}_{2m-1}$ and $\bar{\epsilon}_{2m}$, become $\bar{\epsilon}$. Therefore

$$\bar{\epsilon} = \frac{t_s^2 \omega (\omega^2 - 3t_b^2)}{[\omega(\omega + t_b) - 2t_b^2][\omega(\omega - t_b) - 2t_b^2]} \tag{11}$$

$$t_{re} = \frac{2t_s^2 t_b^3}{[\omega(\omega + t_b) - 2t_b^2][\omega(\omega - t_b) - 2t_b^2]} \tag{12}$$

which comes from (7b), (7c), and (7a). Here $\omega = E - a$. Figure 1(b) shows the geometrical structure of the PPV chain after renormalization.

In the following calculations, it was found that the role of the site energies a is just to shift all energy values by the amount a, and that they do not affect the values of the resulting t_{re} and $\bar{\epsilon}$. We do not study impurities or disorder here. So the original site energies, $\epsilon_{2m-1,1}^b, \ldots, \epsilon_{2m-1,6}^b, \epsilon_{2m-1}$, and ϵ_{2m} (all assumed to have the same value, denoted as a) may be set to zero in this investigation.

2.3. Contributions from electron–electron interactions

The single-electron spectrum of (2) will be changed by the π-electronic interactions, H_{e-e}, and by interparticle correlations, which are important factors in the optical excitation and optical non-linearity. Most authors use the PPP model to describe the Hamiltonian of π-conjugated polymers, in which the π-electron interaction term is parametrized by an Ohno potential, and decoupled by the HF approximation [3, 7, 8]. In this study, we are concerned with the band energy gap instead of the polaron effect and the related polarization effects. We will also treat the system as a rigid lattice [3, 9] and assume that lattice vibrations of the system will not affect the band gap to a large extent. Then, the HF approximation will be applied to decouple the interaction term H_{e-e} [3, 7, 8].

PPV is centrosymmetric and thus has C_2 symmetry. Some π-electronic interaction terms from the parametrized Ohno potential, V_{ij} (see (6)), counteract each other. For example, the π-electrons on sites $2m$ and $2m + 1$ of the vinylene unit in a PPV unit will experience repulsive Coulomb interactions: $V_{2m-2,2m}$ and $V_{2m,2m+2}$ or $V_{2m-1,2m+1}$ and $V_{2m+1,2m+3}$ from the nearby PPV units (one on its left and another on its right) with identical magnitudes ($V_{2m-2,2m} = V_{2m,2m+2}$ and $V_{2m-1,2m+1} = V_{2m+1,2m+3}$) but opposite directions. As for other non-nearest-neighbour π-electron interactions, the same consideration applies. Therefore these π-electron repulsive interactions need not be considered in the calculations. However, the π-electron interaction $V_{2m-1,2m}$ (crossing a benzene ring) in the PPV unit cell is unique and is not counteracted by any other interaction terms. Also, other non-nearest-neighbour non-symmetrical interactions are not counteracted. For instance, the π-electrons on a vinylene unit experience the Coulomb forces from the benzene rings on their left and their right, which are not counteracted. Nevertheless, they contribute a negligible amount, because the non-nearest-neighbour bond-charge densities are so small when compared to the nearest-neighbour ones. Thus, we only consider the nearest-neighbour π-electronic interactions for the carbon atoms in this study.

It is assumed that the mean value of the π-electron density operator, $\langle n_{i\sigma} \rangle$, shows no fluctuation and is exactly $1/2$, which is equivalent to working in the bond-order-wave (BOW) phase. Because there is no magnetic effect, $\langle n_{i\sigma} \rangle = \langle n_{i\bar{\sigma}} \rangle$. Under this assumption, the terms containing U in H_{e-e} vanish and the long-range Coulomb-interaction terms, V_{ij}, do not contribute to the site energies in the HF approximation. If we do not make the assumption that $\langle n_{i\sigma} \rangle$ is $1/2$, the site energies will have additional terms containing factors like $U\langle n_{i\sigma} \rangle$ or $V_{ij}\langle n_{i\sigma} \rangle$ which only shift the zero of energy. Then H_{e-e} becomes [16]

$$
\begin{aligned}
H_{e-e}^{HF} = &- \sum_{m,\sigma} V_s[(C_{2m-1,\sigma}^\dagger C_{2m-1,1,\sigma} + C_{2m-1,1,\sigma}^\dagger C_{2m-1,\sigma})\Delta_s - (\Delta_s)^2] \\
&- \sum_{m,\sigma} \sideset{}{'}\sum_{s,s'} V_b[(C_{2m-1,s,\sigma}^\dagger C_{2m-1,s',\sigma} + C_{2m-1,s',\sigma}^\dagger C_{2m-1,s,\sigma})\Delta_b - (\Delta_b)^2] \\
&- \sum_{m,\sigma} V_s[(C_{2m-1,4,\sigma}^\dagger C_{2m,\sigma} + C_{2m,\sigma}^\dagger C_{2m-1,4,\sigma})\Delta_s - (\Delta_s)^2] \\
&- \sum_{m,\sigma} V_0[(C_{2m,\sigma}^\dagger C_{2m+1,\sigma} + C_{2m+1,\sigma}^\dagger C_{2m,\sigma})\Delta_0 - (\Delta_0)^2] + H_{v-units}^{HF} + H_{p-units}^{HF} \\
= &\, H_{p-nn}^{HF} + H_{p-nnn}^{HF} + H_{v-nn}^{HF} + H_{v-nnn}^{HF}
\end{aligned} \tag{13}
$$

where $\Delta_s \equiv \langle C_{2m-1,1,\sigma}^\dagger C_{2m-1,\sigma} \rangle = \langle C_{2m-1,4,\sigma}^\dagger C_{2m,\sigma} \rangle$, $\Delta_b \equiv \langle C_{2m-1,s',\sigma}^\dagger C_{2m-1,s,\sigma} \rangle$, and $\Delta_0 \equiv \langle C_{2m+1,\sigma}^\dagger C_{2m,\sigma} \rangle$. $\langle \cdots \rangle$ means the ground-state expectation value; $\sum_{s,s'}'$ means the sum over the nearest-neighbour sites on the benzene rings. Here, Δ_s, Δ_b, and Δ_0 are the bond-charge densities on the single bond between the benzene ring and the vinylene bond,

the benzene ring bonds, and the vinylene double bond, respectively (see the appendix for expressions for them). Because Δ_s, Δ_b, and Δ_0 are all constant, their square terms in H_{e-e}^{HF} may be omitted in the calculation.

Due to the absence of the on-site Coulomb interaction U in H_{e-e}^{HF}, the electron correlation effect arising from U has in fact been removed from the system. However, this does not mean that there is no correlation between the π-electrons, because the long-range Coulomb interaction V_{ij} is still operative in H_{e-e}^{HF}. In the HF approximation the part of the correlation effects arising from the electrons with the same spin is included. As a first-order approximation, the residual interaction $H_{res} = H_{e-e} - H_{e-e}^{HF}$ will also be omitted because, as a perturbation, it contributes only to a small degree [17].

Although the on-site Coulomb interactions U are not included in the resulting Hamiltonian, H_{e-e}^{HF}, in the HF approximation in the BOW phase, its role is partly taken, through the Ohno formula, by (6). The role of U is to affect the electrons' localizability. Thus, as U increases, the localization of the π-electrons will increase, and hence the overlap between two adjacent atomic orbitals decreases and the corresponding bond-charge density also decreases.

In the tight-binding approximation that the SSH Hamiltonian was based on, the nearest-neighbour bond-charge densities, $\langle C_i^\dagger C_{i\pm1}\rangle$, are the main contributions, and other non-nearest-neighbour bond-charge densities like $\langle C_i^\dagger C_{i\pm2}\rangle$ and $\langle C_i^\dagger C_{i\pm3}\rangle$ are negligible. The non-nearest-neighbouring interaction terms relating to the phenylene units, H_{p-nnn}^{HF}, and the non-nearest-neighbouring interaction terms relating to the vinylene units, H_{v-nnn}^{HF}, may be omitted. This is why we only consider the nearest-neighbour interactions. We may renormalize H_{p-nn}^{HF} to $-\sum_{m,\sigma}\Delta t_{ee}^{re}(C_{2m-1,\sigma}^\dagger C_{2m,\sigma} + C_{2m,\sigma}^\dagger C_{2m-1,\sigma})$. Then we have

$$
\tilde{H}_{re}^{HF} = -\sum_{m,\sigma}\Delta t_{ee}^{re}(C_{2m-1,\sigma}^\dagger C_{2m,\sigma} + C_{2m,\sigma}^\dagger C_{2m-1,\sigma})
$$
$$
- \sum_{m,\sigma}\Delta t_{ee}^0(C_{2m,\sigma}^\dagger C_{2m+1,\sigma} + C_{2m+1,\sigma}^\dagger C_{2m,\sigma}). \tag{14}
$$

Here $\Delta t_{ee}^0 = V_0\Delta_0$ is the HF correction of the electron–electron interactions with respect to the vinylene double bond, and Δt_{ee}^{re} is the correction of the electron–electron interactions with respect to the phenylene unit which is determined by

$$
\Delta t_{ee}^{re} = \frac{2(V_s\Delta_s)^2(V_b\Delta_b)^3}{|[E(E+V_b\Delta_b) - 2(V_b\Delta_b)^2][E(E-V_b\Delta_b) - 2(V_b\Delta_b)^2]|}. \tag{15}
$$

Finally, by adding (10b) and (14) together, we obtain a renormalized effective single-band Hamiltonian for PPV:

$$
\tilde{H}_{eff} = \sum_{m,\sigma}\bar{\epsilon}(n_{2m-1,\sigma} + n_{2m,\sigma}) - \sum_{m,\sigma}t_0'(C_{2m,\sigma}^\dagger C_{2m+1,\sigma} + C_{2m+1,\sigma}^\dagger C_{2m,\sigma})
$$
$$
- \sum_{m,\sigma}t_{re}'(C_{2m-1,\sigma}^\dagger C_{2m,\sigma} + C_{2m,\sigma}^\dagger C_{2m-1,\sigma}). \tag{16}
$$

Here t_0' and t_{re}' are given by

$$
t_0' = t_v + \Delta t_{ee}^0 \tag{17}
$$
$$
t_{re}' = t_{re} + \Delta t_{ee}^{re}. \tag{18}
$$

In the momentum space, $\tilde{H}_{eff}$ is easily diagonalized as

$$
E_{eff} = \sum_k(\epsilon_{k_c}n_{k_c} - \epsilon_{k_v}n_{k_v}) \tag{19}
$$

where $\epsilon_{k_c} = |\bar{z}_{k_c}| + \bar{\epsilon}$ and $\epsilon_{k_v} = -(|\bar{z}_{k_v}| - \bar{\epsilon})$. Here,

$$
|\bar{z}_k| = \sqrt{(t_0' + t_{re}')^2 - 4(t_0't_{re}')\sin^2(kd/2)}
$$

and ϵ_{k_c} and ϵ_{k_v} are the conduction band and the valence band energy spectra. Due to the renormalization, the conduction band and the valence band are not symmetric with respect to the zero energy level. The band energy gap, denoted by E_{gap}^{HF}, is given by $2|\bar{z}_{k_F}| = 2(t_0' - t_{re}')$ at $k_F = \pi/d$; that is,

$$E_{gap}^{HF} = E_{gap}^0 + \Delta E_{gap} \tag{20}$$

where ΔE_{gap} is the correction of the electron–electron interaction to the energy band gap. Because the original PPV system has been transformed to an equivalent single and double model like that of PA, the band gap is opened as for PA at the k-point $k_F = \pi/d$ of the reduced Brillouin zone [3]. Here the definition of d is as follows. We take the direction of the line drawn by passing through the centres of the benzene rings along the x-axis and denote the length of the effective single bond projected along the x-axis as b, and the length of the double bond along the x-axis as a. Then the lattice period is $d = a + b$ with $a = R_{2m,2m+1} \cos\theta_1$ and $b = R_{2m-1,2m} \cos\theta_2$, where θ_1 (θ_2) is angle between the vinylene double bond $R_{2m,2m+1}$ (=1.345 Å) (the effective single bond $R_{2m-1,2m}$) and the x-axis. $R_{2m-1,2m}$ may be determined from geometric relations for the vinylene double bond, the effective single bond, and the angle between them.

3. Determination of the effective hopping parameter

3.1. The Green's function and energy spectra

The effective single-band Hamiltonian of the PPV has been constructed above. The next important step is to determine the values of the effective hopping parameter t_{re} and the effective site energy $\bar{\epsilon}$. For this, we introduce the Green's function for the renormalized PPV system [17]:

$$G_{ij}(t - t') = -i\langle\,|\mathcal{T}[C_{i\sigma}(t)C_{j\sigma}^\dagger(t')]|\,\rangle \tag{21}$$

where $|\,\rangle$ denotes the ground state of the renormalized PPV system.

$$C_{j\sigma}^\dagger(t) = \exp(i\tilde{H}_0 t)C_{i\sigma}^\dagger \exp(-i\tilde{H}_0 t)$$

is the Heisenberg operator. In the energy domain, $G_{ij}(t - t')$ is transformed into $G_{ij}(E)$ which satisfies the following coupled set of linear equations:

$$EG_{ij}(E) = \delta_{ij} + \bar{\epsilon}_i G_{ij}(E) + \sum_l t_{il} G_{lj}(E). \tag{22}$$

When the system is in the ground state, the diagonal Green's function contains all of the information of the energy spectrum. The energies of the system can then be obtained from the poles of the diagonal matrix element $G_{ll}(E)$. Because all of the effective site energies are the same, the Green functions for even sites and odd sites are identical. From (22), we obtain

$$G_{ll}(E) = \cfrac{1}{E - \bar{\epsilon} - \cfrac{t_v^2}{E - \bar{\epsilon} - \cfrac{t_{re}^2}{\cdots}} - \cfrac{t_{re}^2}{E - \bar{\epsilon} - \cfrac{t_v^2}{\cdots}}}. \tag{23}$$

Here E is the energy spectrum of the renormalized PPV. Equation (23) is the continued-fraction form of the Green's function. If we apply a different cut-off to the continued-fraction part, we may have different systems with distinct energy distributions. Note that when $\bar{\epsilon}$ and t_{re} are inserted into (23), the E-values obtained are those of the original PPV system.

(1) For a two-effective-site system without a term for hopping between these two effective sites, $G_{ll}(E)$ is

$$G_2(E) = \frac{1}{E - \bar{\epsilon}}.$$ (24)

It can be seen from the expression for $\bar{\epsilon}$ (see (11)) that the corresponding original system is just a phenylene unit. From the poles of (24) we obtain a polynomial equation in E, whose solution yields the energies of the original system: $E = 0$ or

$$
\begin{aligned}
E_4 &= +\sqrt{\frac{(5t_b^2 + t_s^2)}{2} + \sqrt{2t_b^4 + \frac{(t_b^2 - t_s^2)^2}{4}}} \\[2mm]
E_3 &= +\sqrt{\frac{(5t_b^2 + t_s^2)}{2} - \sqrt{2t_b^4 + \frac{(t_b^2 - t_s^2)^2}{4}}} \\[2mm]
E_2 &= -\sqrt{\frac{(5t_b^2 + t_s^2)}{2} - \sqrt{2t_b^4 + \frac{(t_b^2 - t_s^2)^2}{4}}} \\[2mm]
E_1 &= -\sqrt{\frac{(5t_b^2 + t_s^2)}{2} + \sqrt{2t_b^4 + \frac{(t_b^2 - t_s^2)^2}{4}}}.
\end{aligned}
$$ (25)

If t_s is taken as zero, equation (25) shows that $E_4 = 2t_b$, $E_3 = t_b$, $E_2 = -t_b$, and $E_1 = -2t_b$, which are just the energies of a single benzene ring. Here the site energies have been omitted. If they were retained, however, we would clearly have $E_4 = a + 2t_b$, $E_3 = a + t_b$, $E_2 = a - t_b$, and $E_1 = a - 2t_b$. Evidently, these four energies correspond to four states of a single benzene ring: $a_{2u}(E_4)$, $e_{1g}(E_3)$, $e_{2u}(E_2)$, and $b_{2g}(E_1)$. The LUMO and the HOMO are the e_{1g} and e_{2u} ones, respectively. The LUMO and the HOMO give the energy difference, $2t_b$, whether the site energies, a, are omitted or not. Thus, equation (25) gives the four real energies of a phenylene unit (eight carbon atoms) with four degenerate levels, and the difference between the LUMO and the HOMO is $E_3 - E_2$.

(2) For a three-effective-site system with hopping parameters t_{re} and t_v for the adjacent sites, $G_{ll}(E)$ reads

$$G_3(E) = \frac{1}{E - \bar{\epsilon} - \dfrac{t_v^2}{E - \bar{\epsilon}} - \dfrac{t_{re}^2}{E - \bar{\epsilon}}}.$$ (26)

The corresponding original system is composed of a phenylene unit and a vinylene unit, which includes a PPV unit. Inserting (12) and (11) into (26), we again obtain a polynomial equation in E. The solution to this algebraic equation gives ten real energy values E. There are nine π-electrons in this system Thus, on the HOMO level there is only one electron site occupied.

(3) For a seven-effective-site system with alternative hopping parameters t_{re} and t_v, $G_{ll}(E)$ becomes

$$G_7(E) = \frac{1}{E - \bar{\epsilon} - \dfrac{t_v^2}{E - \bar{\epsilon} - \dfrac{t_{re}^2}{E - \bar{\epsilon} - \dfrac{t_v^2}{E - \bar{\epsilon}}}} - \dfrac{t_{re}^2}{E - \bar{\epsilon} - \dfrac{t_v^2}{E - \bar{\epsilon} - \dfrac{t_{re}^2}{E - \bar{\epsilon}}}}}.$$ (27)

The corresponding original system is composed of three phenylene units and three vinylene units, which includes three PPV units. Similarly, inserting (12) and (11) into (27), we can obtain a polynomial equation in E. The solution to this algebraic equation gives twenty real energy values E. Evidently, there are three degenerate levels in the empty molecular orbitals and the occupied molecular orbitals, respectively. On the HOMO level there is one π-electron site occupied. Note that the present method cannot be used to establish which level is degenerate.

3.2. Calculation results

In our calculations we adopt the following two sets of parameters—referred to as set (I) [8, 18] and set (II) [7]:

(I) $t_v = 2.32$ eV, $t_s = 1.74$ eV, $t_b = 2.11$ eV, and $U = 5.05$ eV. The electron–electron interactions are given by the Ohno formula:

$$V_{m,n} = 1/\sqrt{[(1/U)^2 + (R_{m,n}/Vr_0)^2]}$$

where $V = 2.63$ eV, $R_{m,n}$ is the distance between carbon atom sites m and n, and $r_0 = 1.4$ Å, the mean value of $R_{m,n}$. The electron–lattice coupling strength is assumed to be 5.23 eV Å^{-1}, which gives V_b, V_s, and V_0 as 2.34 eV, 2.26 eV, and 2.40 eV, respectively. The six bond lengths of the benzene ring are taken to be equal to 1.39 Å; the bond length between the benzene ring and the vinylene double bond is 1.45 Å, and the vinylene double-bond length is 1.35 Å.

(II) $t_v = 2.6$ eV, $t_s = 2.2$ eV, $t_b = 2.4$ eV, $U = 8$ eV, and

$$V_{m,n} = U/\kappa\sqrt{(1 + 0.6117R_{m,n}^2)}$$

which gives V_b, V_s, and V_0 as $5.42/\kappa$ eV, $5.29/\kappa$ eV, and $5.51/\kappa$ eV, respectively, where the $R_{m,n}$ are taken as those in (I). Here κ is taken as 2, 2.4, and 3, respectively.

The more levels of the continued fraction we take, the longer the renormalized system is taken to be. Because it is not practical to simultaneously resolve equations (12), (11), and (23) with an infinite continued fraction, and, moreover, when PPV has more than eight unit cells the band energy gap has reached a fixed value [3], only finite levels of the continued fraction are considered in actual calculations. Table 1 lists the calculation results for one PPV unit cell, three PPV unit cells, and ten PPV unit cells. Table 1 shows that the values of t_{re} decrease with increasing numbers of PPV unit cells and that increasing the number of PPV unit cells decreases the intervals between the LUMO and HOMO levels.

Table 1. The computational results in the first two rows are based on the parameters $t_v = 2.32$ eV, $t_s = 1.74$ eV, and $t_b = 2.11$ eV from (I); those in the last two rows are based on the parameters $t_v = 2.6$ eV, $t_s = 2.2$ eV, and $t_b = 2.4$ eV from (II).

Single PPV unit			Three PPV units			Ten PPV units		
E	$\bar{\epsilon}$	t_{re}	E	$\bar{\epsilon}$	t_{re}	E	$\bar{\epsilon}$	t_{re}
1.32 (LUMO)	−1.07	1.31	1.05 (LUMO)	−0.70	1.02	0.90 (LUMO)	−0.56	0.92
−1.32 (HOMO)	1.07	1.31	−1.05 (HOMO)	0.70	1.02	−0.90 (HOMO)	0.56	0.92
1.35 (LUMO)	−1.21	1.60	1.01 (LUMO)	−0.76	1.28	0.87 (LUMO)	−0.62	1.20
−1.35 (HOMO)	1.21	1.60	−1.01 (HOMO)	0.76	1.28	−0.87 (HOMO)	0.62	1.20

On putting the energy value of the HOMO or the LUMO into (12) and (15), we obtain the corresponding effective hopping parameter values, t_{re}, and the electron–electron interaction corrections, Δt_{ee}^{re}. According to these values, we obtain the corresponding band energy gap, E_{gap}^{HF}.

Table 1 lists the energy values of the LUMO and HOMO and the corresponding effective hopping parameters, t_{re} and $\bar{\epsilon}$. It is seen that for the different initial parameters: t_v, t_s, and t_b, the values of t_{re} and $\bar{\epsilon}$ obtained are somewhat different but their differences are never very large.

Table 2 lists the values of the band energy gap determined for the renormalized PPV polymer corresponding to the different values of t_{re} using two sets of different parameters, sets (I) and (II). Note that the values in table 2 are in fact obtained without considering the angle ($\sim 120°$) between the phenylene unit and vinylene unit in the PPV unit. Thus, the resultant band energy gap may be a little larger.

Table 3 lists the values obtained considering this angle in the calculations. These values are smaller than those in table 2.

Table 2. $E_{gap}^0 = 2(t_v - t_{re})$, $\Delta E_{gap} = 2(\Delta t_{ee}^0 - \Delta t_{ee}^{re})$, and $E_{gap}^{HF} = E_{gap}^0 + \Delta E_{gap}$. All quantities are in units of eV.

	Ten PPV units	t_v	t_{re}	E_{gap}^0	ΔE_{gap}	E_{gap}^{HF}
(I)	$U = 5.05$	2.32	0.92	2.79	0.85	3.65
(II)	$U = 6, \kappa = 1.2$	2.6	1.20	2.80	0.51	3.32
(II)	$U = 6, \kappa = 1.6$	2.6	1.20	2.80	0.99	3.79
(II)	$U = 6, \kappa = 2$	2.6	1.20	2.80	0.88	3.68
(II)	$U = 6, \kappa = 2.1$	2.6	1.20	2.80	0.80	3.60
(II)	$U = 6, \kappa = 2.2$	2.6	1.20	2.80	0.69	3.49
(II)	$U = 8, \kappa = 1.6$	2.6	1.20	2.80	0.51	3.32
(II)	$U = 8, \kappa = 1.8$	2.6	1.20	2.80	0.83	3.63
(II)	$U = 8, \kappa = 2$	2.6	1.20	2.80	0.96	3.76
(II)	$U = 8, \kappa = 2.4$	2.6	1.20	2.80	0.97	3.77
(II)	$U = 8, \kappa = 3$	2.6	1.20	2.80	0.62	3.42

Table 3. $E_{gap}'^0$, $\Delta E_{gap}'$, and $E_{gap}'^{HF}$ obtained taking into consideration the angle of 120° between the phenylene unit and the vinylene unit. All quantities are in units of eV.

	Ten PPV units	$E_{gap}'^0$	$\Delta E_{gap}'$	$E_{gap}'^{HF}$	E_{gap}
(I)	$U = 5.05$	2.61	0.79	3.42	3.2 (HF) [8]
(II)	$U = 6, \kappa = 1.6$	2.63	0.93	3.55	3.3 (GW) [5]
(II)	$U = 6, \kappa = 2$	2.63	0.88	3.45	3.6 (HF) [7]
(II)	$U = 6, \kappa = 2.1$	2.63	0.75	3.38	3.64 (HF) [18]
(II)	$U = 8, \kappa = 1.8$	2.63	0.78	3.40	
(II)	$U = 8, \kappa = 2$	2.63	0.90	3.52	
(II)	$U = 8, \kappa = 2.4$	2.63	0.91	3.54	

Note that the results in table 2 were obtained without considering the geometric configuration of PPV; that is, we treat the effective single bond and the double bond as purely one dimensional. Therefore, the calculated $E_{gap}^0 = 2(t_v - t_{re})$ and the resultant E_{gap}^{HF} may be larger than the actual values. In fact, the phenylene unit and the vinylene unit are at an angle, which makes the effective PPV system a zigzag one (quasi-one dimensional). Thus,

the band energy gap ($2|z_{k_F}|$) along the x-axis direction should be multiplied by a factor. The factor is determined by the geometric parameters of the PPV unit. If the angle between the effective single bond and the double bond is assumed to be 120°, we then obtain smaller values of E'^0_{gap}, $\Delta E'_{gap}$, and E'^{HF}_{gap}. It is seen that the values of E'^{HF}_{gap} are within a reasonable range. See table 3.

4. Discussion

When some E-values are equal to t_b or any multiple of t_b, t_{re} and $\bar{\epsilon}$ from (11) and (12) will become divergent. When the site energies, a, are included, the divergence will be at $t_b + a$ and $2t_b + a$. These E-values cannot be inserted in (11) and (12) to determine t_{re} or $\bar{\epsilon}$. In renormalization language, the values of E equalling t_b or multiples of t_b make the renormalized electron system deviate from its fixed point, and so we avoid them.

In the renormalization calculations, there are two standard points which can be used which are inherent to PPV polymer. They are the intervals, δ ($=E_{LUMO} - E_{HOMO}$), between the LUMO and HOMO levels for a single PPV unit and an infinite PPV chain, respectively, for the given parameters. The interval, δ, decreases with increasing number of repeated PPV units and reaches a fixed value when the numbers are rather large. For PPV, the intervals, δ, for the ten-unit systems and those for the systems with more than ten units are almost the same. For instance, $\Delta\delta = \delta$(ten PPV units) $- \delta$(eleven PPV units) $= 0.009$ (for the data set (I)) or 0.011 (for the data set (II)). Thus, the ten-PPV-unit system is sufficient to represent an infinite PPV chain. On the other hand, the main absorption peaks of the experimental absorption spectra of PPV and MEH-PPV (a derivative of PPV) are measured at 2.5 eV [19] and 2.4 eV [3]. These result from the transition of an electron in the HOMO level to the LUMO level under the excitation of a photon by the applied electric field. Thus, choosing these energies, E_{LUMO} or E_{HOMO}, to determine the effective hopping of the renormalized single-band PPV system (corresponding to a very long PPV system) is natural and reasonable. Furthermore, the desired effective hopping value t_{re} of the renormalized system should satisfy the following requirements: (i) it should be smaller than t_s and t_b; and (ii) the effective hopping t_{re} must reproduce the main absorption peak at the photon energy 2.4 eV or 2.5 eV. Using the renormalized single-band model Hamiltonian, we did indeed reproduce the main absorption peak[4].

The results in table 1 show that the effective hopping values, t_{re}, obtained for ten PPV units from the data sets (I) and (II) are different (0.92 eV and 1.20 eV). But the differences between t_{re} and t_v for the sets (I) and (II) are almost the same. This yields almost identical non-interacting band energy gaps, E^0_{gap}, of 2.8 eV (table 2) or 2.63 eV (table 3). There is also a similar case for the effective site energies. The different resultant band energy gaps, E^{HF}_{gap}, result from the electron–electron interaction parameters and the chosen screening strength.

Using the data set (I) where $U = 5.05$ eV, we obtain the band energy gap of 3.65 eV (table 2) or 3.42 eV (table 3). As a comparison, the author of [18] gave $E^{HF}_{gap} = 3.64$ eV using the data set (I), while the authors of [8] found that $E^{HF}_{gap} = 3.2$ eV using the same data set (I). Using the data set (II), we found that when $U = 6$ eV and $1.2 \leqslant \kappa \leqslant 2.2$, the band energy gap is within the range between 3.32 eV and 3.79 eV (table 2). When κ is between 1.6 and 2.1, the band energy gap is between 3.79 eV and 3.60 eV (table 2) or 3.55 eV and 3.38 eV (table 3). When κ is 1.2 or 2.2, the band energy gap is 3.32 eV or 3.49 eV, respectively. Except for $\kappa = 1.2$ and 2.2, E^{HF}_{gap} decreases with κ increasing from 1.6 to 2.1

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[4] We have used this model to calculate the 1^1B_u exciton state and found that its main absorption peak lies near 2.4–2.5 eV.

(tables 2 and 3). When $U = 5.05$ or 6 eV the system is not in the strong-electron-correlation region. Thus, our HF effective Hamiltonian H_{e-e}^{HF} not containing the on-site Coulomb U may work reliably.

We notice that the electron–electron interaction Hamiltonian forms in [3, 7, 8, 18] are a little different from ours. These differences are mainly reflected in the U-term. Because in our U-term we have extracted 1/2 from the ground-state charge density, the HF decoupling leads to the vanishing of this term, while the authors of [3, 7, 8, 18] did not extract 1/2 from the ground-state charge density, so the HF decoupling did not lead to the vanishing of this U-term. Thus in their Hamiltonians the on-site Coulomb U was kept. That is why our results for the band energy gap are a little different from theirs, for the same data sets (I) and (II). Although the U-interaction was kept in their Hamiltonians, their calculations were still within the HF mean-field theory (the Coulomb-correlation model for the exciton [4]) and did not include the whole electron correlation effect. In the single-configuration interaction (SCI), the electron correlation effect does not emerge [17].

When $U = 8$ eV, the system seems to go into a strong-correlation region. The electron correlation comes into effect. But our effective Hamiltonian is based on HF approximation, without keeping the U-term (the reason for this is explained in the previous paragraph). So $U = 8$ eV seems not to be a suitable value to use. However, for the organic molecular systems, the electron–electron interaction is parametrized as an Ohno form [11] which connects the on-site Coulomb U and the long-range Coulomb interaction V_{ij}. For the organic molecular systems the difference between the on-site Coulomb U and the nearest-neighbour Coulomb interaction V may not be so big (usually $U \sim 2V$–$3V$ or so [13]), For instance, as we already know, the calculations [20] for an isolated benzene ring yield that $U = 16.93$ eV and the nearest-neighbour long-range Coulomb interaction V is 9.03 eV which is not small compared with the U-value. Note that there is no magnetic benzene molecule observed at such a U-value (at a pπ-orbital). Another characteristic of organic molecular systems is the screening effect which will reduce U and V [16]. These are reflections of the individuality of the organic molecular systems. Therefore, in the calculations [3, 7], the screening constant κ was considered. It is seen from our calculational results in tables 2 and 3 that when $U = 8$ eV we still obtain reasonable values of E_{gap}^{HF} which only show small differences when compared with those from calculations using a HF Hamiltonian keeping the U-term [3, 7, 8, 18]. Thus for our effective Hamiltonian not keeping the U-term in the HF approximation, the larger U-value (8 eV) is still appropriate for use in the calculations.

When $U = 8$ eV, we find that the band energy gap is between 3.32 eV and 3.77 eV for κ from 1.6 to 3, while it is between 3.63 eV and 3.77 eV for κ from 1.8 to 2.4. Except for $\kappa = 3$ and 1.6, E_{gap}^{HF} increases with κ increasing from 1.8 to 2.4 (table 3). The $\kappa = 2$ case gives $E_{gap}^{HF} = 3.76$ eV (table 2) or 3.52 eV (table 3) which is a little different from the result in [3, 7] which was $E_{gap}^{HF} = 3.6$ eV. This difference could be, as stated in the previous paragraph, due to the different U-terms and the differences between the approaches used here and in [3, 7].

We see from (15) that some V_b-values may make $(E - V_b \Delta_b)$ very small for the given E_{HOMO} or E_{LUMO}, in which case Δt_{ee}^{re} would become much larger. In such a case, this may produce a smaller E_{gap}^{HF}: it may even be close to zero or negative. Thus, V_b cannot be determined if it is close or equal to E_{HOMO}/Δ_b or E_{LUMO}/Δ_b. If it is, this would make Δt_{ee}^{re} very large (even exceeding Δt_{ee}^0) or divergent. This causes breakdown of the present renormalization approach. This means a limitation of the present renormalization scheme to certain interaction parameters. Because V_b is determined by the U-value and κ through (6), some values of U and κ are prohibited in the present approach. For instance, $\Delta E_{gap} = -0.53$ for $U = 6$ eV and $\kappa = 1$, so $E_{gap}^{HF} = 2.27$ eV, and $\Delta E_{gap} = -0.16$ for $U = 8$ eV and $\kappa = 1.4$,

so $E_{gap}^{HF} = 2.64$ eV, and $\Delta E_{gap} = -1.65$ for $U = 8$ eV and $\kappa = 1.2$, so $E_{gap}^{HF} = 1.16$ eV, which is not true for PPV polymer. Thus, the present renormalization scheme is not suitable for those parameters. Nevertheless, for the data sets (I) and (II), the present method still works well.

The complete band energy gap should read $\mathcal{E}_{gap} = E_{gap}^{HF} + E_{gap}^{c}$, where E_{gap}^{c} is a contribution from the interparticle corrections. According to the *ab initio* calculation for PPV in [5], the band energy gap was 3.3 eV, which included the exchange–correction effects. Because we are not aware of the actual parameters used in [5], we cannot judge the contribution E_{gap}^{c} from the differences between 3.3 eV and our results in table 2 and table 3.

In the ground state of the system, the band energy gap may be determined from the difference between the conduction band edge (LUMO) and the valence band top (HOMO). We may use $\mathcal{E}_{gap} = E_{gap} + E_{gap}^{c}$ in discussing the band energy gap. In the excited state of the system where an electron has been excited from the valence band to the conduction band, in addition to those features that it was necessary to consider in the former case, the polarization effects and the lattice relaxation accompanying the moving electron and the moving hole remaining in the valence band need to be considered. In this case we may have an extra term and have $\mathcal{E}_{gap} = E_{gap} + E_{gap}^{c} + E_{gap}^{pol}$, where E_{gap}^{pol} is the contribution from the polarization and the lattice relaxation. When we study the polaron–exciton problem, we should consider those factors in determining the band energy gap.

5. Conclusions

Our calculated results show that the values of the band energy gap obtained for ten PPV units are close to those in references [3, 5, 7, 8, 18]. The small differences between ours and those in [3, 5, 7, 8, 18] as regards E_{gap}^{HF} may result from the different U-terms used and the differences between the individual techniques. In the present model approach, the many-band nature of PPV has been converted into a single-band one (we only use the HOMO and LUMO states of the original PPV system) with an effective hopping parameter t_{re} (0.92 eV from the data set (I) or 1.20 eV from the data set (II)) and the effective site energy $\bar{\epsilon}$ (-0.56 eV from the data set (I) or -0.62 eV from the data set (II)). The electron–electron interaction effect is treated by HF approximation and renormalized as $\tilde{H}_{re}^{HF}$. The parameters before and after the renormalization have a clear physical connection.

The present model calculation provides a simple but practical approach to investigation of the electronic structure of PPV. The advantage is that we can consider the main optical non-linear excitations of a very long conjugated polymer with regularly embedded benzene rings using a SSH-type single-band Hamiltonian. Another advantage is that it could be used to consider the atomic substitution problem related to the electron structure of the conjugated polymers. For the existing data for PPV [3, 7, 8, 18], the present renormalization scheme works well. Further modification is needed to include the correlation effect arising from the residual interaction H_{res}.

Appendix

The bond charge densities Δ_s and Δ_0 are given by the following elliptic integrals:

$$\Delta_s = \frac{1}{\pi} \int_0^{\pi/2} \frac{2x_0 \cos^2(x) - z_0}{\sqrt{1 - (1 - z_0^2) \sin^2(x)}} \, \mathrm{d}x \tag{A.1}$$

$$\Delta_0 = \frac{1}{\pi} \int_0^{\pi/2} \frac{2x_0 \cos^2(x) + z_0}{\sqrt{1 - (1 - z_0^2) \sin^2(x)}} \, \mathrm{d}x \tag{A.2}$$

where

$$\begin{aligned}
x_0 &= \frac{t_s}{t_v + t_s} = \frac{t^0 - \delta t}{2t^0} \\
z_0 &= \frac{t_v - t_s}{t_v + t_s} = \frac{\delta t}{t^0}.
\end{aligned} \tag{A.3}$$

Here t^0 is the bond length of the vinylene unit without 'dimerization' and δt is the 'dimerization' on the vinylene unit. Assume that the bond lengths within the benzene rings are all equal; the bond charge density Δ_b may then be approximated as

$$\Delta_b \simeq \frac{1}{\pi} \int_0^{\pi/2} \cos(x) \, \mathrm{d}x = \frac{1}{\pi}. \tag{A.4}$$

The value of Δ_b should be larger than Δ_s, since the bond length on the benzene ring is shorter than that between the benzene ring and the vinylene unit [8, 21].

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