Polaron-pair binding due to interchain coupling in conjugated polymers

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By including both interchain hopping and electron-electron interaction within the context of the Takayama–Lin-Liu–Maki continuum model, and using the (nearly) degenerate perturbation method, we have studied characteristics of the interchain polaron-pair state in conjugated polymers, namely, its binding energy and the transition rate from an intrachain polaron exciton to an interchain polaron pair. It is found that the polaron-pair binding energy due to interchain Coulomb correlation is typically smaller than that due to interchain hopping. We introduce a small energy difference ε between intrachain and interchain excitations to distinguish their different lattice relaxations; we are then able to establish a two-level model, which can be solved exactly to obtain the transition probability. When ε is small enough, the solution is just a first-order degenerate perturbation result, i.e., it is proportional to a $t^{\perp}$ binding term; when ε is large, then it becomes dependent on a $(t^{\perp})^2$-binding term. In both cases, the interchain electron-correlation effect always appears in first order and is found not to influence the intrachain to interchain transition.

Conjugated polymers are not strictly one-dimensional arrays. Several experiments indicate that the formation of interchain polaron pairs is the origin for photoconductivity[1] and photoinduced-absorption[2,3] phenomena. Raman studies have shown that in many instances conjugated polymers consist of many short conjugated segments separated by defects;[4] in this case, the interchain concept has also to be taken in a more general sense in order to comprehend the hopping process between disconnected segments of the same chain. Bässler *et al.* have carried out site-selective luminescence experiments on polyparaphenylenevinylene (PPV), and found that the incoherent relaxations of the excitations, due to both interchain and intrachain inhomogeneous broadenings, are responsible for the photoluminescence, a feature that indicates the importance of considering the interchain interactions.[5]

Baeriswyl and Maki,[6] and Danielson and Ball[7] have investigated the interchain coupling effects via (i) adding an interchain hopping term $t^{\perp}$ in the continuum Takayama–Lin-Liu–Maki (TLM) model[8] and (ii) considering second-order perturbation (which neglects the contribution of the midgap-state transitions). These authors concluded that there occurs a strong interchain soliton confinement, proportional to $(t^{\perp})^2$; however, the confinement for the polaron is extremely small.[6] From the study of molecular crystal models, Emin has given an argument, later on confirmed by Gartstein and Zakhidov, that even a very small interchain hopping $(t^{\perp}/t^{\parallel} \sim 0.01)$ could destroy the formation of one-dimensional (1D) large polarons due to diffusions to other chains.[9] This point was further demonstrated by Vogl and Campbell on the basis of a local-density-functional band structure;[10] these authors found that in a 3D crystalline structure, there does not appear any intragap level when polarons or even bipolaronlike defects are present. Mizes and Conwell have reproduced this result within a simple two-chain model; they found, however, that conjugation defects can stabilize the appearance of polarons.[11] This

therefore rationalizes the experimental evidence for the existence of polarons. In light of recent photoexcitation experiments on PPV, Mizes and Conwell have also studied the electronic structure of Coulomb-bound interchain polaron pairs and tried to explain the results of photoinduced-absorption experiments on the basis of the formation of such pairs.[12]

In this paper, we include both interchain electron-phonon and electron-electron interactions in the TLM continuum model for two chains, in order to provide exact solutions for a two-level system, which models both the interchain polaron pair and intrachain polaron excitons. To avoid the complication related to the lattice relaxations on the two chains [which would imply to carry out a Franck-Condon (FC) analysis in the adiabatic approximation], we introduce a phenomenological parameter that allows us to distinguish the unperturbed intrachain polaron-exciton and interchain polaron-pair excitation energies.

The interchain coupling Hamiltonian consists of two parts:

$$H_1 = -\sum_{n,\sigma} t_n^{\perp}(c_{1n,\sigma}^{\dagger} c_{2n,\sigma} + \text{H.c.}) \,,$$

$$H_2 = \sum_{n,\sigma,\sigma'} V_n^{\perp}(c_{1n,\sigma}^{\dagger} c_{1n,\sigma} - \tfrac{1}{2})(c_{2n,\sigma'}^{\dagger} c_{2n,\sigma'} - \tfrac{1}{2}) \,,$$

$$t_n^{\perp} = t_1 + (-1)^n t_2 \,,$$

$$V_n^{\perp} = V_1 + (-1)^n V_2 \,,$$

where $c_{in,\sigma}$ is the destruction operator for an electron at site n in the ith chain with spin σ, and $t^{\perp}$ and $V^{\perp}$ are the interchain hopping parameter and e-e interaction term, respectively. Note that either in a $P2_1/a$ or in a $P2_1/n$ structure, adjacent carbon atoms on one chain couple to hydrogen atoms in different chains. We assume that the two chains are in-phase, which corresponds to a $P2_1/a$ structure, as supported by the results of the 3D local-

density-approximation (LDA) calculations[10] and by experiment.[13] Strickly speaking, a two-chain system cannot represent a full 3D structure; however, here, we take into account the major features of the 3D system by simply allowing the interchain parameters to be different for adjacent sites.

Making the transformation from a discrete to a continuum model by virtue of

$$u(x_j) = \frac{(-1)^j}{\sqrt{2}}(c_{2j} - ic_{2j+1}),$$

$$v(x_j) = \frac{i(-1)^j}{\sqrt{2}}(c_{2j} + ic_{2j+1}),$$

where u, v are the two components of the spinor wave function $\Psi^\dagger(x) = [u^*(x), v^*(x)]$, we obtain

$$T = -\sum_\sigma \int \frac{dx}{a} \Psi_\sigma^\dagger(1x)(t_1 - t_2\sigma_2)\Psi_\sigma(2x),$$

$$V = \sum_{\sigma,\sigma} \left\{ \tfrac{1}{2}V_1 \int \frac{dx}{a} [\Psi_\sigma^\dagger(1x)\Psi_\sigma(1x)\Psi_\sigma^\dagger(2x)\Psi_\sigma(2x) + \Psi_\sigma^\dagger(1x)\sigma_2\Psi_\sigma(1x)\Psi_\sigma^\dagger(2x)\sigma_2\Psi_\sigma(2x)] \right.$$

$$\left. + \frac{V_2}{2} \int \frac{dx}{a} [\Psi_\sigma^\dagger(1x)\Psi_\sigma(1x)\Psi_\sigma^\dagger(2x)\sigma_2\Psi_\sigma(2x) - \Psi_\sigma^\dagger(1x)\sigma_2\Psi_\sigma(1x)\Psi_\sigma^\dagger(2x)\Psi_\sigma(2x)] \right\},$$

where σ_2 is the second Pauli matrix and a is the lattice constant.

We construct the interchain (positive and negative) polaron-pair state vector as

$$|1\rangle = \frac{1}{\sqrt{2}}(c_{s1}^\dagger c_{a2} - c_{s2}^\dagger c_{a1})|G_1 G_2\rangle$$

and the intrachain polaron-exciton state as

$$|2\rangle = \frac{1}{\sqrt{2}}(c_{s1}^\dagger c_{a1} - c_{s2}^\dagger c_{a2})|G_1 G_2\rangle,$$

where $C_{si}^\dagger$ (C_{ai}) is the creation (destruction) operator for an electron in the upper (lower) intragap polaron level on the ith chain while G_i is the (half-filled) ground state of the ith chain. The states $|1\rangle$ and $|2\rangle$ are unperturbed with respect to interchain interactions. Note that we have not taken the plus sign in the linear combinations describing the two states; it can indeed be verified that the t^1 term only couples the above two antibonding forms. The mean-field contribution of V^1 simply renormalizes t^1, while the fluctuation term is found to have only diagonal elements with the above two states. We give all the matrix elements below:

$$T_{11} = T_{22} = V_{12} = 0,$$

$$\Gamma_{12} = \Gamma_{22} = \int \frac{dx}{a} \{\Psi_s^\dagger(1x)(t_1 - t_2\sigma_2)\Psi_s(2x) + \Psi_a^\dagger(1x)(t_1 - t_2\sigma)\Psi_a(2x)\},$$

$$V_{11} = -\frac{V_1}{4} \int \frac{dx}{a} [\Psi_a^\dagger(1x)\Psi_s(1x)\Psi_s^\dagger(2x)\Psi_a(2x) + \Psi_s^\dagger(1x)\Psi_a(1x)\Psi_a^\dagger(2x)\Psi_s(2x)$$

$$+ \Psi_a^\dagger(1x)\sigma_2\Psi_s(1x)\Psi_s^\dagger(2x)\sigma_2\Psi_a(2x) + \Psi_s^\dagger(1x)\sigma_2\Psi_a(2x)\Psi_a^\dagger(2x)\sigma_2\Psi_s(2x)]$$

$$- \frac{V_2}{4} \int \frac{dx}{a} [\Psi_a^\dagger(1x)\Psi_s(1x)\Psi_s^\dagger(2x)\sigma_2\Psi_a(2x) + \Psi_a^\dagger(1x)\Psi_a(2x)\Psi_4^\dagger(2x)\sigma_2\Psi_s(2x)$$

$$+ \Psi_a^\dagger(1x)\sigma_2\Psi_s(1x)\Psi_s^\dagger(2x)\Psi_a(2x) + \Psi_s^\dagger(1x)\sigma_2\Psi_a(2x)\Psi_a^\dagger(2x)\Psi_s(2x)],$$

$$V_{22} = -\frac{V_1}{4} \int \frac{dx}{a} [\Psi_a^\dagger(1x)\Psi_a(2x)\Psi_s^\dagger(2x)\Psi_s(2x) + \Psi_s^\dagger(1x)\Psi_s(1x)\Psi_a^\dagger(2x)\Psi_a(2x) + \Psi_a^\dagger(1x)\sigma_2\Psi_a(1x)\Psi_s^\dagger(2x)\sigma_2\Psi_2(2x)$$

$$+ \Psi_s^\dagger(1x)\sigma_2\Psi_s(1x)\Psi_a^\dagger(2x)\sigma_2\Psi_a(2x)]$$

$$- \frac{V_2}{4} \int \frac{dx}{a} [\Psi_a^\dagger(1x)\Psi_a(1x)\Psi_s^\dagger(2x)\sigma_2\Psi_s(2x) + \Psi_s^\dagger(1x)\Psi_s(1x)\Psi_a^\dagger(2x)\sigma_2\Psi_a(2x) + \Psi_a^\dagger(1x)\sigma_2\Psi_a(1x)\Psi_s^\dagger(2x)\Psi_s(2x)$$

$$+ \Psi_s^\dagger(1x)\sigma_2\Psi_s(1x)\Psi_a^\dagger(2x)\Psi_a(2x)].$$

$\Psi_s(ix)$ [$\Psi_a(ix)$] is the spinor wave function for the upper (lower) polaron midgap level in the ith chain. The above V terms are evaluated in the same way as Wu and Kivelson[14] have done in the "g-ology" approach for intrachain e-e interactions. The midgap polaron-state (unperturbed) wave functions, as obtained by Campbell and Bishop,[15] are given below:

$$u_s(x) = \frac{\sqrt{\kappa}}{4}[(1-i)s_+ + (1+i)s_-] ,$$

$$v_s(x) = \frac{\sqrt{\kappa}}{4}[(1+i)s_+ + (1-i)s_-] ,$$

$$\Psi_a(x) = \sigma_2\Psi_s(x) ,$$

$$s_{(\pm)} = \mathrm{sech}[\kappa(x \pm x_\sigma)] ,$$

$$2x_0 = Wa/(\Delta_0\sqrt{2})\ln(\sqrt{2}+1) \sim 1.24\xi_0; \quad \kappa = 1/(\sqrt{2}\xi_0) .$$

After some algebra (see the Appendix), we have

$$T \equiv T_{12} = T_{21} = \kappa t_1 \int dx\, s_+(1x)s_+(2x)$$

$$= \kappa t_1 \int dx\, \mathrm{sech}(\kappa x)\mathrm{sech}[\kappa(x-1)]$$

$$= 2t_1 \frac{\kappa l}{\sinh(\kappa l)} ,$$

$$V \equiv V_{11} = V_{22}$$

$$= -\frac{V_1}{4}\kappa^2 a \int dx\,\{\mathrm{sech}(\kappa x)\mathrm{sech}[\kappa(x-l)]\}^2$$

$$= -\kappa a\frac{V_1}{3}; \quad \in l = 0$$

$$= -\kappa a V_1 \frac{\kappa l\coth(\kappa l)-1}{[\sinh(\kappa l)]^2} ; \quad \in l \ne 0 .$$

l is the distance between two polaron centers on adjacent chains. Note that for a polaron state, both t_2 and V_2 contributions vanish for in-phase alignment. It is noted that as $l \to \infty$, both T and V go to zero, with V more quickly (exponentially) than T.

With all the matrix elements given above, we obtain a two-level model: $H_{11} = \varepsilon_p + V$, $H_{22} = \varepsilon_p - \varepsilon + V$, $H_{12} = H_{21} = T$, where ε_p is the polaron-pair electronic energy; ε is a parameter that characterizes the difference in the unperturbed intrachain and interchain polaron-pair energy due to their different lattice relaxations. (Note that the lattice relaxation takes a much longer time than the electronic excitation and we have not taken full account of both intrachain and interchain relaxations; we have simply introduced the parameter ε to distinguish them.) The eigenvalues are obtained as

$$\lambda = \varepsilon_p + V - (\varepsilon \pm \sqrt{\varepsilon^2 + 4T^2})/2 .$$

For $\varepsilon \to 0$, $\lambda = \varepsilon + V \pm T$, i.e., this corresponds to a degenerate first-order perturbation result. For $\varepsilon \gg T$, the solution becomes second order in T. In the latter case, one needs also to consider all the continuum band states, as calculated previously.[6,7] We define the binding energy of the interchain polaron pair as the difference between the total energy of the $l = 0$ case and that of the $l \to \infty$ case:

$$E_b = -V(0) + \sqrt{T^2(0) + \varepsilon^2/4} - \varepsilon/2 .$$

The interchain electron-electron correlation gives a contribution on the order of $V_1/30$ and is inversely proportional to the coherence length, as was first demonstrated in the perturbation calculations of Wu and Kivelson.[14] The state-of-the-art LDA 3D band-structure calculations[10] provide an estimate for $t^\perp$ around 0.12 eV; from

the work of Mizes and Conwell,[12] $V^\perp$ is on the order of 1 eV. Taking these values, the interchain polaron-pair binding energy due to $V^\perp$ is only about 0.03 eV, which is much smaller than the contribution due to $t^\perp$. Note that we have not calculated the mean-field contribution of $V^\perp$ to $t^\perp$. For small ε, the interchain polaron-pair binding energy is about half that of the intrachain pair.[16,5]

Suppose that at time $t = 0$, the system corresponds to a photoexcited intrachain polaron exciton, $|2\rangle$. Due to interchain coupling, this excitation will evolve to an interchain polaron-pair state $|1\rangle$, which is described by the time-dependent Schrödinger equation. The time-dependent state vector is

$$\Psi(t) = c_1(t)e^{-iH_{11}t/h}|1\rangle + c_2(t)e^{-iH_{22}t/h}|2\rangle .$$

Combining the initial condition $c_1(0) = 0$, $c_2(0) = 1$, and the normalization condition $|c_1(t)|^2 + |c_2(t)|^2 = 1$, we get the time-dependent transition probability

$$|c_1(t)|^2 = \frac{4T^2}{\varepsilon^2 + 4T^2}\sin^2(\omega t); \quad \hbar\omega = \sqrt{T^2 + \varepsilon^2/4} .$$

Due to the fact that $V_{11} = V_{22}$, the transition rate does not depend on $V^\perp$. The averaged (over one period) transition probability is $T^2/(T^2 + \varepsilon^2/4)$; this means that the difference ε in lattice-relaxation energy between the intrachain and interchain polarons makes the interchain transition process more difficult.

The interchain transition is thus dependent on the difference in lattice conformations between intrachain and interchain excitations. In the case of polyacetylene, Jeyadev and Schrieffer have studied the interchain polaron hopping bandwidth[17] and obtained the FC factor to be about 0.1; this means that the interchain polaron mobility is reduced by a factor of 10 due to lattice relaxation, in other words, ε is qualitatively large. We have carried out a similar calculation on PPV and found that the FC factors are 0.62 for polaron hopping and 0.13 for bipolaron hopping.[18] The former value is much larger than that of polyacetylene (PA), a fact due to the presence of phenyl rings, which prevents the lattice to relax as much. From this, we conclude that the interchain polaron mobility in PPV is higher than in PA, i.e., the ε value is smaller for PPV than PA.

To conclude, we have calculated the interchain polaron-pair binding energy and transition rate by considering both interchain hopping and electron-electron interactions. The latter contribution to the binding energy of the polaron pair is found to be much less significant than that due to the former term. The interchain polaron transition is only determined by the hopping term (which could take account of a mean-field renormalization due to electron-electron interactions). The lattice-relaxation effect, which is less important in PPV than in PA, hinders the interchain transition. A full consideration of these effects deserves further studies.

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APPENDIX

Let $y = e^{2x} + 1$ and $a = e^{2l} - 1$, then the integral for the V term can be written as

$$I = \int_{-\infty}^{+\infty} dx \, \text{sech}^2(x)\text{sech}^2(x - l)$$

$$= \int_{1}^{\infty} dy \, 8(1+a) \left[\frac{1}{y(y+a)^2} - \frac{1}{y^2(y+a)^2} \right] .$$

If $a = 0$, ($l = 0$), then $I = \frac{4}{3}$. If $a > 0$, then we can make the following factorization:

$$\frac{1}{y(y+a)^2} = \frac{1}{a^2 y} - \frac{1}{a^2(y+a)} - \frac{1}{a(y+a)^2} ,$$

$$\frac{1}{y^2(y+a)^2} = -\frac{1}{a^3 y} + \frac{1}{a^2 y^2} + \frac{2}{a^3(y+1)} + \frac{1}{a^2(y+a)^2} .$$

It is then possible to perform the integrations for each term above. Note that the factorization does not permit an extrapolation to $a = 0$.

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