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Optical spectra in conducting polymers: Breaking of symmetries

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Within a continuum electron-phonon-coupled model, theoretical calculations are presented for the optical absorption due to polarons in conducting polymers. We show that the symmetries of the Su-Schrieffer-Heeger model for these systems have to be broken, and a realistic physical model is introduced for this purpose. As a result of the additional electron-phonon coupling, the experimental signatures such as absorption intensities can now be explained quite satisfactorily. Several other mechanisms including electron-electron interactions are discussed as well.

I. INTRODUCTION

Since the early theoretical work on optical absorption from polarons in conducting polymers[1] there has been quite a number of theoretical[2,3] and experimental[4–7] investigations on this topic. As a general result it has turned out that both the absorption pattern and also its change with doping was found to be in accordance with the early predictions which were done in the continuum limit of the Su-Schrieffer-Heeger (SSH)-like model. There is, however, one shortcoming of the original SSH-like model, namely, the fact that the intensity ratio of different intragap absorption lines for the polaron was predicted to be quite small, but found experimentally to be much greater. It has become quite clear in recent investigations[3,8] that the main cause of this difference is the exceptional high symmetry of the original SSH model. There have been some attempts to improve these calculations by considering different kinds of extensions of the SSH model: these include diatomic polymers,[9,10] the influence of next-nearest-neighbor interactions,[11] and the possible influence of electronic interactions, as Hubbard-type Coulombic interactions[2,12–16] and different density-hopping couplings.[17]

In the next section we will shortly describe the original model and discuss its symmetry. We then propose an additional symmetry breaking interaction between π and σ electrons. In Sec. III the consequence for optical-absorption experiments is studied and investigated in detail for polarons. In the following section related problems are discussed under the consideration of electron-electron interactions. By this investigation we show that the general underlying principle of symmetry breaking can explain the intensity ratio in absorption found experimentally.

II. MODEL HAMILTONIANS AND SYMMETRIES

The simplest microscopic model of a (degenerate) π-electron system is the discrete Su-Schrieffer-Heeger (SSH) Hamiltonian[18]

$$H_{\rm SSH}=-\sum_{n,s}[t_0+\alpha(u_{n+1}-u_n)](c^{\dagger}_{n,s}c_{n+1,s}+\text{H.c.})+\frac{K}{2}\sum_{n}(u_{n+1}-u_n)^2\;. \qquad (2.1)$$

Here $c^{\dagger}_{n,s}$ creates an (π-)electron of spin s at site n, and u_n is the displacement of the nth site from its undistorted position. The hopping matrix element t_0, the electron-phonon coupling constant α, and the spring constant K are material parameters and have to be determined from experiment. For *trans*-CH_x we have $t_0\simeq 2.5$ eV, $\alpha=4.1$ eV/Å, and $K=21$ eV/Å^2. Appropriate to the system discussed in the Introduction we consider one conduction electron per site, i.e., a half-filled band, in which case the Hamiltonian (2.1) is unstable to a (Peierls) dimerization. We therefore introduce the continuum limit[19] of (2.1), i.e., integrate out the k_F oscillations, and arrive at

$$H_{\rm TLM}=\sum_{s}\int\frac{dy}{a}\left\{\frac{1}{8\pi t_0\lambda}\Delta^2(y)+\psi^{\dagger}_{s}(y)[-iv_F\partial_y\sigma_3+\Delta(y)\sigma_1]\psi(y)\right\}. \qquad (2.2)$$

Here $\lambda=2\alpha^2/\pi t_0K$ and $v_F=2at_0$, where a is the undistorted lattice constant. The (staggered) lattice displacement is described by $\Delta(y)$ and the electron field by the two-component spinor $\psi^{\dagger}_{s}=(u^{*}_{s},v^{*}_{s})$. The electron spectrum is linearized around the Fermi level. This continuum limit is valid if the excitations studied are extended over many lattice spacings.

The SSH [or the Takayama–Lin-Lin–Maki (TLM), respectively,] model in this form has to be extended in order to account for the nondegenerate ground state of most systems discussed in the Introduction. This extension has been introduced by Brazovskii and Kirova[20] and can easily be incorporated into the solutions of the TLM model (cf., e.g., Ref. 1). We therefore do not discuss this extension here.

Variation of $H_{\rm TLM}$ (2.2) leads to the single-particle electron wave-function equations:

$$\varepsilon_n u_{ns} = -i v_F \partial_y u_{ns} + \Delta(y) v_{ns} \,,$$
$$\varepsilon_n v_{ns} = i v_F \partial_y v_{ns} + \Delta(y) u_{ns} \tag{2.3}$$

and the self-consistency equation for the electronic gap

$$\Delta(y) = -\pi v_F \lambda \sum_{\substack{\text{occ}\\ \text{level}}} v_{ns}^{*} u_{ns} + u_{ns}^{*} v_{ns} \ . \tag{2.4}$$

The continuum equations (2.3) have essentially the form of single-particle Dirac equations in the presence of a potential $\Delta(y)$. The partial soliton ("reflectionless potential") properties of these equations have been studied previously.[21] In addition they possess two additional symmetries which we want to focus on.

First there is charge conjugation symmetry (CCS).[22] In the discrete version of the model (2.1) this is reflected by $c_n \rightarrow (-1)^n c_n^{\dagger}$, while for the continuum model (2.2) this means $\psi(x) \rightarrow -\sigma_2 K \psi(x)$, where K is the "complex-conjugate-operator." Both transformations leave the Hamiltonians (2.1) and (2.2), respectively, invariant. They correspond to a pairing of electron and hole states with respect to the Fermi energy. This symmetry has been appreciated before[1] and the need for its breaking has been discussed.

Second there is supersymmetry (SUSY).[23] This additional symmetry has been emphasized in our earlier publications,[8] and here we just want to recall the main features. SUSY can be understood formally by considering the model Hamiltonian (2.2) as the "square root" of a supersymmetric Hamiltonian H: $H = H_{\text{TLM}}^2$ [with the electronic part of (2.2) only]. The smallest ($N = 1$) representation of a supersymmetric algebra now requires that there are operators $Q, Q^{\dagger}$ such that $H = \frac{1}{2}\{Q, Q^{\dagger}\}$ with

$$[H, Q] = 0, \quad \{Q^{\dagger}, Q^{\dagger}\} = 0 = \{Q, Q\} \ . \tag{2.5}$$

In our case we have $Q^{\dagger} = [+\partial_y + \Delta(y)]\left(\begin{smallmatrix} 0 & 0 \\ 1 & 0 \end{smallmatrix}\right)$, and the (anti)commutators (2.5) are fulfilled. This symmetry can also be expressed in terms of a double commutator:

$$[H, \sigma_3] = \{H_{\text{TLM}}, [H_{\text{TLM}}, \sigma_3]\} = 0 \ . \tag{2.6}$$

Physically this means that a state at energy $+E \neq 0$ is paired with a state at $-E$. The model for a diatomic ($A = B$) polymer breaks CCS but (2.6) is still fullfilled. In consequence the polaron levels of ths model are still located symmetrically around midgap.

Viewed from SUSY the CCS corresponds to the Fermi number operator in this formalism[23] Both symmetries are therefore connected in some way. In consequence CCS can be broken while leaving SUSY unbroken (up to a zero energy shift), whereas breaking SUSY automatically destroys CCS. But before we discuss the need for introducing explicit symmetry breaking terms, we want to remark that, e.g., the SUSY can be broken *spontaneously*: although H_{TLM} conserves SUSY the ground state of this model (the uniformly dimerized state) as well as the polaron solution are not invariant under this symmetry. The kink solution on the other hand is supersymmetric as it is an $E = 0$ solution of H. This corresponds very nicely to the situation in various models in statistical physics and elementary particle theory.

As has been shown[1] this simple model for conjugated π systems has some significant predictions for optical-absorption experiments, which can be (and are) tested: The polaron solution (for details see Ref. 21) is characterized by the existence of two localized levels within the electronic gap which are located symmetrically around midgap. This feature is directly related to SUSY. In addition the total intensity from the transition from the (filled) valence band to the lower polaron level (low-energy peak, LEP) is much higher[1] than the one for the high-energy peak (HEP) (the transition valence-band to upper polaron level). This second feature on the other hand is closely related to CCS.[1] These predictions have been measured in various systems, such as polythiophene,[4] polyparaphenylene,[5] and others,[6] and one finds: The intensity ratio is of the order 1.5 (in contrast to the predicted 12) and there are hints that the levels are not located symmetrically around midgap.[7] In addition photoluminescence experiments suggest a breaking of CCS.[24]

There have been some attempts[8,9,11] to achieve such a breaking and various breaking mechanisms have been proposed. A simple mechanism which will be the main topic of this paper has been put forward[8] recently by the present authors. We want to consider an additional interaction of the π electrons with the σ electrons (i.e., the lattice) via a term describing the contribution to the elastic energy of the lattice depending on the π-electron density on each site:

$$H_{\beta} = \beta \alpha^2 \sum_{n,s} c_{ns}^{\dagger} c_{ns} (u_{n+1} + u_{n-1} - 2u_n)^2 \ . \tag{2.7}$$

This electron-lattice coupling (β) has the advantage of being a single-particle, short-range CCS and SUSY breaking contribution to the simple model (2.1). In the continuum limit H_{β} reads

$$H_{\beta} = \beta \sum_{s} \int \frac{dy}{a} \Delta^2(y) \psi_s^{\dagger}(y) \psi_s(y) \ . \tag{2.8}$$

In consequence we have an additional term in the equation of motion (2.3) as well as an alteration of the self-consistency equation (2.4) (cf. Ref. 8). In the following section we want to discuss in detail the features of this model, especially the polaron solution, and compare with experimental results.

There is also the possibility of introducing alternating onsite energies into the SSH model, i.e., to construct a model for a $(A = B)_x$ polymer.[9] This model breaks CCS, but still maintains SUSY which accounts for analytic solutions of this model. Since direct physical realization has only been found recently[10] such a model cannot account for the symmetry breaking in other systems. Secondly a next-nearest-neighbor hopping[11] also breaks CCS (and SUSY as well). Note that a constant next-nearest-neighbor hopping produces an energy shift $\psi^{\dagger}\psi$ in the continuum limit in the same order as TLM (this has been considered by Kivelson and Wu[25]) whereas Danielson and Ball[11] include a coupling of this hopping to the phonons and thus obtain a true symmetry breaking effect. Thirdly the coupling of the electronic density to local phonons (intramolecular modes) (Ref. 26) has been formulated specifically for CH_x and the results cannot be translated to other polymers of this class. Formally the symmetry breaking effect corresponds to those discussed in Sec. IV. A fourth alternative has been put forward recently by Kakano.[27] Here the onsite electronic energies are affected by the lattice distortions of the adjacent sites, and therefore this interaction has a structure similar to (2.7) but with the lattice entering only linearly. In consequence this introduces a second-order parameter in the continuum limit (cf. Ref. 27). The conclusions drawn from this model for a kink excitation are then similar to the ones discussed in the next section, the polaron excitation, however, has not been discussed by Kakano. Additional electron-electron interactions we want to comment on in Sec. IV.

III. OPTICAL ABSORPTION

The ground state (uniform dimerization) of the SFB model [$H_{\mathrm{TLM}}+H_\beta$, Eqs. (2.2) and (2.7)] can be solved analytically and has been discussed[8] already. We therefore focus directly on the nonlinear excitations of this model. As analytic solutions for these excitations are not available we proceed via *consistent*[8] perturbation expansions. Towards this end we expand *all* quantities, energies ε_n, wave functions ψ, and gap parameters Δ starting from the TLM values (which correspond to the case $\beta \equiv 0$):

$$\begin{aligned} \Delta(y) &= \Delta^T(y)+\beta\Delta^\beta(y) , \\ f(y) &= f^T(y)+\beta f^\beta(y) , \\ \varepsilon_n &= \varepsilon_n^T+\beta\varepsilon_n^\beta . \end{aligned} \tag{3.1}$$

(For computational convenience we use transformed wave functions $f_\pm = u \pm iv$.) The equation of motion (2.3) then yields an inhomogeneous differential equation for the perturbational functions f^β, the self-consistency equation is solved (in this order) with one parameter r only which is a measure of the width of kink or polaron, respectively. Then the total energy (per site) is computed and minimized with respect to r. Only the last step is performed numerically, the other can be done analytically. For details we refer to the Appendix. Here we want to remark only that the perturbational functions f^β break the CCS *maximally*, i.e., $f^\beta_{\varepsilon>0} = -\sigma_3 f^\beta_{\varepsilon<0}$.

For a single kink excitation we find the localized level at $\varepsilon_K^\beta = \frac{1}{3}\Delta_0^{T2}$ moved out of its former position at midgap $\varepsilon_K^T = 0$ (Δ_0^T being the size of the uniform dimerization). The gap functions $f_\pm^\beta$ have already been given elsewhere (cf. Ref. 8), for completeness we give the correction Δ^β to the electronic gaps (n is the occupation number for the localized level):

$$\Delta^\beta = 4\pi\lambda\Delta_0^2\left(\tfrac{1}{4}-\tfrac{1}{3}n\right)\frac{\tanh(y/\xi_0)}{\cosh^2(y/\xi_0)} . \tag{3.2}$$

The main results we want to emphasize are those for the polaron solution. We find that due to broken SUSY both localized levels are moved out of their symmetrical position by the same amount of $\varepsilon_P^\beta = \frac{2}{3}(1-\omega_0^2)[2\omega_0 -(\omega_0^2-1)\frac{4}{5}]/\omega_0^2$ with $\pm\omega_0$ being the unperturbed polaron levels of the TLM model [see Fig. 1(b)]. The corresponding localized functions and the correction to the gap $\Delta(y)$ are quite complicated and lengthy so that they will not be reported here. In Fig. 2 the full gap function $\Delta(y)$ for the polaron is shown together with the correction $\Delta^\beta(y)$. Note that the contribution from Δ^β is 30% at the center of the polaron distortion. Again we refer the reader to the Appendix for more details.

In calculating the optical-absorption coefficient $\alpha(\omega)$ we proceed in analogy to Ref. 1. The expression for $\alpha(\omega)$ reads

$$\alpha(\omega) = A/\omega \sum_{\{1,2\}} n_{1,2}\,|M_{1,2}|^2\delta(\omega-\varepsilon_1-\varepsilon_2) \tag{3.3}$$

with $M_{1,2} = \langle 2|\sigma_1|1\rangle$ for a transition from state $|1\rangle$ to state $|2\rangle$. Using the expansions for the wave functions and energies (3.1) we arrive at (cf. the Appendix)

$$\alpha(\omega) = \alpha_{\mathrm{TLM}}(\omega)+\beta\delta\alpha(\omega) \tag{3.4a}$$

with $\alpha_{\mathrm{TLM}}(\omega)$ the unperturbed TLM result (Ref. 1) and

$$\begin{aligned} \delta\alpha = A\frac{\Delta_0^T}{\omega}\xi_0\int dk\,|\,&\mathrm{Re}(M_{1,2}^T)\mathrm{Re}(M_{1,2}^\beta) \\ &+\mathrm{Im}(M_{1,2}^T)\mathrm{Im}(M_{1,2}^\beta)\,|\,\delta(\omega-\varepsilon_1-\varepsilon_2) , \end{aligned} \tag{3.4b}$$

which is valid up to first order in β.

The results for the kink have been reported elsewhere.[8] Here we only reiterate that due to the shift of the localized state out of the middle of the gap there will be a splitting of the midgap absorption peak of a single kink. From the observed broad midgap absorption we can therefore deduce an upper bound on the parameter β; it turns out that this bond is $\beta\Delta_0^T \leq 0.2$, which is small enough so that a perturbational treatment of H_β is valid.

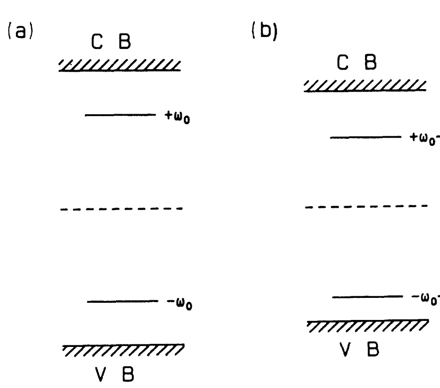

FIG. 1. (a) The electronic structure of polarons in the SSH model: valence band (VB), conduction band (CB), and two localized states at $\pm\omega_0$ symmetric around the Fermi level (dotted line). (b) The electronic structure of polarons in the generalized model with $\beta\neq0$: valence band (VB), conduction band (CB), and two localized levels which are asymmetric around the Fermi level (dotted line).

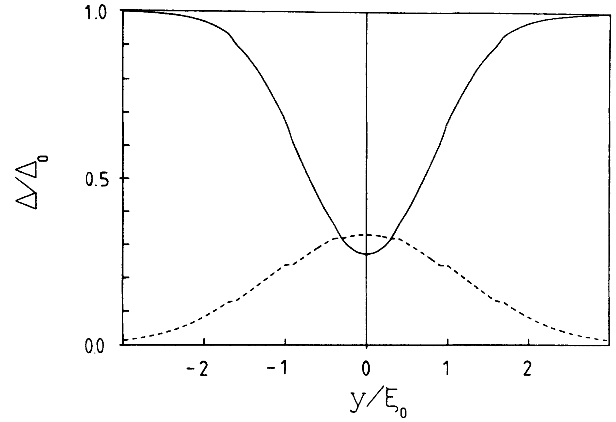

FIG. 2. Full gap function $\Delta(y)$ (solid line) together with the correction $\Delta^{\beta}(y)$ (dashed line) for $\beta\Delta_0^T=0.1$.

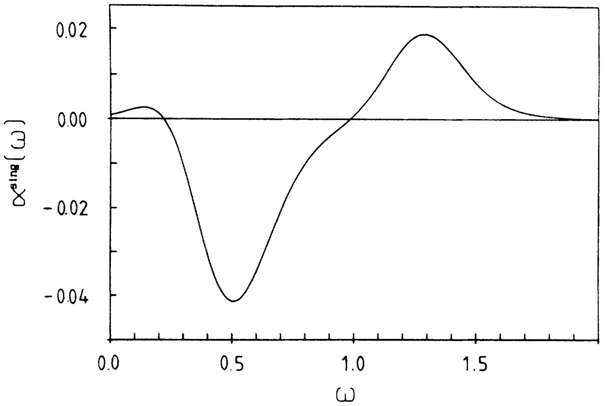

FIG. 4. The singular part $\alpha^{\rm sing}$ of the optical-absorption coefficient shows the transfer of intensity from the low-energy peak to the high-energy peak. Both peaks have been convoluted with a Gaussian to simulate experimental broadening (cf. Ref. 1).

In the remainder of this section we want to focus on the results for various (bi) polarons. First we find that due to the presence of the H_β interaction bipolarons will be stabilized in contrast to the pure TLM case: we find a *finite* width of the bipolaron (in the TLM case this is infinite, cf. Fig. 3). Second we can show that the additional interaction transfers intensity from the low-energy peak to the high-energy peak. Studying only the most divergent terms of $\Delta\alpha(\omega)$ [Eq. 3.4(b)] at the thresholds, respectively, we get the results depicted in Fig 4. This transfer of oscillator strength is responsible for the better agreement of our model with the experimental results compared to the pure TLM model. To demonstrate this fact further we have calculated the intensity ratio of the high-energy peak to the low-energy peak. This is shown in Fig. 5 for various values of the symmetry breaking parameter β as function of the position of the localized levels ω_0. We find a drastic (compared to the TLM prediction) reduction of this ratio as function of β for reasonable values of ω_0 ($\omega_0=0.36\Delta_0$ for polythiophene[4]).

We illustrate the resulting absorption spectra $\alpha(\omega)$ for different polaronic excitations. We have convoluted the theoretical results for $\alpha(\omega)$ with a Gaussian function to represent reasonable (experimental) broadening. Figure 6 shows the absorption spectra for electron and hole bipolaron ($n_+=n_-=0$ or 2), and a single (electron) polaron ($n_+=1, n_-=2$). [Here $n_\pm$ denotes the occupation of the higher (lower) localized level, respectively.] Note that due to the broadening (which is the same here as in Ref. 1) the splitting of the peaks arising from the asymmetric position of the levels is not visible.

As mentioned before there is some experimental evidence[7] that the bipolaronic levels are not located symmetrically around midgap in accordance with our calculations. Vardeny *et al.*[7] have reported photoinduced measurements in polythiophene (PT) where they observed

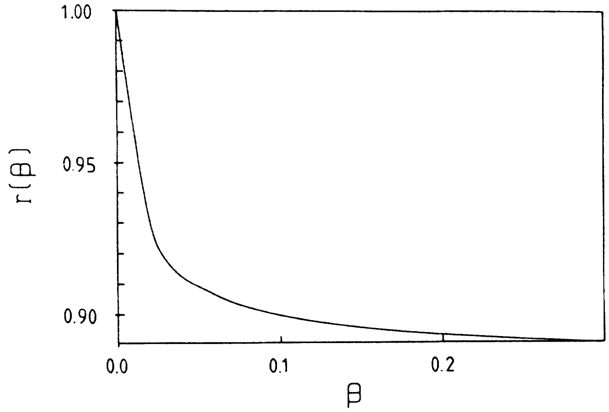

FIG. 3. $r(\beta)$ for the bipolaron. The TLM value $r=1$ corresponds to an infinite width of this excitation. For any $r<1$ this width is finite.

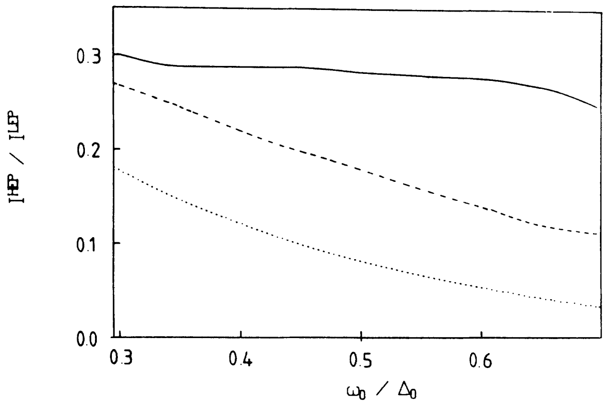

FIG. 5. Ratio of intensity high-energy peak to low-energy peak as function of position of the localized levels within the gap for various values of the symmetry breaking parameter β: $\beta=0.0$ (TLM) (dotted line), $\beta=0.2/\Delta_0$ (dashed line), and $\beta=0.3/\Delta_0$ (solid line).

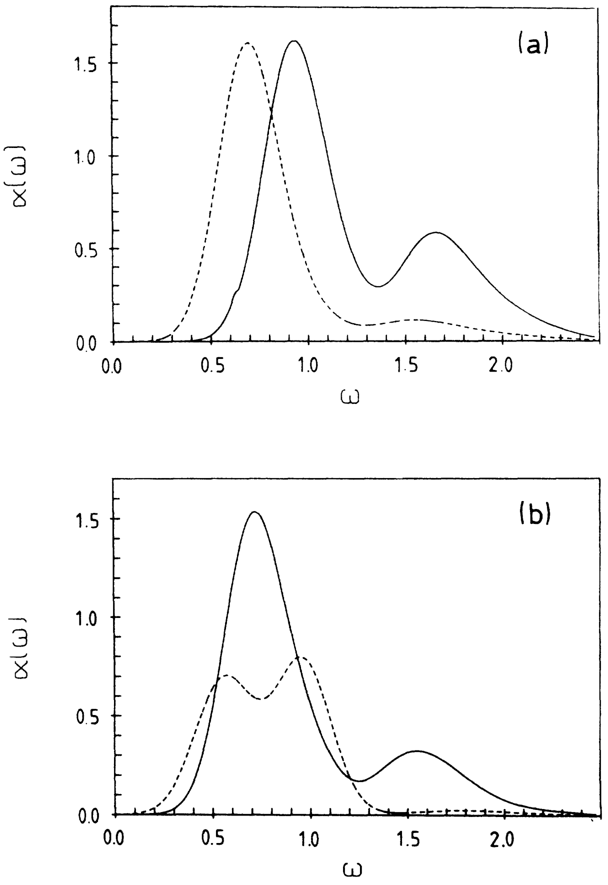

FIG. 6. Optical-absorption spectrum (in arbitrary units) below the gap $\omega=2\Delta_0$ with a Gaussian broadening of $\sigma=0.14\Delta_0$, dashed line; $\beta=0.0$ (TLM), solid line, $\beta=0{:}3/\Delta_0$: (a) single bipolaron with $\omega_0=0.36\Delta_0$; (b) single (electron) polaron with $\omega_0=0.49\Delta_0$. Note that two of the three polaron peaks have merged into one with this broadening.

two asymmetric peaks at 0.45 and 1.25 eV, respectively, with corresponding electronic gap of $2\Delta=2.2$ eV. These levels are assigned to photogenerated spinless bipolarons, the strong deviation from a symmetric position around midgap is accompanied by an intensity ratio I (HEP): I(LEP)$\,=1{:}1.5$ in contrast to the TLM result which gives a ratio of 1:12. A detailed numerical investigation[28] of the excitation spectrum in doped PT within the Hückel theory has also shown that the polaronic and bipolaronic levels are located asymmetrically with respect to the center of the gap.

IV. ELECTRON-ELECTRON INTERACTIONS

So far only electron-lattice interactions have been considered in order to understand the electronic structure of conducting polymers. It has been suggested though that electron-electron interactions do play an important role in these systems.[29] These lowest-order Coulomb interactions have been modeled mostly in terms of Hubbard-type correlation terms:

$$H_c=\frac{U}{2}\sum_{n,s}c^{\dagger}_{ns}c_{ns}c^{\dagger}_{n\,-s}c_{n\,-s}+\frac{V}{2}\sum_{n,s,s'}c^{\dagger}_{ns}c_{ns}c^{\dagger}_{n\,+1s'}c_{n\,+1s'}\,, \tag{4.1}$$

where only onsite (U) and nearest-neighbor (V) correlations are taken into account. Various methods have been employed to study the influence of these Coulomb terms on the ground-state (uniform dimerization) properties of the SSH (or TLM) model, these include quantum Monte Carlo methods,[12] Gutzweiler *Ansatz*,[13] and Hartree-Fock approximation (HF).[14–16] Only a few attempts have been made to extend these methods for excited states (e.g., kinks and/or polarons) as well.[14,2] Grabowski *et al.*[15] have calculated the influence of the Coulomb terms U and V on the total energy of an exciton. They have used a HF *Ansatz* for the discrete model in order to obtain corrections to the single particle energies ε_k, but they did not calculate corrections to the wave functions and therefore to the optical-absorption strength. So far only an unrestricted HF *Ansatz* has been used to obtain some information about the gap structure of polarons or excitons, respectively. This approximation yields (in the continuum limit) y-dependent effective fields which have to be determined self-consistently in a way analogous to the gap function $\Delta(y)$ (2.4). It turns out that the mathematical structure of the effective Hamiltonian after the HF has been introduced corresponds to perturbations of the form we have considered in the preceding sections.[2] As a consequence the effective Hamiltonian does break the CCS whereas the full model (3.1) for the Coulomb interactions is invariant under CCS. It is clear that Coulomb interactions which are modeled through coupling of electronic densities as it is the case with Hubbard U (and V) terms conserve CCS. The breaking of CCS is introduced by the HF because one of the effective fields used in HF couples field operators from two different electronic densities. Therefore the results from HF calculations have to be interpreted with this caveat.

For these reasons we have also studied additional non-Hubbard electronic interactions which can be expressed as density depending hopping terms (with some amplitude W for this process):

$$H_W=-W\sum_{n,s}c^{\dagger}_{ns}c_{ns}[(c^{\dagger}_{n\,+1-s}+c^{\dagger}_{n\,-1-s})c_{n\,-s}+\text{H.c.}]\,. \tag{4.2}$$

This Hamiltonian explicitly breaks CCS through the hopping contributions. Interactions of this kind have also been considered by Kivelson *et al.*[30] The W term (4.2) corresponds to the $X(0)$ term in Ref. 30. There it has been shown that the inclusion of bond-charge-density terms leads to a decrease in the magnitude of the dimerization for the ground state of the model similar to our results. Baeriswyl *et al.*[31] and Gammel and Campbell[32] argue, however, that interactions of this type are negligible compared to the Hubbard terms. The HF treatment of the contribution (4.2) to the original SSH Hamiltonian (2.1) does not alter the underlying symmetries and is therefore more trustworthy than for Hubbard-type interactions. The results, however, do correspond to those found for the Hubbard terms (Ref. 2), i.e., one finds [as for the additional electron-lattice interaction H_β (2.6)] a stabilization of the bipolaron excitation as well as a transfer of oscillator strength from the low-energy peak to the high-energy peak and a shift of the localized levels within the gap. Since these results for the U and V terms have been published already we do not present here the analogous results for the W interaction.

In contrast to the extended SSH models considered so far there is another class of Hamiltonians, the Pariser-Parr-Pople (PPP) Hamiltonians,[33] which involves explicit electron-electron interactions. It is possible to derive a continuum version of this theory via unrestricted HF methods and to consider some properties of the excited states. A direct comparison with the results presented in this chapter is very difficult. The PPP kinks are amplitude-phase solitons, while the TLM (or SSH) kinks are pure amplitude solitons; PPP polarons are even more complicated than PPP kinks on account of the four gap parameters of the PPP model.

V. CONCLUSIONS

In the preceding sections we have presented the experimental facts that make it necessary to extend the simple Su-Schrieffer-Heeger model for conducting polymers. Physically this means that the various symmetries underlying the SSH model such as charge conjugation symmetry and supersymmetry have to be broken. We have discussed various mechanisms which achieve this breaking of symmetries, these electron-electron as well as electron-lattice interactions. The influence of these interactions on the different nonlinear excitations of these systems has been studied and detailed experimental signatures of the optical absorption coefficient have been predicted. Whereas electron-electron interactions could be treated only in Hartree-Fock approximation the electron-lattice interaction could be handled in a systematic perturbational calculation.

The main features of the additional interaction are transfer of oscillator strength from the low-energy peak to the high-energy peak for the various polaronic excitations, shift of the localized levels within the gap out of their symmetric position and a resulting splitting of the absorption peaks. This first signature agrees very well with recent experimental results in polythiophene and polyparaphenylene, respectively. For the other features there are some experimental hints, a more convincing agreement, however, is still missing.

So far the physical systems we have been concerned with are polymers belonging to the class characterized by the existence of a backbone of conjugated bonds, the drosophila of which being polyacetylene. On the other hand other classes of polymers have been discussed,[34] such as the polysilylenes, polygermylenes, and polyanilines, which can be modeled by similar methods as the conjugated polymers. It turns out that these systems show polaronic type excitation of the polyacetylene form as well. From this we expect the results presented here do carry over to the other polymer classes *cum granu salis*. The role of symmetries in these substances, however, has still to be clarified.

ACKNOWLEDGMENT

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APPENDIX

In order to perform a perturbational calculation with respect to the additional interaction (2.7) (characterized by the parameter β) we start from the one-particle equation for the electrons

$$(H_T+\beta H_\beta)f=\varepsilon f \tag{A1}$$

with $H_T=-iv_F\sigma_1\partial_y-\Delta^T(y)\sigma_2$ and $H_\beta=\Delta^{T2}(y)\mathbb{1}$. Using the expansions (3.1) the first-order terms yield (neglecting Δ^β at the moment)

$$(\varepsilon^T-H_T)f^\beta=(H_\beta-\varepsilon^\beta)f^T \tag{A2}$$

for both gap and band functions f. This is an inhomogeneous differential equation with the H_T as differential operator. The wave functions f^β are composed from the unperturbed (TLM) solution plus a special solution of (A2). In order to determine these special solutions we diagonalize the left-hand side of (A2) through multiplication with (ε^T+H_T) from the left:

$$Df^\beta=I(y) \tag{A3}$$

with $D=[\varepsilon^{T2}-\Delta^{T2}(y)+v_F^2\partial_y^2]\mathbb{1}+v_F[\partial_y\Delta^T(y)]\sigma_3$ and the inhomogeneity $I(y)=(\varepsilon^T+H_T)(H^\beta-\varepsilon^\beta)f^T$. The special solution $\bar{f}^\beta$ can now be constructed with the help of the Green's function of (A3); it has the general form

$$\begin{aligned}\bar{f}^\beta=&-f_1(y)\int^y dy'\frac{1}{W}I(y')f_2(y')\\&+f_2(y)\int^y dy'\frac{1}{W}I(y')f_1(y')\end{aligned} \tag{A4}$$

with $f_1(y),f_2(y)$ a system of fundamental solutions of the homogeneous part of (A3) and W the corresponding Wronski determinant.

The general solution of (A2) $f^\beta=\bar{f}^\beta+cf^T$ contains two constants which have to be determined by physical arguments: $f^\beta\sim f^T$ for $y\to\infty$, i.e., $f^\beta\sim e^{iky}$ for band and e^{-y/ξ_0} for gap functions, and thus the eigenvalue ε^β is fixed; second, for large y the gap correction $\Delta^\beta(y)$ has to agree with the ground-state value Δ_0^β. This then determines the arbitrary contribution c of (homogeneous) TLM solutions.

For the kink excitation Eq. (A2) can be sholved directly. In this case the correction to the gap function reads

$$\bar{f}_0^\beta(y)=\begin{bmatrix}0\\ i\dfrac{1}{3(\xi_0)^{1/2}}\Delta_0^T\tanh(y/\xi_0)/\cosh(y/\xi_0)\end{bmatrix} \tag{A5}$$

with the corresponding energy shift

$$\varepsilon_0^\beta=\Delta_0^{T2}/3\ . \tag{A6}$$

Since the energy shift for the bands is

$$\varepsilon^\beta=\Delta_0^{T2} \tag{A7}$$

the localized state in the gap is moved out from the center of the gap by an amount of $-\frac{2}{3}\beta\Delta_0^{T2}$. This will lead to a splitting of the corresponding absorption peaks as described in Ref. 8.

From (A4) we can calculate the corrections to the band functions:

$$\bar{f}^{\beta}_{k+}(y)=\frac{i}{3}N_k\varepsilon_k^T e^{iky}\left[\frac{1}{1+\xi_0^2k^2}[\xi_0 k/\cosh^2(y/\xi_0)-i\tanh(y/\xi_0)(4+5\xi_0^2k^2)-\xi_0 k\tanh^2(y/\xi_0)]\right.$$
$$\left.-4e^{-2iky}I_k(y)[\xi_0 k-i\tanh(y/\xi_0)]\right], \tag{A8a}$$

$$\bar{f}^{\beta}_{k-}(y)=\frac{i}{3}N_k\Delta_0^T e^{iky}\{-1/\cosh^2(y/\xi_0)-3i\xi_0 k\tanh(y/\xi_0)$$
$$\times[\tfrac{1}{3}k^2\xi_0^2-1+\tfrac{2}{3}\tanh^2(y/\xi_0)-ik\xi_0]/(1+\xi_0^2k^2)+4e^{-2iky}I_k(y)(1+k^2\xi_0^2)\}, \tag{A8b}$$

with

$$N_k=\frac{1}{\sqrt{L}}\Delta_0^T/\varepsilon_k^T,\quad \varepsilon_k^T=\Delta_0^T[(1+k^2\xi_0^2)]^{1/2}$$

and (A9)

$$I_k(y)=\int^y dy'/\xi_0 e^{2iky'}\tanh(y'/\xi_0).$$

With these wave functions the corrections for the gap $\Delta^\beta(x)$ and the optical-absorption coefficient $\alpha^\beta(\omega)$ can be calculated. $\Delta^\beta(y)$ follows from the variation of the total energy $\langle H_T+H_\beta\rangle$ with respect to Δ together with the expansion (3.1):

$$\Delta^\beta(y)=\pi v_F\lambda\sum_{\substack{\text{occ}\\ \text{levels}}}\mathrm{Re}(f^{T+}\sigma_2 f^\beta)-\Delta^T(y)f^{T+}1f^T. \tag{A10}$$

[This is the linearized version (in β) of the full self-consistency equation as given in Ref. 8.] In order to perform the summation over the occupied states in (A10) (which corresponds to an integration over k) in closed form we replace

$$\tanh(y/\xi_0)\rightarrow\begin{cases}-1, & y\le-\xi_0\\ y/\xi_0 & -\xi_0\le y\le\xi_0\\ 1, & \xi_0\le y.\end{cases} \tag{A11}$$

We then finally arrive at

$$\Delta^\beta(y)=2\pi\lambda\Delta_0^2(\tfrac{1}{4}-\tfrac{1}{3}n)\tanh(y/\xi_0)/\cosh^2(y/\xi_0), \tag{A12}$$

where n denotes the number of electrons which occupy the localized level.

The correction to the matrix element which enters the absorption coefficient [cf. (3.3)] follows from:

$$M^\beta_{1,2}=\tfrac{1}{2}\int dy(f_2^{T+}\sigma_1 f_1^\beta+f_2^{\beta+}\sigma_1 f_1^T) \tag{A13}$$

which in turn yields for linearized $|M|^2$

$$|M_{1,2}|^2=(1+2\beta c)|M^T_{1,2}|^2$$
$$+2\beta(\mathrm{Re}M^T_{1,2}\mathrm{Re}M^\beta_{1,2}+\mathrm{Im}M^T_{1,2}\mathrm{Im}M^\beta_{1,2}). \tag{A14}$$

The TLM matrix elements for the transition to the localized level are pure imaginary (cf. Ref. 1). The wave functions have the symmetries

$$f^T_{\varepsilon>0}=\sigma_3 f^T_{\varepsilon<0},\quad f^\beta_{\varepsilon>0}=-\sigma_3 f^\beta_{\varepsilon<0} \tag{A15}$$

and therefore we have the relations

$$M^T_{v,0}=-M^{T*}_{0,c},\quad M^\beta_{v,0}=M^{\beta*}_{0,c}, \tag{A16}$$

where v,c stands for valence ($\varepsilon<0$) and conduction ($\varepsilon>0$) band, respectively, and 0 for the localized level.

The matrix elements (A14) can then be simplified to

$$|M_{v,0}|^2=(1+2\beta c)|M^T_{v,0}|^2$$
$$+\beta\pi\frac{(\xi_0)^{1/2}}{L^{1/2}}\frac{1}{\cosh\pi k\xi_0/2}m, \tag{A17}$$
$$|M_{0,c}|^2=(1+2\beta c)|M^T_{0,c}|-\beta\pi\frac{(\xi_0)^{1/2}}{L^{1/2}}\frac{1}{\cosh\pi k\xi_0/2}m$$

with $m=\mathrm{Im}M^\beta_{v,0}$. Neglecting the contribution of the homogeneous solution c we find that intensity from the transition localized level to conduction band is transferred to the transition valence band to localized level.

The calculations for the polaron are done in the same way. One has to remember, however, that the polaron is characterized by a parameter $r=\kappa_0\xi_0=\tanh(2\kappa_0 y_0)$ (cf. Ref. 1) characterizing the spatial extend of this solution. This value has to be determined by a minimization of the total energy $E(r)$. This total energy contains (up to the first order in β) the (unperturbed) TLM energy, the occupied one particle energies $\sum_{\substack{\text{occ}\\ \text{levels}}}\varepsilon^\beta$, and the contribution due to Δ^β in the electronic part $\sum_{\substack{\text{occ}\\ \text{levels}}}\frac{1}{2}\int dy f^{T+}[-\sigma_2\Delta^\beta(y)]f^T$ as well as in the lattice energy $1/(2\pi t_0\lambda)\int dy\,\Delta^T(y)\Delta^\beta(y)$.

The correction to the energies for the band states is the same as for the kink $\varepsilon^\beta=\Delta_0^{T2}$, for the localized levels we find

$$\varepsilon^\beta_\pm=\Delta_0^{T2}\left[1-\frac{2}{3}\frac{r^2}{1-r^2}(2\sqrt{1-r^2}-\tfrac{4}{5}r^2)\right] \tag{A18}$$

independent of occupation. [The unperturbed result is $\varepsilon_{\pm}^{T} = \pm\Delta_0^T(1-r^2)^{1/2}$]. $\varepsilon_{\pm}^{\beta}$ yields a shift of the levels in the *same* direction, as it is the case for the band states. From this we find the property of maximal symmetry breaking for the $\bar{f}^{\beta}$ functions: comparing negative energy $\varepsilon < 0$ with positive energy $(\varepsilon > 0)$ states we find

$$D_{>} = D_{<}, \quad \varepsilon_{>}^{T} = -\varepsilon_{<}^{T}, \quad H_{>}^{T} = -H_{<}^{T}, \quad H_{>}^{\beta} = H_{<}^{\beta} ,$$
$$\varepsilon_{>}^{\beta} = \varepsilon_{<}^{\beta}, \quad f_{>}^{T} = \sigma_3 f_{<}^{T} ,$$

from which (A15) follows directly, for kinks as well as polarons. This can be seen explicitly in Eqs. (A5) and (A8).

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