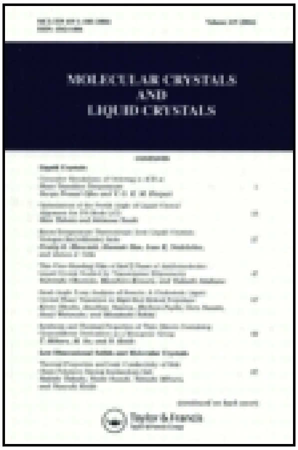

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

# Theoretical Studies of Charged Defect States in Doped Polyacetylene and Polyparaphenylene

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Version of record first published: 19 Dec 2006.

To cite this article: J. E. Brédas , R. R. Chance & R. Silbey (1981): Theoretical Studies of Charged Defect States in Doped Polyacetylene and Polyparaphenylene, Molecular Crystals and Liquid Crystals, 77:1-4, 319-332

To link to this article: http://dx.doi.org/10.1080/00268948108075251

*Mol. Cryst. Liq. Cryst.*, 1981, Vol. 77, pp. 319–332
0026-8941/81/7701-0319$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

# THEORETICAL STUDIES OF CHARGED DEFECT STATES IN DOPED POLYACETYLENE AND POLYPARAPHENYLENE

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Received for publication September 7, 1981

Defect state calculations have been performed for polyacetylene and polyparaphenylene in the framework of the Su, Schrieffer, and Heeger Hamiltonian. In polyacetylene, the study of the energetics of the separation of the radical (neutral defect)-ion(charged defect) pair induced upon doping indicates that the two defects tend to remain close to each other. This results in the formation of polarons whose binding energy is estimated to be of the order of 0.05 eV. Absorption spectra at low doping levels are consistent with polaron formation. Interaction between polarons leads to the formation of charged solitons. In poly(p-phenylene), defects are always correlated in pairs. Upon doping, polarons are formed (binding energy ~ 0.03 eV), with the relaxation of the lattice extending over about four rings. Calculations suggest the possibility of bipolarons (doubly charged defects) that yield conductivity without Pauli susceptibility.

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*Fellow of the Belgian National Science Foundation (Aspirant FNRS)

## I. INTRODUCTION

In the past few years, much interest has been devoted world-wide to conjugated organic polymers that can be made conducting upon doping with electron donors or acceptors. Among these systems are polyacetylene[1], poly(p-phenylene),[2] poly(p-phenylene sulfide),[3,4] and polypyrrole.[5] So far, polyacetylene, PA, has been the most studied compound. A reason for this is that the degenerate ground state that exists in all-trans PA suggests the presence of topological kinks or so-called soliton defects.[6-10] On the basis of the soliton model, many unusual properties have been predicted for all-trans PA, including the possibility of a conductivity mechanism involving charged solitons that carry no spin. Other polymers, such as poly(p-phenylene), PPP, do not possess degenerate ground states and are therefore not expected to accommmodate solitons. However, experimental transport properties of PPP and PA are very similar. In order to make a comparison between polyacetylene and poly(p-phenylene), we have applied to both systems the same theoretical model, based on the approaches of Pople and Walmsley[6] and Su, Schrieffer, and Heeger.[8]

Section II is devoted to polyacetylene. We first describe the model and then apply it to the study of energetics of the separation of pairs of defects induced upon doping. Interactions between holes (polarons) are described and the band structure evolution is presented for a lattice of holes and a lattice of charged solitons. Experimental data for optical absorption of radical anions in finite-chain polyenes are used to demonstrate that dopant-induced optical absorption in PA can be understood with a polaron model. In Section III, we detail the model used to treat the defect states in PPP, study the energetics of pairs of defects, and finally compare PPP with PA. It must be borne in mind that these models are based on a simple one electron theory and neglect correlation effects which can be important. Interchain interactions and presence of the dopant ion are also neglected.

## II. DEFECT STATES IN POLYACETYLENE

In the present model, all-trans PA is Peierls distorted and two energetically equivalent resonance forms can be derived (Fig. 1). The Peierls distortion opens up a gap at the Fermi level of the order of 1.4-1.9 eV, making pristine PA semiconducting.

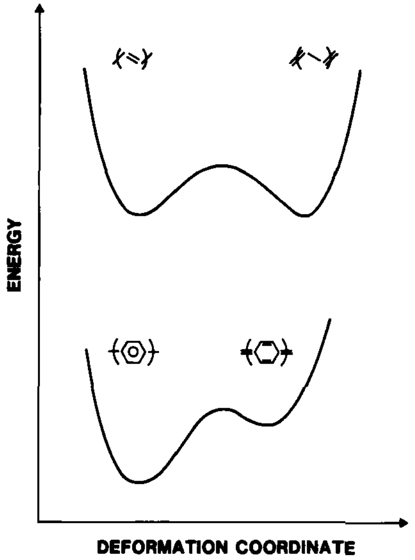


FIGURE 1 Sketch of potential energy curves for polyacetylene showing two energetically equivalent structures, and poly-paraphenylene showing two inequivalent structures.

In order to understand the properties of undoped and doped all-trans polyacetylene, a soliton model has been developed by many authors.[6-10] We now briefly summarize some of its characteristics. The soliton model, based originally on the ideas of Pople and Walmsley,[6] involves the presence of topological kinks along the chains extending over several bonds. Going from the left to the right of the defect, the phase of the bond length alternation is reversed. As the structures to the left and to the right of the defect are energetically degenerate, the defect is expected to be able to move almost freely along the chain, in the manner of a solitary wave. The soliton defect carries spin 1/2 when neutral but no spin when charged. The presence of such a defect introduces a localized electronic state at mid gap.

Numerical calculations used to study the energetics of the soliton formation have usually been performed in the framework of Huckel theory with $\sigma$ bond compressibility.

This is the case of the Su, Schrieffer and Heeger (SSH) adiabatic Hamiltonian.[8] Bond-order bond-length relationships of the Coulson type can also be used.[11] In both approaches, parameters are chosen such as to reproduce the band width, the band gap, and the dimerization pattern and both approaches lead to the same numerical results. A cautionary note is in order regarding the extreme crudity of these theoretical models - whether based on Pople and Walmsley or SSH approaches. Absolute energies obtained from the model, as well as geometries (defect extensions), should be viewed qualitatively with emphasis on trends and internally consistent comparisons.

The energy of an isolated soliton defect can be optimized as a function of its width. We have used a bond order-bond length relationship with a gap of 1.4 eV, a band width of 10 eV, and a degree of bond length alternation of 0.14Å. All calculations have been performed on cyclic polyenes containing at least 110 carbon atoms. The optimal width of the soliton is found to be ~14 bonds (half width: $\ell = 7$), corresponding to an energy for the defect $E_d \simeq 0.45$ eV in close agreement with SSH results.[8] This means that the energy to create a positively charged soliton is 0.25 eV smaller than the 0.7 eV required by a vertical ionization process. However, during the doping process, the transfer of an electron from the chain toward an acceptor molecule creates a radical-cation on the chain, i.e., a charged defect and a neutral defect. It is then relevant to study the energetics of the separation of these two defects. A product of hyperbolic tangent functions is used to describe the bond alternation suppression between the two interacting defects. We have studied the separation of (i) two neutral defects, (ii) a charged and a neutral defect, and (iii) two charged defects. In each case, the width of the defects has been optimized. Results are presented in Fig. 2.

When the two defects are widely separated, we naturally obtain the isolated defect results. As expected, two neutral defects formed by the breaking of a double bond tend not to separate but to recombine, leaving no deformation on the chain ($\ell \to 0$). Two identically charged defects repel each other leading to two isolated charged solitons. When the two charged defects are close to each other, the deformation they provoke is very strong ($\ell > 13$); when they are widely separated the corresponding energy is 0.5 eV lower with respect to two vertical ionization processes.

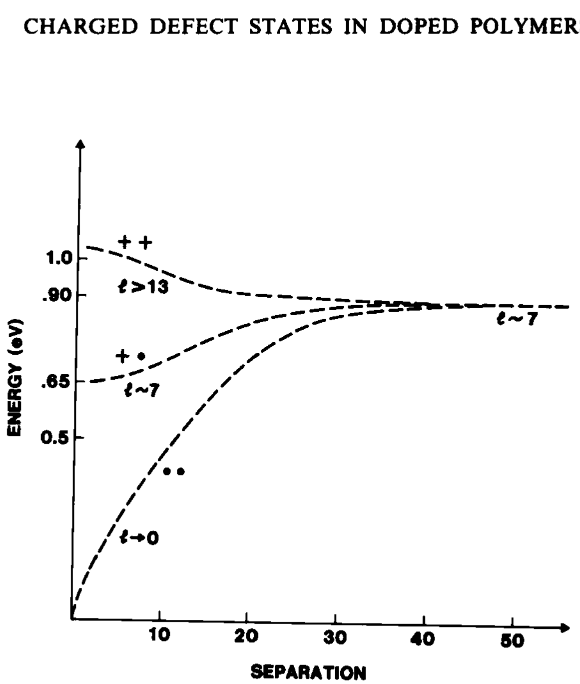


FIGURE 2 Energetics of separation of two defects on polyacetylene chain with . . indicating two radicals (neutral solitons), + + indicating two cations (charged solitons) and + . indicating a radical cation (or polaron for small separations). The quantity ℓ defines the extent of the chain deformation due to the effect. The units for the abscissa and ℓ are number of carbon atoms.

We now turn to the interaction between a neutral and a charged defect. We find that the energy is smallest, 0.65 eV, when the two defects are in close proximity, i.e., a polaron is formed. (Our conclusion that the radical and the ion are attractive is consistent with the trends predicted by Lin-Liu and Maki[12] for large defect pair separations.) With respect to a vertical ionization process, at 0.7 eV, the polaron binding energy is ~ .05 eV, in close agreement with Bishop's results[13] in the continuum limit. The total deformation is relatively small, extending only over ~ 15 bonds for two nearest-neighbor defects -a result which is also in agreement with Bishop. In Fig. 3, we present the difference in the band picture when going from two isolated defects (two localized states at mid gap) to two interacting defects. In the latter the electronic states interact leading to a bonding and an antibonding state within the gap.

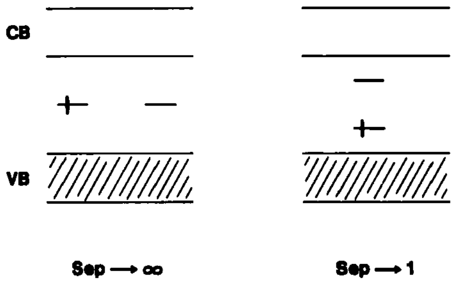


FIGURE 3 Interaction of charged and neutral soliton in polyacetylene. States appear at midgap for infinite separation but interact and split as indicated when the separation approaches one bond.

We now address the question of the interaction between two polarons. To study this interaction, we have considered two polarons with the charged defects located at fixed positions. The neutral defects are gradually pulled away from the charged defects, approach each other, and finally recombine leaving two charged solitons. (FIG. 4) For two polarons widely separated (E ~ 2 x .65 eV = 1.3 eV), that process leads first to the formation of four isolated defects (E ~ 4 x .45 eV = 1.8 eV), before eventually the recombination of the two radicals leaves only two charged solitons (E ~ 2 x 0.45 eV = 0.9 eV). At 2.0% (homogeneous) doping level (charges about 50 sites apart), the barrier indicated in Fig. 4 is still of the order of 0.1 eV. The barrier disappears at around 3% doping level (charges about 35 sites apart) and at 4% doping level neutral defects readily recombine, leading to a lattice of charged solitons.

These results indicate that, within our model, at very low (homogeneous) doping levels, polarons are preferentially formed. Two proximal polarons can interact leading to two charged solitons. (Note that charge transfer could also take place from a neutral soliton formed during the cis-trans isomerization process. This leads to a charged soliton.)[14] At higher doping levels, charged solitons are the dominant feature. Looking at the band structure, we first form bonding-antibonding states in the gap related to the polarons, ~ 0.3 eV above (below) the top (bottom) of the valence (conduction) band. In the context of acceptor doping, the bonding states are half occupied. Creation of positive charged solitons leads to empty states at mid-gap. Increase in the doping level results in the broadening of the states in the gap and the formation of bands. As already mentioned,[8,12,15] at higher doping levels conductivity could occur through charged solitons (carrying no spin). When the soliton band merges with the valence band, carriers with spin can contribute to the conductivity. At very high doping levels, our ab initio Hartree-Fock calculations on Li-doped polyacetylene[16] show that bond-length alternation is depressed, solitons are no longer present, and conductivity is due to the closure of the Peierls gap.

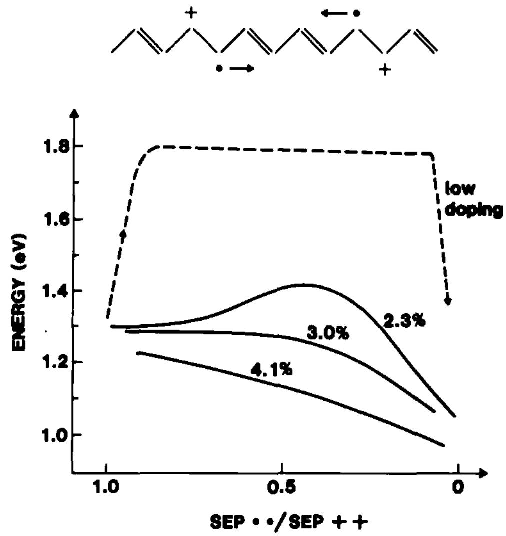


FIGURE 4 Interaction between two radical-cations (or holes or polarons) in polyacetylene. The horizontal axis is the ratio of the radical separations to the charge separations so that the right extreme of the figure represents the formation of two charged solitons from two polarons. Doping levels as mole per cent are indicated.

The midgap absorption which appears at ~ 0.8 eV when polyacetylene is doped[17,18] has been taken as evidence for the generation of solitons on doping. Since our model shows that the formation of polarons is energetically favored over solitons at low doping levels, the question arises as to whether or not polarons are responsible for, or contribute to, the observed midgap absorption. A polaron in polyacetylene introduces three new transitions as depicted in Fig. 5. Table I gives our calculated energies for these transitions (normalized by the energy gap) for radical-ion separations of 1,3,5, and 7 bonds. Note that the average absorption energy expected with the polaron model is also about midgap.

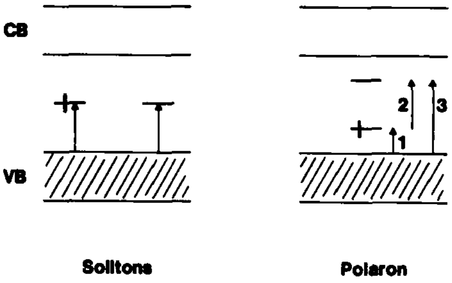
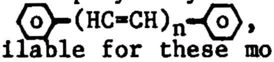


FIGURE 5 Schematic representation of dopant-induced optical transitions in polyacetylene for solitons and polarons.

Table I. Energies ($E_d$), defect level positions ($\varepsilon_d$), and transition energies for charged defects in polyacetylene. The transition energies - $E_1$, $E_2$, and $E_3$- are normalized by the bandgap energy for comparison to experiments.

| Separation | $E_d$ (eV) | $\varepsilon_d$ (eV) | $E_1$ | $E_2$ | $E_3$ |
|---|---|---|---|---|---|
| 1 | .652 | ±.434 | 0.20 | 0.62 | 0.81 |
| 3 | .656 | ±.395 | 0.23 | 0.56 | 0.79 |
| 5 | .667 | ±.357 | 0.25 | 0.50 | 0.75 |
| 7 | .680 | ±.318 | 0.28 | 0.45 | 0.73 |
| "Experiment"................... | | | 0.30 | 0.44 | 0.55 |

We now consider charged defect absorption observed in model compounds for polyacetylene. We choose the diphenylpolyenes (DPP), , since there are rather extensive data[19] available for these molecules with $n = 1$ to 6. Because we are interested in the extrapolation of oligomer data to the polymer, we must appropriately "correct" the DPP data. We accomplish this correction by defining an effective conjugation length, $n_{eff} = n + A$, such that the absorption energy of DPP with n double bonds is equal to that of a polyene with $n + A$ double bonds.[20] The absorption energies are plotted versus $1/n_{eff}$, which according to theory and experiment should yield a roughly linear relationship.[21] Results are shown in Figure 6. We find $A = 2.7$; in other words, stilbene ($n = 1$) absorbs at about the same energy as octatriene ($n + A \simeq 4$). The extrapolation to $n_{eff} = \infty$ yields $E_g = 1.8$ eV, in good agreement with experiment.[17]

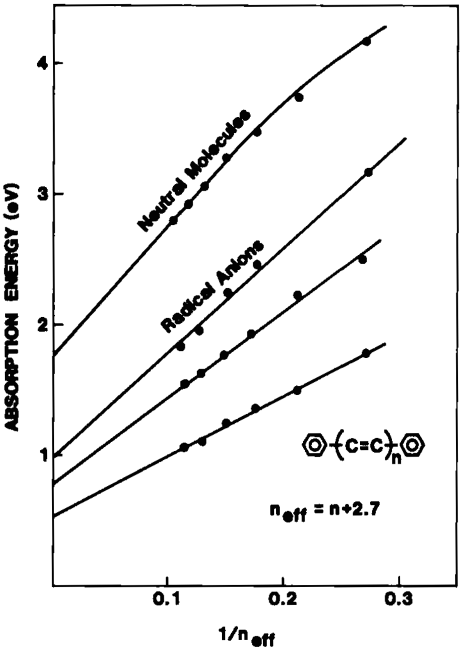


FIGURE 6 Optical absorption energy versus the reciprocal of the "effective" number of double bonds for diphenyl polyenes (neutral molecules and radical anions). The solid line through the neutral molecule data represents data for polyenes (with extrapolation) taken from the literature.[20]

We also show in Fig. 6 the transition energies for radical anions as obtained by Hoijtink and van der Meij.[19] The data are roughly linear with $1/n_{eff}$ and extrapolate to 0.5, 0.8, and 1.0 eV. These data, after normalizing by the 1.8 eV bandgap, are compared to theory in Table I. The radical anions correspond to negatively charged polarons, i.e. to donor doping of polyacetylene for which a broad (~ 1 eV wide) transition centered at about 0.7 eV has been observed.[18] Thus the extrapolated radical anion absorption data are quite consistent with the experimental observations for donor doped polyacetylene. We may conclude that polaron absorption offers a satisfactory explanation for the midgap absorption in doped polyacetylene and that the soliton explanation is nonunique.

## III. DEFECT STATES IN POLYPARAPHENYLENE

Polyparaphenylene consists of benzene rings linked in para position. Bonds lengths within the rings are ~ 1.40Å; bonds lengths between the rings are ~ 1.50Å.[22] The band gap is of the order of 3.5 eV.[2] A resonance form can be derived that corresponds to a quinoid structure. The major difference with respect to all-trans polyacetylene is that the two forms are not energetically degenerate, the quinoid structure being less stable in energy (Fig. 1). When we discuss defects in PPP, it is important to recognize that the connectivity in PPP makes it very different from polyacetylene. For physical values of the transfer integrals, we find that no midgap ($\varepsilon = 0$) state is possible for the defect structures considered here. As a result defects will interact in pairs even in the low concentration limit.

Calculations on PPP are performed in the framework of a bond-order bond-length relationship of the Coulson type.[11] Parameters are chosen such as to reproduce the geometry of the benzenoid structure, the band gap (3.5 eV), and the band width of the highest occupied $\pi$-orbital (3.2 eV).[23]

The model we have chosen for dealing with pairs of defects (Fig. 7) is derived directly from polyacetylene. We consider that the deformation toward a quinoid structure is maximum in the middle of the defect and gradually decreases toward the edge of the defect to lead back to the benzenoid structure. Such behavior can be simulated by a product of hyperbolic tangent functions (Fig. 7). The optimization of the energy for a pair of defects now depends on two factors: the number of rings, N, over which the defect extends and the factor entering the hyperbolic tangent function which determines the amplitude of the deformation in the middle of the defect.

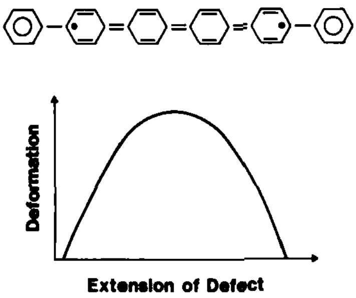


FIGURE 7 Deformation model for polyparaphenylene chain based on product of hyperbolic tangent functions.

Our results describe three effects: First, for two neutral defects (radicals), the minimum of energy is, of course, obtained when they recombine, leaving no deformation. Second, for a charged defect interacting with a neutral defect a polaron is formed whose binding energy is of the order of 0.03 eV (to be compared with 0.05 eV in all-trans polyacetylene) and whose extension is over about 4 rings. It must be pointed out that the deformation associated with the polaron is relatively soft: in the middle of the defect the bonds within the rings change by ~ 0.025Å while the bonds between the rings by some 0.05Å. The presence of the polaron introduces two states, bonding and anti-bonding, in the gap - the bonding state being ~ 0.2 eV above the top of the valence band. Third, for two positively charged defects (bipolaron) the deformation is stronger, about twice as large as in the previous case, and the defect has a larger extension, of the order of 5 rings. (Note that as no Coulomb repulsion has been introduced in these preliminary calculations, this constitutes a lower limit to the width of the defect.) These two trends, large deformation and large defect extension, can be understood by the fact that they both result in pushing up the bonding state in the gap, ~ 0.6 eV above the valence band edge, making the ionization process easier. The gain in total energy obtained with respect to two vertical ionizations is of the order of 0.4 eV (to be compared with 0.5 eV in the case of polyacetylene). A very important feature of these results is that they point out the possibility of formation of bipolarons in doped polyparaphenylene (Fig. 8). Similar behavior can be expected for cis-PA, which, like PPP, does not have a degenerate ground state.

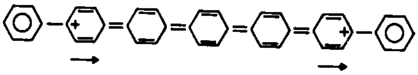


FIGURE 8 Bipolaron on polyparaphenylene chain

As the doping level increases, bipolaron states in the gap can broaden and lead to the formation of bands, as in the case of polyacetylene. Conductivity could then arise from the motion of bipolarons, which can be viewed as pairs of correlated charged defects carrying no spin. This picture is supported by the magnetic data of Peo et al.[24] that indicate a very low Pauli susceptibility in the metallic regime of $SbF_5$ doped PPP.

In summary, we want to emphasize that our model calculations on charged defect states in all-trans PA and PPP indicate that these two conducting compounds are much more similar than previously thought, despite the absence of a degenerate ground state in PPP. At low doping levels, polaron formation is expected for both PA and PPP with similar polaron binding energies and similar defect extensions. At higher doping levels two polarons interact to produce two uncorrelated charged solitons in PA and a bipolaron or correlated charged soliton-antisoliton pair, in PPP. We must emphasize once more that all these calculations, as well as those of references 6-10, are based on a very crude one-electron model which neglects all electron correlation effects. These effects may play a substantial role in the energetics.[25]

## IV. ACKNOWLEDGEMENTS

Helpful discussions with R.H. Baughman, L.W. Shacklette, and R.L. Elsenbaumer are gratefully acknowledged. This work was supported in part by the National Science Foundation (#DMR-7908307).

## REFERENCES

1. H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, J. Chem. Soc. Chem.Commun., 578 (1977).
2. L.W. Shacklette, R.R. Chance, D.M. Ivory, G.G. Miller, and R.H. Baughman, Synth. Met. 1, 307 (1979).
3. J.F. Rabolt, T.C. Clarke, K.K. Kanazawa, J.R. Reynolds and G.B. Street, J. Chem. Soc. Chem. Commun., 347 (1980).
4. R.R. Chance, L.W. Shacklette, G.G. Miller, D.M. Ivory, J.M. Sowa, R.L. Elsenbaumer and R.H. Baughman, J. Chem. Soc. Chem. Commun., 348 (1980).
5. K.K. Kanazawa, A.F. Diaz, R.H. Geiss, W.D. Gill, J.F. Kwak, J.A. Logan, J.F. Rabolt and G.B. Street, J. Chem. Soc. Chem. Commun., 854 (1979).
6. J.A. Pople and S.H. Walmsley, Mol. Phys. 5, 15 (1962).
7. M.J. Rice, Phys. Lett. A 71, 152 (1979); M.J. Rice and J. Timonen, Phys. Lett. A 73, 368 (1979).
8. W.P. Su, J.R. Schrieffer, and A.J. Heeger, Phys. Rev. Lett. 42, 1698 (1979); Phys. Rev. B 22, 2209 (1980).
9. S.A. Brazovskii, JETP Lett. 51, 342 (1980).
10. H. Takayama, Y.R. Lin-Liu, and K. Maki, Phys. Rev. B 21, 2388 (1980).
11. See, for example, L. Salem, Molecular Orbital Theory of Systems (W.A. Benjamin, New York, 1966).
12. Y.R. Lin-Liu and K. Maki, Phys. Rev. B 22, 5754 (1980).
13. A. Bishop in "Proceedings of the International Conference on Low Dimensional Conductors", Boulder, Colorado, August 1981.
14. S. Ikehata, J. Kaufer, T. Woerner, A. Pron, M.A. Druy, A. Sivak, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. Lett. 45, 1123 (1980).
15. E.J. Mele and M.J. Rice, Phys. Rev. B 23, 5397 (1981).
16. J.L. Brédas, R.R. Chance, and R.J. Silbey, J. Phys. Chem. 85, 756 (1981).
17. C.R. Fincher, Jr., M. Ozaki, A.J. Heeger, and A.G. MacDiarmid, Phys. Rev. B 19, 4140 (1979).
18. T. Chung, A. Feldblum, A.J. Heeger, and A.G. MacDiarmid, J. Chem. Phys. in press.

19. G.J. Hoijtink and P.H. van der Meij, Phys. Chem. Neue Folge 20, 1 (1959).
20. R.H. Baughman and R.R. Chance, J. Polym. Sci. Polym. Phys. Ed. 14, 2037 (1976) and references therein.
21. See, for example, D. Yarkony and R. Silbey, Chem. Phys. 20, 183 (1977).
22. Y. Delugeard, J. Deusuche, and J.L. Baudour, Acta. Cryst. B32, 702 (1976).
23. J.L. Brédas, R.R. Chance, R.H. Baughman, and R. Silbey, Int. J. Quantum Chem., in press; J. Chem. Phys., in press.
24. M. Peo, S. Roth, K. Dransfeld, B. Tieke, H. Gross, A. Grupp, and H. Sixl, Solid State Commun. 35, 119 (1980).
25. A.A. Ovchinnikov, I.I. Ukrainskii, and G.V. Kventsel, Ups. Fiz. Nauk. 108, 575 (1972).