Green's-function study of optical properties of polymers: Charge-transfer exciton spectra of polydiacetylenes

S. Suhai*

*Lehrstuhl für Theoretische Chemie der Friedrich-Alexander-Universität Erlangen—Nürnberg,
Egerlandstrasse 3, D-8520 Erlangen, West Germany*
(Received 15 September 1983)

The visible optical spectrum of two typical polydiacetylene (PDA) crystals, poly[2,4-hexadiyne-1,6-diol-bis-(p-toluene sulfonate)] (PTS) with an acetylene-like structure and poly[5,7-dodecadiyne-1,2-diol-bis-(phenylurethane)] (TCDU) with a butatriene-like structure, is investigated with the use of a first-principles Green's-function formalism of charge-transfer exciton theory. The energy-band structures of the ground state are calculated first at the Hartree-Fock level with nonlocal exchange and they are corrected afterward for electron correlation effects using the electron-polaron model of Toyozawa. The electron-hole interaction $\hat{H}_{e,h}$ is treated by first-order perturbation theory in the framework of the Lax-Koster-Slater resolvent method as proposed by Takeuti. The influence of screening on $\hat{H}_{e,h}$ is also investigated with the help of an $\vec{r}$-dependent static dielectric function. The results show that correlation corrections play an important role in the calculation of the optical spectrum since they substantially modify the Green's function of the host crystal as well as $\hat{H}_{e,h}$. Both the singlet and triplet excitons are found to be delocalized with a radius of 25—30 Å in PDA's: the Frenkel exciton contributes only ~30% of the binding energy. The calculations predict the first-singlet absorption maximum for PTS at 2.1—2.2 eV and for TCDU at 1.7—1.8 eV, with an exciton bandwidth of ~2.9 and ~3.5 eV, respectively. The exciton binding energy is found to be ~0.4 eV for both systems. Triplet levels are located at 0.8—0.9 eV below the singlets at $K=0$ and they form relatively flat bands. The theoretical ionization potentials are 5.7 and 5.0 eV for PTS and TCDU crystals, respectively.

I. INTRODUCTION

The optical properties of polydiacetylene (PDA) crystals have been the subject of a number of experimental[1–40] and theoretical[41–44] investigations. These polymers are unique among the newly discovered highly conducting organic polymers in that single crystals of considerable size can be synthesized from them.[45–48] These crystals contain a very low concentration of defects and are characterized by an extensive electron delocalization along the main polymer chain. Numerous PDA crystals have been synthesized with different side groups and their physical properties have been investigated (for recent reviews see Refs. 49—52). The PDA conjugated backbone exhibits one of the two mesomeric structures represented by the acetylenic, $[=RC-C\equiv C-CR=]_n$ and the butatriene, $[-RC=C=C=CR-]_n$ bonding sequences.

The mostly studied PDA crystal with an acetylene pattern is poly[2,4-hexadiyne-1,6-diol-bis-(p-toluene sulfonate)] (PTS), for which the side group R is $-CH_2OSO_2C_6H_4CH_3$. It crystallizes with the monoclinic $(P2_1/c)$ structure containing two polymer repeat units in the elementary cell.[53] Its visible spectrum consists of a complex series of transitions starting with a strong absorption edge and an associated reflection peak at ~16 000 cm^{-1} (~2 eV).[1–6] The absorption is highly anisotropic and it has been initially interpreted as an interband transition since the absorption profile shows the form of a van Hove singularity characteristic for the den-

sity of states in a quasi-one-dimensional (quasi-1D) band. The absence of photoconductivity at the absorption maximum near to 2 eV casts doubt, however, on this interpretation.[3,8] In fact, the above-mentioned singularity in the line shape appears also for a 1D exciton band. The observation of surface polaritons[22] as well as signs of an excitonic behavior in the resonance Raman spectra[4] supports the original suggestion of Bloor et al.[1] that the first absorption peak is due to excitons. Changes in the backbone conformation may substantially modify, however, the optical spectrum of PDA's offering in this way a very sensitive tool to detect structural phase transitions.

A well-known crystal with butatriene-like chain geometry is poly[5,7-dodecadiyne-1,2-diol-bis-(phenylurethane)] TCDU, for which the side group R is $-(CH_2)_4OCONHC_6H_5$. It undergoes a first-order phase transition at low temperatures (<100 K) or at high pressures (>5 kbar). This transition is reversible and it can be detected by resonance Raman[13] as well as by optical[33] spectroscopy. At room temperature (phase II) the backbone structure appears closer to the butatriene structure though distortions in both the $-(CH_2)_4$—linkage and in the polymer backbone have been observed.[54] The lowest-energy optical transition occurs in phase II at ~18 500 cm^{-1} (~2.3 eV) while it is reduced to ~15 300 cm^{-1} (~1.9 eV) in phase I. This red shift has been attributed to a butatriene-to-diacetylene bond reorganization[13] though this assignment is not supported by theoretical considerations. In our calculations, the geometrical data of the

butratriene-like high-temperature phase of TCDU have been used.

The purpose of the present paper is to calculate exciton levels for both crystals from first-principles formalism and to investigate the effect of the above-mentioned structural differences on the optical properties. The organization of this paper is as follows: In Sec. II we present the formalism of charge-transfer exciton theory in its first-principles implementation. The electron-polaron method which obtains correlation corrections to the Hartree-Fock (HF) one-electron bands will be briefly described in Sec. III and it is applied to the calculation of quasiparticle energy bands in PDA's. The exciton spectra are calculated in Sec. IV using both the HF and quasiparticle energy bands. The theoretical results are discussed and compared with experimental results in Sec. V.

II. FIRST-PRINCIPLES FORMALISM OF CHARGE-TRANSFER EXCITON THEORY

Organic polymer crystals represent a special class of solids from the point of view of their optical properties. The traditional methods to treat bound electron-hole pairs[55] are inapplicable to them: their monomeric units are strongly (covalently) interacting, therefore, intracellular and intercellular excitations must be treated on the same footing. This is in clear contradiction to the Frenkel model, based on the assumption that the excited electron primarily shares a unit cell with the hole. On the other hand, the dielectric screening in these materials is certainly too weak to produce Wannier-Mott—type excitons with a large radius. A theoretical framework to bridge the gap between the above two limits of the exciton picture has been proposed by Takeuti.[56] It is based on the Green's-function formalism developed earlier by Lax[57] and by Koster and Slater[58] to treat lattice vibrations and impurity states, respectively. A similar method has been worked out also by Altarelli and Bassani[59] which is based on a Fredholm-type solution of the integral equation determining the expansion coefficients of the exciton wave function.

To obtain quantitative results Takeuti had to assume at that time simple parabolic bands and he had to restrict himself to the diagonal part of the electron-hole interaction matrix. These restrictions are, however, not necessary and the purpose of the present paper is to present a first-

principles calculation of the excitonic levels in PDA in which no semiempirical approximations are made in evaluating the matrix elements of the Green's function and the electron-hole (e-h) interaction. It seems to be especially recommended to avoid the use of empirical parameters if typical correlation effects such as excitonic binding are investigated in extended systems. Semiempirical schemes contain, namely, parameters adjusted to describe the experimentally observed properties of relatively small molecules. The effect of correlation is built, therefore, ab ovo into these parameters and their use in a perturbation theoretical scheme to calculate e-h attraction may lead to inconsistent results. On the other hand, we may also have situations in infinite systems not appearing for a few atoms, for which the parameters were optimized. These may be the reasons why Takeuti's scheme has led to a comparatively large exciton binding energy of ~ 2.3 eV in a semiempirical π-electron study on polyenes.[60]

In deriving the e-h interaction we start from the Hamiltonian (in atomic units):

$$\hat{H} = \int \psi^\dagger(x)[-\tfrac{1}{2}\Delta + V_p(x)]\psi(x)d^3x$$
$$+ \tfrac{1}{2}\int\int \psi^\dagger(x)\psi^\dagger(x')\frac{1}{|x-x'|}$$
$$\times \psi(x')\psi(x)d^3x\,d^3x' , \qquad (1)$$

where x represents the spatial and spin variables $x \equiv (\vec{r},\sigma)$ and $V_p(x)$ is the periodic potential due to the ions. The field operators $\psi(x),\psi^\dagger(x)$ obey the usual fermion commutation rules and will be expanded using as a basis the complete orthonormal set of Wannier spin orbitals belonging to the valence bands (VB's) and conduction bands (CB's), respectively:[61,62]

$$\psi(x) = \sum_l a_{lv}w_v(x-l) + \sum_l a_{lc}w_c(x-l) , \qquad (2)$$

$$\psi^\dagger(x) = \sum_l a_{lv}^\dagger w_v^*(x-l) + \sum_l a_{lc}^\dagger w_c^*(x-l) , \qquad (3)$$

where the notation $w_j(x-l) \equiv w_j(\vec{r}-\vec{R}_l)x_j(\sigma)$ is used ($\vec{R}_l$ stands for the lattice vector of the cell in which the Wannier function is localized). Substituting Eqs. (2) and (3) into (1) and separating the one- and many-particle terms we obtain

$$\hat{H} = \hat{h} + \hat{g} , \qquad (4)$$

$$\hat{h} = \sum_{l,m} a_{lc}^\dagger a_{mc} h_{lm}^c + \sum_{l,m} a_{lv}^\dagger a_{mv} h_{lm}^v , \qquad (5)$$

$$\hat{g} = \tfrac{1}{2} \sum_{l_1,\ldots,l_4} \sum_{j_1,\ldots,j_4} a_{l_1j_1}^\dagger a_{l_2j_2}^\dagger a_{l_3j_3} a_{l_4j_4} g \begin{bmatrix} l_1 & l_2 \\ j_1 & j_2 \end{bmatrix} \begin{bmatrix} l_3 & l_4 \\ j_3 & j_4 \end{bmatrix} , \quad j_i = v,c . \qquad (6)$$

The monoelectronic and bielectronic integrals are defined here by

$$h_{lm}^j = \int w_j^*(x-l)[-\tfrac{1}{2}\Delta + V_p(x)]w_j(x-m)d^3x, \quad j=v,c , \qquad (7)$$

$$g \begin{bmatrix} l_1 & l_2 \\ j_1 & j_2 \end{bmatrix} \begin{bmatrix} l_3 & l_4 \\ j_3 & j_4 \end{bmatrix} = \int\int w_{j_1}^*(x-l_1)w_{j_2}^*(x'-l_2)\frac{1}{|x-x'|}w_{j_3}(x'-l_3)w_{j_4}(x-l_4)d^3x\,d^3x' . \qquad (8)$$

To obtain more transparent expressions, we introduce at this point the particle-hole picture using the operators $a_l^\dagger \equiv a_{lc}^\dagger$ and $a_l \equiv a_{lc}$ for the creation and destruction of a particle in the conduction band and similarly $d_l^\dagger \equiv a_{lv}$ and $d_l = a_{lv}^\dagger$ in the case of a hole in the valence band. In terms of these operators, we can construct the wave function of an exciton through the following steps.

(i) First, we create an e-h pair from the completely filled n-electron valence band $\Phi = d_{l_1} \cdots d_{l_{N_c}} \Phi_0$ (Φ_0 is the vacuum) with a separation $\vec{R}_s$:

$$\Psi_{l+s, l} = a_{l+s}^\dagger d_l^\dagger \Phi . \tag{9}$$

(ii) As the second step, stationary eigenstates with quasimomentum $\vec{K}$ are formed in the Bloch form

$$\Psi_{s, \vec{K}} = N_c^{-1/2} \sum_l \exp(i\vec{K}\cdot\vec{R}_l) a_{l+s}^\dagger d_l^\dagger \Phi , \tag{10}$$

where N_c is the number of elementary cells in the crystal.

(iii) Finally, the wave function of an exciton with momentum $\vec{K}$ is formed as a linear combination of symmetry adapted e-h pair functions with different separation:

$$\Psi_{\vec{K}} = \sum_s \Omega_{s, \vec{K}} \Psi_{s, \vec{K}} . \tag{11}$$

The weight of the different charge-transfer components in the excitonic wave function can be determined by solving the Schrödinger equation

$$\hat{H}\Psi_{\vec{K}} = E_{\vec{K}} \Psi_{\vec{K}} , \tag{12}$$

providing also the exciton band structure $E_{\vec{K}}$. For this purpose we partition the Hamiltonian by substituting the particle-hole operators in Eqs. (4)–(6). After some algebra we obtain

$$\widetilde{H} = E_{\mathrm{HF}} + \hat{H}_e + \hat{H}_h + \hat{H}_{e,h} , \tag{13}$$

where $E_{\mathrm{HF}} = \langle \Phi | \hat{H} | \Phi \rangle$ is the energy of the completely filled valence band in the HF approximation and

$$\hat{H}_e = \sum_{l,m} a_l^\dagger a_m \left\{ h_{lm}^c + \sum_p \left[g \begin{bmatrix} l & p \\ c & v \end{bmatrix} \begin{bmatrix} p & m \\ v & c \end{bmatrix} \right. \right.$$
$$\left. \left. -g \begin{bmatrix} p & l \\ v & c \end{bmatrix} \begin{bmatrix} p & m \\ v & c \end{bmatrix} \right] \right\}$$
$$= \sum_{l,m} a_l^\dagger a_m \langle w_c(x-l) | \hat{F} | w_c(x-m) \rangle , \tag{14}$$

$$\hat{H}_h = -\sum_{l,m} d_m^\dagger d_l \left\{ h_{lm}^v + \sum_p \left[g \begin{bmatrix} l & p \\ v & v \end{bmatrix} \begin{bmatrix} p & m \\ v & v \end{bmatrix} \right. \right.$$
$$\left. \left. -g \begin{bmatrix} p & l \\ v & v \end{bmatrix} \begin{bmatrix} p & m \\ v & v \end{bmatrix} \right] \right\}$$
$$= -\sum_{l,m} d_m^\dagger d_l \langle w_v(x-l) | \hat{F} | w_v(x-m) \rangle , \tag{15}$$

$$\hat{H}_{e,h} = -\sum_{l_1, \ldots, l_4} a_{l_1}^\dagger a_{l_4} d_{l_3}^\dagger d_{l_2} \left[g \begin{bmatrix} l_1 & l_2 \\ c & v \end{bmatrix} \begin{bmatrix} l_3 & l_4 \\ v & c \end{bmatrix} \right.$$
$$\left. -g \begin{bmatrix} l_2 & l_1 \\ v & c \end{bmatrix} \begin{bmatrix} l_3 & l_4 \\ v & c \end{bmatrix} \right] . \tag{16}$$

To obtain $\widetilde{H}$, we neglected in Eq. (13) those contributions from $\hat{H}$ which contain more than two electron or hole operators, respectively. Since the wave function $\Psi_{\vec{K}}$ contains only one e-h pair operator, the matrix elements of those terms are automatically zero. The Wannier functions are not eigenfunctions of the Fock operator $\hat{F}$, it is, therefore, worthwhile to switch to a Bloch representation to calculate the matrix elements of $\hat{H}_e$ and $\hat{H}_h$ with the exciton wave functions $\Psi_{s, \vec{K}}$. The Wannier basis w is related to the Bloch one φ by the unitary transformation

$$w_j(\vec{r}-\vec{R}_l) = N_c^{-1/2} \sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_l)\varphi_{j,\vec{k}} . \tag{17}$$

In fact, the $\varphi_{j,\vec{k}}$'s are at our disposal since the band-structure problem

$$\hat{F}\varphi_{j,\vec{k}} = \epsilon_{j,\vec{k}}\varphi_{j,\vec{k}} \tag{18}$$

has been solved previously for various PDA's using atomic basis sets of different quality.[63] The above transformation is still not a trivial problem since the localization properties of the w's sensitively depend on the phase of the φ's which is undetermined in Eq. (18). We shall return to this problem later and substitute now only the w's in Eqs. (14) and (15) and form the matrix elements of $\hat{H}_e$ and $\hat{H}_h$. After some algebraic computations we obtain

$$\langle \Psi_{r, \vec{K}} | \hat{H}_e | \Psi_{s, \vec{K}} \rangle = N_c^{-1} \sum_{\vec{k}} \exp[i\vec{k}\cdot(\vec{R}_r - \vec{R}_s)]\epsilon_{c, \vec{k}} , \tag{19}$$

$$\langle \Psi_{r, \vec{K}} | \hat{H}_h | \Psi_{s, \vec{K}} \rangle = N_c^{-1} \sum_{\vec{k}} \exp[i\vec{k}\cdot(\vec{R}_r - \vec{R}_s)]$$
$$\times (-\epsilon_{v, \vec{k}-\vec{K}}) . \tag{20}$$

On the right-hand side of Eq. (12) we need, furthermore, the matrix element of $E_{\vec{K}}$, which can be written in the form

$$\langle \Psi_{r, \vec{K}} | E_{\vec{K}} | \Psi_{s, \vec{K}} \rangle = N_c^{-1} E_{\vec{K}} \sum_{\vec{k}} \exp[i\vec{k}\cdot(\vec{R}_r - \vec{R}_s)] . \tag{21}$$

Applying now the resolvent method[57,58] for the perturbation $\hat{H}_{e,h}$ and fixing the origin of the energy by setting $E_{\mathrm{HF}} = 0$ in Eq. (13), we can write

$$\Psi_{\vec{K}} = [E_{\vec{K}} - (\hat{H}_e + \hat{H}_h)]^{-1}\hat{H}_{e,h}\Psi_{\vec{K}} . \tag{22}$$

Substituting this into Eq. (11), multiplying from the left-hand side with $\Psi_{s,\vec{K}}$, and integrating we obtain

$$\Omega_{r,\vec{K}} = \sum_s \sum_t \langle \Psi_{r,\vec{K}} | [E_{\vec{K}} - (\hat{H}_e + \hat{H}_h)]^{-1}$$

$$\times | \Psi_{s,\vec{K}} \rangle \langle \Psi_{s,\vec{K}} | \hat{H}_{e,h} | \Psi_{t,\vec{K}} \rangle \Omega_{t,\vec{K}} .$$

$$(23)$$

The matrix elements of the e-h interaction are again easy to calculate using the expansions of $\Psi_{s,\vec{K}}$ from Eq. (16) and we obtain for them in terms of the w's

$$\langle \Psi_{s,\vec{K}} | \hat{H}_{e,h} | \Psi_{t,\vec{K}} \rangle = - \sum_u \exp(-i\vec{K}\cdot\vec{R}_u)$$

$$\times \left[g \begin{bmatrix} s+u & 0 \\ c & v \end{bmatrix} \begin{bmatrix} u & t \\ v & c \end{bmatrix} \right.$$

$$\left. -g \begin{bmatrix} 0 & s+u \\ v & c \end{bmatrix} \begin{bmatrix} u & t \\ v & c \end{bmatrix} \right]$$

$$\equiv V^{(v,c)}(\vec{R}_s, \vec{R}_t, \vec{K}) . \qquad (24)$$

Collecting all the calculated terms from Eqs. (19)–(21) and (24), and substituting them into Eq. (23), we arrive at a system of homogeneous linear equations for the determination of the unknown coefficients $\Omega_{t,\vec{K}}$:

$$\Omega_{r,\vec{K}}^{(v,c)} = \sum_s \sum_t G^{(v,c)}(\vec{R}_r, \vec{R}_s, E_{\vec{K}}) V^{(v,c)}(\vec{R}_s, \vec{R}_t, \vec{K}) \Omega_{t,\vec{K}}^{(v,c)} .$$

$$(25)$$

$G^{(v,c)}(\vec{R}_r, \vec{R}_s, E_{\vec{K}})$ stands here for the matrix element of the Green's function belonging to the periodic crystal. It can be easily calculated using the results of previous band-structure calculations[63,64] as

$$G^{(v,c)}(\vec{R}_r, \vec{R}_s, E_{\vec{K}}) = N_c^{-1} \sum_{\vec{k}} \frac{\exp[i\vec{k}\cdot(\vec{R}_r - \vec{R}_s)]}{E_{\vec{K}} - (\epsilon_{c,\vec{k}} - \epsilon_{v,\vec{k}-\vec{K}})} .$$

$$(26)$$

In summary, we can determine the exciton band structure $E_{\vec{K}}$ in the following steps.

(i) From the HF energy bands $\epsilon_{j,\vec{k}}$ we calculate the matrix elements of the Green's function, using Eq. (26) in the region of the HF gap where excitonic levels can be expected.

(ii) We transform the Bloch functions to a set of optimally localized Wannier functions (see below) and calculate the matrix elements of the e-h interaction in the whole Brillouin zone (BZ) using Eq. (24).

(iii) Finally, we determine $E_{\vec{K}}$ by finding the zeros of the determinant $D = |\underline{G}\,\underline{V} - \underline{I}|$, where I is the unit matrix, and solve the system of equations of (25) to calculate the normalized values of $\Omega_{r,\vec{K}}$.

From the numerical point of view, step (i) is the simplest one and amounts only to a few percent of the total computational efforts. Since the HF bands of PDA's show a relatively simple shape,[63] the only problem in calculating elements of $\underline{G}$ arises from the fact that for more distant neighbors the integrand in Eq. (26) has an oscillatory character due to the exponential factor. We have had, however, very good experience by using for its integration the Gauss-Legendre method which has been applied also in our crystal-orbital calculations to obtain the long-range parts of the density matrix.

The most time consuming part of the calculations is the evaluation of the matrix elements $V^{(v,c)}(\vec{R}_s, \vec{R}_t, \vec{K})$ defined by Eq. (24). For the purpose of the construction of the Fock operators $\hat{F}$, as a first step in the HF calculation, the bielectronic integrals are calculated in terms of atomic basis functions (in our case Gaussians), which are used to construct the Bloch functions. The transformation (17) produces Wannier functions expanded in the same basis set:

$$w_j(\vec{r} - \vec{R}_l) = \sum_t \sum_q f_{qj}(\vec{R}_t - \vec{R}_l) \chi_q(\vec{r} - \vec{R}_t - \vec{R}_q) , \qquad (27)$$

where $\chi_q(\vec{r} - \vec{R}_t - \vec{R}_q)$ is a linear combination (contraction) of Gaussians centered at the position $\vec{R}_q$ in the elementary cell with lattice vector $\vec{R}_t$. The $w_j(\vec{r} - \vec{R}_l)$ itself is centered around the cell $\vec{R}_l$, while the coefficients $f_{qj}(\vec{R}_t - \vec{R}_l)$ give a measure of the extension of the tail over neighboring cells. For an efficient calculation of the e-h interaction matrix elements, it is very important to keep these tails as short as possible. We obtained very reasonably localized Wannier functions in PDA's by making use of the undetermined phase of the φ's as obtained from Eq. (18). Together with a given $\varphi_{j,\vec{k}}$ we obtain, namely, a whole group of eigenfunctions in the form $\widetilde{\varphi}_{j,\vec{k}} = \varphi_{j,\vec{k}} \exp(i\lambda_{j,\vec{k}})$, which belong to all the same eigenvalue. This degree of freedom can be used to influence various properties (symmetry, real or complex nature, localization) of the w's (Refs. 65–68) by an appropriate choice of the phase factor. We found, after comparison of different methods,[68] that the most efficient localization is provided by the maximization of the zero cell contribution of the functional

$$I(\lambda_{j,\vec{k}}) = \int w_j^*(\vec{r}) z^2 w_j(\vec{r}) d^3 r , \qquad (28)$$

where the z axis is identical to the chain direction. This variational procedure provides, besides localization, one more degree of freedom which can be used to keep the w's real (by applying the auxiliary condition $\lambda_{j,\vec{k}} = -\lambda_{j,-\vec{k}}$ in the whole BZ).

The zeros of the function $D(E_{\vec{K}})$ were found finally by

localizing first the regions of its sign change in a preliminary step and then iterating to each solution with a finer mesh. Since $D(E_{\vec{K}})$ turned out to be a rather slowly varying function, a simple interpolation scheme was enough to find its zeros in 8—10 iteration steps with an accuracy of $|D| < 10^{-7}$. The energy values $E_{\vec{K}}$ contain at least five significant digits in eV in this case. The corresponding excitonic wave-function components $\Omega_{r,\vec{K}}$ were obtained by a subsequent solution of the system of homogeneous linear equations. With the above conditions their accuracy was better then four significant digits.

III. ELECTRON CORRELATION EFFECTS IN POLYDIACETYLENES

The first applications of the previously described formalism to calculate excitonic levels in PDA's led to rather disappointing results at the HF level: The excitation energies were still in error of about 2 eV (as we will show in the next section). Since there are basically three important ingredients in the calculation (the one-electron dispersions, the band gap, and the e-h interaction matrix), it was not difficult to find out in test calculations that the position of excitonic levels is most sensitive to the value of the single-particle gap. On the other hand, we know from a number of previous investigations[69-75] that reasonable values for this quantity can be obtained also only if correlation effects are included in the calculations (assuming, of course, that the size of the atomic basis set is properly saturated in this respect).

The most important part of the remaining error in the gap can be eliminated, therefore, only if we take into account the changes in correlation upon creating a hole in the valence band and setting an extra electron into the conduction band. In a previous work[74] we described in more detail how these correction terms can be calculated in the framework of Toyozawa's electron-polaron theory[76] using first-principles matrix elements. The major steps of such a calculation, which have been performed in this work also for the PDA's in question, are the following.

(i) The correlation energy per unit cell of the crystal E_{corr} is calculated using second-order Møller-Plesset perturbation theory (MPPT) as a sum of individual electron-pair contributions (correlation "bonds") $e(i,\vec{k}_i;j,\vec{k}_j)$. Each e contains a large number of contributions from various double-scattering processes of the type $(\varphi_{i,\vec{k}_i}\varphi_{j,\vec{k}_j}) \rightarrow (\varphi_{a,\vec{k}_i+\vec{q}}\varphi_{b,\vec{k}_j-\vec{q}})$, i.e., virtual double excitons.

(ii) The creation of a hole in the valence band means to break first all correlation bonds of the corresponding electron, leading to a negative self-energy correction of the electron in the N-particle system $\Sigma_v^{(N)}(e)$.

(iii) At the same time, the creation of an empty state in the valence band increases the remaining pair correlations in the $(N-1)$-particle system due to extra scattering processes involving the new hole. This gives rise to a hole self-energy in the N-particle system $\Sigma_v^{(N)}(h)$. Since the hole stabilizes itself, less energy is needed for its creation

than without correlation effects, i.e., this correction is always positive.

(iv) If we set an extra electron into a conduction band state, it establishes first its correlation bonds with the particles in the filled valence band. This is the electronic self-energy in the $(N+1)$-particle system $\Sigma_c^{(N+1)}(e)$ which is always negative.

(v) Finally, the occupation of a state which has been empty in the N-particle system reduces the number of possible scatterings and, therefore, the pair correlations in the $(N+1)$-particle system are smaller than in the N-particle system. This gives rise to a positive hole self-energy correlation $\Sigma_c^{(N+1)}(h)$.

In terms of the above terminology, each particle in the solid is surrounded by a cloud of virtual excitons constituting its pair correlations, i.e., the bare HF particles are transformed to polarons. The corresponding quasiparticle energies can be obtained as ionization potentials and electron affinities of the correlated N-particle system. Collecting the above discussed contributions, we obtain for the energy of a polaron in the quasiparticle valence band

$$\epsilon_v(\mathrm{polaron}) = \epsilon_v(\mathrm{HF}) + \Sigma_v^{(N)}(e) + \Sigma_v^{(N)}(h) , \qquad (29)$$

and in the new conduction band

$$\epsilon_c(\mathrm{polaron}) = \epsilon_c(\mathrm{HF}) + \Sigma_c^{(N+1)}(e) + \Sigma_c^{(N+1)}(h) . \qquad (30)$$

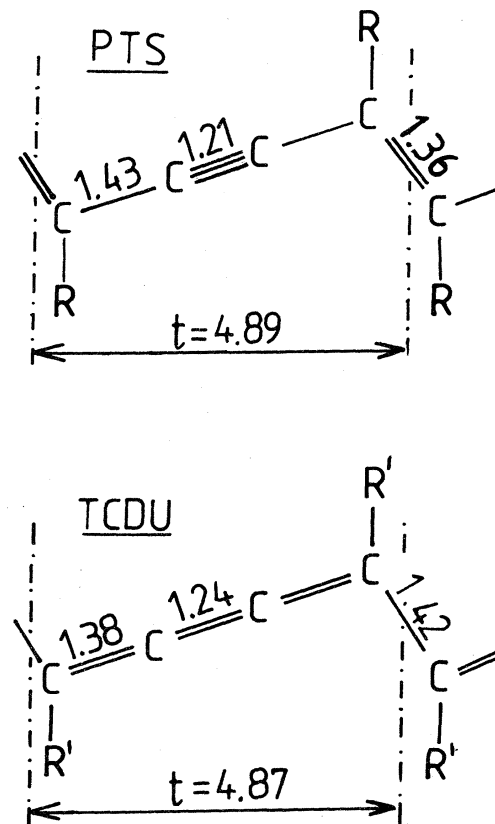We performed the calculations with the above outlined

FIG. 1. Geometrical structure of the unit cell for the PTS and TCDU backbones, respectively, used in the calculations (distances are given in Å).

TABLE I. Total energy per elementary cell calculated with two different atomic basis sets at the HF and correlated levels. E_{corr} is obtained by second-order MPPT and ΔE is the energy needed for the PTS$\rightarrow$TCDU backbone structural transition.

	E_{PTS} (a.u.)	E_{TCDU} (a.u.)	ΔE (kcal/mole)
HF/STO-3G	-150.5735	-150.5553	11.42
HF/6-31G**	-152.5215	-152.5074	8.85
E_{corr}/STO-3G	-0.271032	-0.276132	-3.20
E_{corr}/6-31G**	-0.544208	-0.549168	-3.11
$E_{HF}+E_{corr}$/STO-3G	-150.8445	-150.8314	8.21
$E_{HF}+E_{corr}$/6-31G**	-153.0657	-153.0566	5.74

method both for the PTS and TCDU backbones of PDA. The side groups have been substituted, as in previous work,[63] by hydrogen atoms. The geometrical structure of the two polymers, shown in Fig. 1, was taken from Ref. 53 for PTS and from Ref. 54 for TCDU, respectively. The first quantity of interest from these results is the total energy per elementary unit in the crystal characterizing the stability of the polymer chains. It is calculated as the sum of electronic and nuclear contributions. Its electronic part has been obtained in this work at two different levels, without correlation ($E = E_{HF}$) and including correlation effects ($E = E_{HF} + E_{corr}$). To calculate E_{corr} only virtual excitations within the valence shell have been taken into account since we are not interested in this work in processes involving core electrons. The values given below for E_{corr} refer, therefore, to the valence-shell correlation energy. The infinite lattice sums had to be performed in direct space with a radius of 16 unit cells to obtain convergent results in the case of the minimal basis.[63] In the meantime, we worked out a more efficient procedure for this summation[64] which results in convergent total energies if the interactions are summed up until the fifth-neighboring diacetylene unit. This program has been used for the calculations with an extended basis set.

To demonstrate the importance of the size of the atomic basis set, especially in the correlation part, we present in Table I results which have been obtained with a minimal basis [expanding the $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals into a linear combination of three Gaussians, STO-3G (Ref. 77)] and with an extended one [containing for carbon six Gaussians for $1s$, four Gaussians for $2s$, and the $2p$'s contracted in a double-ξ manner and five d's: for hydrogen again four s-type Gaussians in a double-ξ contraction and a set of p functions 6-31, G** (Refs. 78 and 79)]. It must be mentioned that according to our previous estimates,[73–75] the latter basis covers in second-order MPPT approximately 70—75% of the full valence-shell correlation in polymers which gives a sound basis to discuss various physical properties in these systems. Two conclusions can be drawn from Table I.

(i) The transition energy very sensitively depends on both the basis set and correlation effects which reduce its value from 11—12 kcal/mole (predicted earlier also by other HF calculations[80]) to 5—6 kcal/mole.

(ii) This latter value is sufficiently small that the energy gain through hydrogen bonds, formed between the side groups of TCDU, can compensate for it and thus lead to a stable crystal structure as proposed by Enkelmann and Lando.[54]

Turning now to the polaron energies entering the Green's function, we present first in Table II the values of the correction terms obtained at the extrema of the conduction and valence bands, respectively, using the extended basis set [in fact, these corrections have been calculated for five points in each band and have been fitted by a trigonometric polynomial to obtain a fine mesh in the BZ for the calculation of the matrix G in Eq. (26)]. As we can see from Table II, the self-energies follow the previously discussed general trends and shift together [according to Eqs. (29) and (30)] the conduction band to lower energies and the valence band to higher energies, respectively. We also observe that the shift $\Sigma_c^{(N+1)}(e) + \Sigma_c^{(N+1)}(h)$ is larger at the top than at the bottom of the conduction band, leading to an effective band narrowing. At the same time, the terms $\Sigma_v^{(N)}(e) + \Sigma_v^{(N)}(h)$ produce a stronger shift at the bottom of the valence band than at its top. This situation is analogous to the Franck-Condon effect in phonon-polaron theory.

We present the obtained band extrema and bandwidths for both systems in Table III. It can be seen that the polaron corrections are really substantial ones reducing the forbidden gap by more than 2 eV. The significant changes of ~ 1.2 eV due to correlation in the ionization potentials (IP) (IP $= -\epsilon_{v,max}$) should also be noted. The changes in band positions and bandwidths of the PTS polymer due to basis-set improvement and inclusion of correlation are shown schematically in Fig. 2 (the situation is very similar for TCDU). According to our previous experience with a number of basis sets with gradually

TABLE II. Self-energy corrections to the HF band eigenvalues calculated by the use of second-order MPPT and the extended 6-31G** atomic basis set (all energies in eV).

		PTS	TCDU
$\Sigma_c^{(N+1)}(e)$	CB max.	-1.652	-1.596
	CB min.	-1.179	-1.126
$\Sigma_c^{(N+1)}(h)$	CB max.	0.267	0.340
	CB min.	0.184	0.231
$\Sigma_v^{(N)}(e)$	VB max.	-0.592	-0.625
	VB min.	-0.883	-0.936
$\Sigma_v^{(N)}(h)$	VB max.	1.724	1.834
	VB min.	2.518	2.626

increasing quality,[73-75] in polymers of this type the values of one-electron levels are practically converged with respect to basis extension at the 6-31 G** level. We can see that the minimal basis very inaccurately represents both bandwidths and forbidden gaps even at the one-electron level. The correlation influences, on the other hand, mostly the value of the gap. It should be noted that inclusion of correlation at the minimal basis level (not shown on the diagram) does not solve the problem: the gap of 8.6 eV is reduced only by less than 1 eV. The use of basis sets of this type should be, therefore, avoided if physical properties closely related to the band structure are investigated.

IV. CALCULATION OF THE EXCITON SPECTRA IN POLYDIACETYLENES

Since the band-structure calculations which form the starting point for the investigation of the exciton spectrum have been performed at the restricted HF level (setting for the same spatial Bloch orbital two electrons with opposite spin) also the Wannier functions as obtained from Eq. (27) conserve this closed-shell property. The e-h pair wave functions $\Psi_{l+s,l}^{(v,c)}$ are, therefore, eigenfunctions of the component of the total spin in the direction of the axis of the quantization. Since the Hamiltonian applied does not contain spin-dependent terms we can take linear combinations of the e-h determinants to form eigenfunctions of a definite spin multiplicity. Substituting the appropriate combinations for singlet and triplet states, respectively, we obtain after simple algebra[55] for the elements of $\underline{V}$ in Eq. (24):
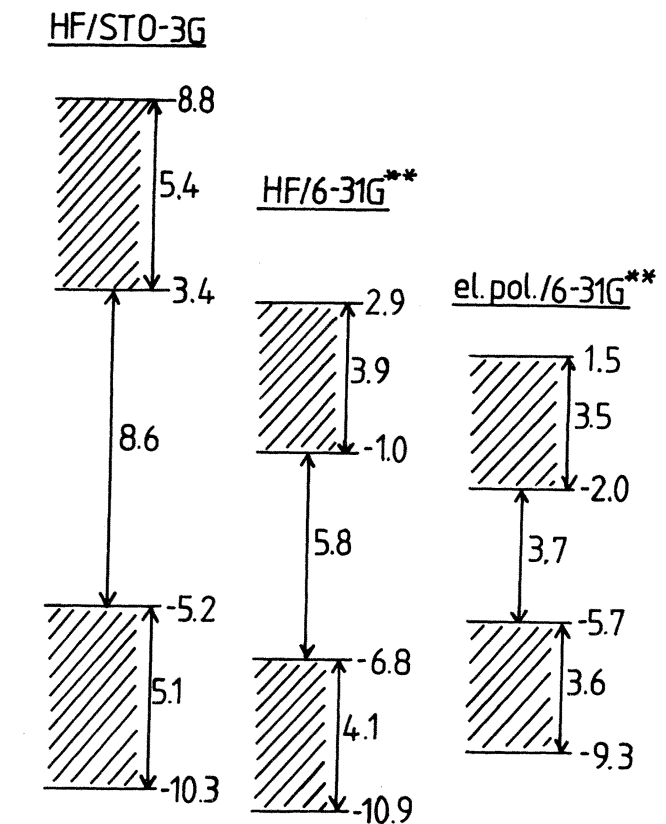

FIG. 2. Effect of basis set improvement (STO-3G to 6-31G**) at the HF level and the importance of correlation (HF to electron polaron) demonstrated on the VB and CB structure of the PTS polymer (all energy values are given in eV).

$$^M V^{(v,c)}(\vec{R}_s,\vec{R}_t,\vec{K}) = - \sum_u \exp(-i\vec{K}\cdot\vec{R}_u) \left[\bar{g} \begin{vmatrix} s+u & 0 \\ c & v \end{vmatrix} \begin{vmatrix} u & t \\ v & c \end{vmatrix} - 2\delta_M \bar{g} \begin{vmatrix} 0 & s+u \\ v & c \end{vmatrix} \begin{vmatrix} u & t \\ v & c \end{vmatrix} \right].$$

(31)

The definition of the bielectronic four-center integrals $\bar{g}$ is the same as those of g in Eq. (8) except for the difference that instead of spin orbitals here only the spatial part of the Wannier functions is used. For true singlet states $\delta_M = 1$ and for triplets $\delta_M = 0$. The lattice sum over $\vec{R}_u$ in Eq. (31) is not a problematic one. The first "Coulomb-type" integral contains exponentially decaying charge distributions on both electrons. The second one (appearing only for singlet excitons) is, from the point of view of the

e-h pair, an exchange contribution but it can be regarded also as a Coulomb-type interaction between two neutral charge clouds. Its leading part is the dipole-dipole coupling, therefore, one does not expect serious problems with its summation. In fact, we obtained reasonably converged results for the exciton energy by letting the index u run until the fifth cellular neighbor. Owing to the tails of the Wannier functions and the fact that their centers are shifted to each other for both electrons, integrals over atomic

TABLE III. Band extrema ($\epsilon_{j,min}, \epsilon_{j,max}$), bandwidths ($\delta\epsilon_j$), and forbidden gaps ($\Delta E_g$) calculated at the HF level and using the electron-polaron model (all energies in eV).

| | PTS | | TCDU | |
	HF	Electron polaron	HF	Electron polaron
$\epsilon_{c,max}$	2.891	1.506	3.754	2.498
$\epsilon_{c,min}$	−1.021	−2.016	−0.924	−1.819
$\delta\epsilon_c$	3.912	3.522	4.678	4.317
$\epsilon_{v,max}$	−6.812	−5.680	−6.211	−5.002
$\epsilon_{v,min}$	−10.940	−9.305	−11.121	−9.431
$\delta\epsilon_v$	4.128	3.625	4.910	4.429
ΔE_g	5.791	3.664	5.287	3.183

TABLE IV. The lowest singlet-exciton energies (at $K=0$) for two polydiacetylene structures obtained by including excitations until the nth neighboring unit cell both at the HF and electron-polaron levels, respectively (all energies in eV).

	PTS		TCDU	
n	HF	Electron polaron	HF	Electron polaron
0	5.282	3.206	4.762	2.901
1	4.718	2.624	4.275	2.317
2	4.319	2.211	3.854	1.925
3	4.107	1.958	3.672	1.550
4	3.994	1.823	3.548	1.392
5	3.965	1.791	3.514	1.366

orbitals must be included until ten neighboring elementary cells. It should be noted here, however, that the dominance of the exchange term (called also "excitation transfer" interaction[55]) in long-range effects is not ab ovo clear since also the first integral in Eq. (31) contains far reaching contributions when near diagonal $(\vec{R}_s \sim \vec{R}_t)$ elements of $\underline{V}$ are calculated. On the other hand, the off-diagonal elements of the Green's function in Eq. (25) decay very fastly, so that the spatial extension of the exciton is determined by the long-range contributions in $\underline{V}$. The lowest singlet exciton energies obtained for both polymers at $K=0$ are presented in Table IV as functions of the number of neighbors for which the exciton is delocalized. We can make the following observations on the basis of these results.

(i) The Frenkel exciton $(n=0)$ represents only a relatively small part of the e-h binding energy ($\sim 30\%$ on the average) for all cases. The exciton must be delocalized at least with a radius of 25—30 Å in the crystal to obtain reasonably convergent excitation energies. This is a consequence of the spread of the wave-function components $\Omega_{s,K}$ which are shown, as a typical example, for the case of PTS singlet excitons in Fig. 3.

(ii) The electron-polaron correction to the HF bands changes fundamentally the exciton energy by reducing its value for both polymers by ~ 2.1 eV. This change is

caused basically by the band-shifting effect of correlation; the band narrowing plays only a secondary role in it.

(iii) The excitation energy obtained for TCDU is in both the HF and electron-polaron schemes lower by ~ 0.4 eV than that of PTS. This difference is similar to but somewhat smaller than the one observed also for the corresponding single-particle gaps (~ 0.5 eV) and seems to be related to the phase differences, observed also in previous works,[43,63,80] in the in-phase and out-of-phase combinations of the π atomic orbitals of the "-yne"- and "-ene"-type bonds in PDA's, respectively.

We can see from these results that the inclusion of polarization-screening effects during the formation of the extra electron and hole states influences profoundly the properties of the exciton. There remains, however, the question to be answered, how does polarization change the e-h interaction by screening $\underline{V}$? The proper solution of this problem presumes the knowledge of the position-dependent dielectric function $\epsilon(\vec{r},t)$ if we are working with integrals over Wannier functions in direct space. Different methods have been proposed for the evaluation of the Fourier transformed of this important quantity, $\epsilon(\vec{q},\omega)$.[81−84] Their implementation at a level of sophistication compatible with the above calculations is a rather intricate problem whose solution is in progress in our laboratory. In terms of this dielectric function, however, we can perform the following preliminary qualitative analysis which shows also the order of magnitude of the corrections we can expect from this side. Taking, for instance, $\epsilon(\vec{q},\omega)$ in the random phase approximation (RPA) as

$$\epsilon_{RPA}(\vec{q},w)=1+\frac{4\pi}{q^2}$$
$$\times \sum_v \sum_c \sum_{\vec{k}} \frac{|\langle \varphi_{c,\vec{k}}|e^{-i\vec{q}\cdot\vec{r}}|\varphi_{v,\vec{k}+\vec{q}}\rangle|^2}{\epsilon_{c,\vec{k}}-\epsilon_{v,\vec{k}+\vec{q}}-\hbar w},$$
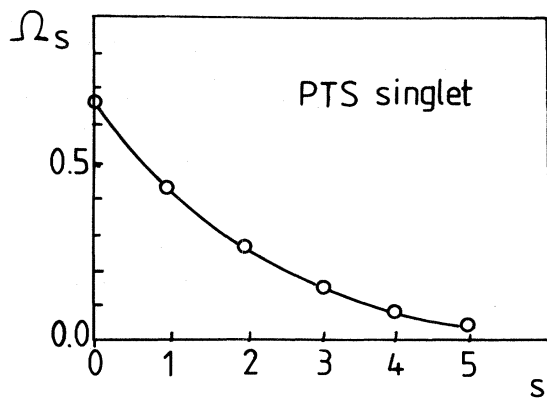
(32)

FIG. 3. Components $\Omega_{s,\vec{K}=\vec{0}}$ of the singlet-exciton wave function in neighboring elementary cells of the PTS crystal calculated with the help of the Green's function of the electron-polaron model.

it can be easily proved[85] that $\epsilon_{RPA}(\vec{q},0)$ converges to a finite ϵ_0 for small values of $\vec{q}$, while it drops rapidly to 1 after a few reciprocal-lattice vectors. This means in terms of our direct space e-h interaction that until the electron and hole share the same elementary cell, no screening of $\underline{V}$ occurs, while for large e-h separations the dielectric constant ϵ_0 can be used. The most interesting is, of course,

the intermediate region of a few elementary cells where the excitonic wave function drops gradually to zero as shown by Fig. 3. Until a more accurate $\epsilon(r)$ will be available, we can make use of the interpolation scheme proposed by Hermanson and Phillips[86,87] by writing

$$\epsilon^{-1}(r) = \epsilon_0^{-1} + [(\epsilon_0 - 1)/\epsilon_0] \exp(-Qr) , \qquad (33)$$

where Q^{-1} plays the role of a characteristic "breakdown" length for dielectric effects. Q is a phenomenological constant related to the Thomas-Fermi wave number[85] and in these calculations we have used for it the value $Q = a^{-1}$ where a is the lattice constant. The screening has been taken into account at the level of the integrals over atomic orbitals (AO's). Since the product of the two Gaussians is again a Gaussian centered for each electron in the weighted middle point of the AO's,[88] we have used the distance of these middle points in calculating the screening between neighboring cells according to Eq. (33). Since the precise value of ϵ_0 belonging to the backbones of PDA's is not known, we have performed these calculations for $\epsilon_0 = 2$, 3, and 5.

The results obtained for both PTS and TCDU are shown in Fig. 4. We can see that around the expected value of $\epsilon_0 \sim 3$ the binding energy of the e-h pair is substantially reduced, the singlet level at $K = 0$ is shifted from 1.79 to 2.16 eV for PTS and from 1.37 to 1.74 eV for TCDU, respectively. The difference between the PTS and

TCDU values, on the other hand, is nearly independent of screening. These results suggest that the first-singlet absorption maximum of PTS should be around 2.1–2.2 eV while that of TCDU is at 1.7–1.8 eV. The width of the exciton band is ~ 2.9 eV for PTS and ~ 3.5 eV for TCDU. There exist also triplet-type solutions to Eq. (25) for both systems. The corresponding exciton bands are relatively flat and start at $^3E_{K=0} = 0.87$ and 0.56 eV for PTS and TCDU, respectively. We did not recalculate the triplet levels using screening but we expect for them a shift similar to that observed for singlets.

V. DISCUSSION AND CONCLUSIONS

The main purpose of this study has been the evaluation of the excitonic levels in an organic solid from first-principles formulation without using any empirically adjusted parameters. Since, according to our knowledge, this is the first attempt in this direction, it may be useful to recapitulate the main steps and approximations made in these calculations, before we compare our results with experiments. The critical evaluation of these approximations gives a hint for the limit of reliability of the results but it also shows how the calculations could be refined in the future.

The exciton states have been calculated in three major steps in this work.

(i) As a zeroth-order wave function, a HF determinant has been calculated for the infinite crystal using a linear combination of atomic orbitals Bloch functions.

(ii) Electron-electron correlation effects, missing from the one-particle picture, have been introduced using Toyozawa's electron-polaron model and second-order MPPT.

(iii) The energy levels of charge-transfer excitons have been found, finally, by treating the electron-hole attraction as a perturbation in the framework of the Lax-Koster-Slater resolvent formalism.

Step (i) is the most straightforward one in studies of this kind. If technical problems such as the handling of a large number of AO integrals and the proper truncation of infinite lattice sums are solved, the only open question here is the size of the AO basis set to be used to expand the Bloch functions. This is certainly system dependent and the proper saturation of the basis must be separately tested for different crystal types. We have found that for hydrocarbon crystals the extended spd set described in Sec. III gives a satisfactory accuracy at the HF level. The inclusion of further (f-type) polarization functions would, of course, further reduce the total energy toward the HF limit, but a number of physically relevant quantities such as one-particle levels, relative conformational energies, etc. would not significantly change in going beyond the spd basis.[64,74,75]

The second step is, on the other hand, a really sophisticated problem and its more accurate solution requires improvements at least in three directions in the future.

(a) According to our previous experience,[73] the basis set must be expanded with further polarization functions to
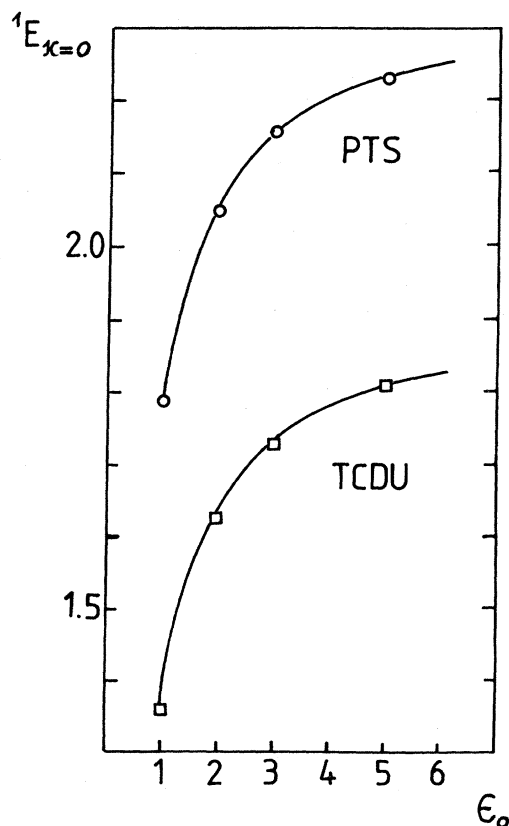

FIG. 4. Effect of dielectric screening on the singlet-exciton energies at $K = 0$. The matrix elements of the e-h interaction have been screened using different values of ϵ_0 in Eq. (33).

obtain the missing part of correlation. At the same time, one must go also beyond second order in perturbation theory. We hope that by using an infinite summation scheme over selected diagrams (which seem to be especially important in infinite systems) it will be possible in the future to cover the major part of the missing $\sim 25-30\%$ of correlation energy. It must be noted, however, that the influence of correlation effects on physical quantities such as the quasiparticle gap is not simply proportional to the correlation content in the wave function. A more systematic study of this problem in the case of polyacetylenes[74] has shown that the corrections become smaller and smaller with increasing correlation and an extrapolation of the results from ~ 70 to 100% reduces the gap only by ~ 0.5 eV.

(b) It must be taken into account, furthermore, that in calculating polaron corrections the HF orbitals of the N-particle system have been used to construct approximate $(N + 1)$-particle wave functions. Though the missing relaxation contributions are probably not large in the outer valence region of the infinite system, they could still somewhat modify the gap. Their calculation using the Green's-function approach is in progress.

(c) Besides electronic correlation, we expect similar polarization effects between electrons (holes) and high-frequency optical phonons (involving especially bond-length modifications) which may lead to the formation of phonon-polaron states with a binding energy of a few tenths of an eV. The above-mentioned three important corrections reduced the quasiparticle gap in polyacetylene by ~ 1 eV (from ~ 3 to ~ 2 eV).[74] Assuming similar corrections also in PDA's, our calculations would predict a gap of 2.5–2.6 eV in PTS and 2–2.1 eV in TCDU, respectively.

The last part of our calculation, step (iii), in the above-mentioned list, involves two major approximations. The first is the restriction to a two-band model. It can be easily seen that even in expanding the field operators in Eqs. (2) and (3) all valence and conduction bands would have been used, the anticommutation of the $a, a^\dagger$ operators belonging to different valence and conduction bands, respectively, would decouple the problem by introducing factors of the type $\delta_{c,c'} \cdot \delta_{v,v'}$ into the matrix elements of the one-particle Green's function. For a more accurate description, therefore, the use of two-particle Green's functions is necessary.

The second approximation here is the use of a phenomenologically determined dielectric function. This made only the estimation of the order of magnitude of screening effects possible. Since the calculation of $\epsilon(\vec{r}, t)$ for PDA's will soon be finished in our laboratory, this part of the calculations will be repeated in the near future to obtain a more appropriate description of this important effect.

As the previously shown details of our results prove, the excitons in both PDA structures are strongly delocalized. The importance of these charge-transfer components has been established previously also in semiempirical π-electron calculation at the Pariser-Parr-Pople level by Philpott[41] in the case of PTS and by Yarkony[43] for both

crystals, though the quantitative details of their results are different from the present ones. Other semiempirical calculations reproduced the band gap at the Hückel[89−91] and $X\alpha$ levels,[92] respectively, without invoking excitonic effects. It is interesting to note, however, that all calculations performed for infinite PDA crystals (including those aiming only at band structures without excitonic effects[63,80,93,94]) predict a larger gap for the butatriene structure than for the diacetylene structure.

Turning now to the comparison of our results with experiments, we note first that different groups agree without exception in the interpretation of the absorption edge at ~ 2 eV in PTS as an excitonic transition. There is a slight uncertainty about the size of the band-to-band gap since in the photon energy region comparable to the gap the processes of creating a bound electron-hole pair (exciton) and a free-charge carrier pair compete with each other. The analysis of the corresponding photoresponse curves is further complicated by temperature effects (possible phase transitions) and by disorder. The comparison of recent results obtained from optical absorption and dc photoconductivity measurements[95−101] indicates that the gap should be in the region of 2.1–2.5 eV. It is to be noted, however, that the upper limit is much more probable since if the excitonic absorption peak would be situated close to the comparatively broad conduction band, its intensity would be much smaller than the observed one. This view is supported by recent electroreflectance studies which relate a strong signal at ~ 2.4 eV in PTS to the fundamental gap.[39] There seems to be, however, general agreement among experimentalists that "a successful interpretative separation of these two processes which would lead to a conclusive determination of the band-gap energy ΔE_g, still remains one of the most important unanswered questions regarding the electronic structure of PTS."[100] It should be remarked in this respect that from the two factors determining the gap (IP and electron affinity) the theoretical value of the former is more reliable and its value of 5.68 eV, obtained for PTS in this work, is in reasonable agreement with experiment [IP$=5.5\pm0.1$ eV (Ref. 40)]. The larger inaccuracy in theoretical electron affinities is related to the previously discussed problem of the nonvariational determination of conduction-band states.

The experimental situation is less clear in the case of TCDU crystals. In earlier work, the higher-absorption energy (as compared with the PTS spectrum) has been assigned to the butatriene-type bonding sequence of this polymer.[13,15,20,28] This assignment is not supported by our results predicting a transition in TCDU which is 0.4 eV lower in energy than the corresponding one in PTS. In fact, another investigation of this problem has also led to the conclusion that the higher-absorption maxima in the high-temperature phases of TCDU are due to distortion of the polymer backbone rather than being a consequence of the diacetylene-to-butatriene phase transition.[33]

The role of such structural deformations in the optical behavior of these polymers together with pressure and strain effects in PDA (Refs. 102−105) is under investigation in our laboratory using the above-described theoretical method. Including also terms into our Hamiltonian

which describe the interaction between the exciton and the electromagnetic field, calculations using the Green's-function formalism are also in progress for the polariton spectra and for nonlinear-optical effects in PDA's.

ACKNOWLEDGMENTS

*Present address: Deutsches Krebsforschungszentrum (German Cancer Research Center), Im Neuenheimer Feld 280, D-6900 Heidelberg, West Germany.

[1] D. Bloor, D. J. Ando, F. H. Preston, and G. C. Stevens, Chem. Phys. 24, 407 (1974).

[2] D. Bloor, G. C. Stevens, P. J. Page, and P. M. Williams, Chem. Phys. Lett. 33, 51 (1975).

[3] B. Reimer and H. Bassler, Phys. Status Solidi A 32, 435 (1975).

[4] D. N. Batchelder and D. Bloor, Chem. Phys. Lett. 38, 37 (1976).

[5] D. Bloor, F. H. Preston, and D. J. Ando, Chem. Phys. Lett. 38, 33 (1976).

[6] D. Bloor and F. H. Preston, Phys. Status Solidi A 37, 427 (1976); 37, 607 (1976).

[7] D. Bloor, Chem. Phys. Lett. 42, 174 (1976).

[8] R. R. Chance and R. H. Baughman, J. Chem. Phys. 64, 3889 (1976).

[9] B. Reimer, H. Bässler, J. Hesse, and G. Weiser, Phys. Status Solidi B 73, 709 (1976).

[10] K. Lochner, B. Reimer, and H. Bässler, Phys. Status Solidi B 76, 533 (1976).

[11] J. Knecht, B. Reimer, and H. Bässler, Chem. Phys. Lett. 49, 327 (1977).

[12] V. Enkelmann and G. Wegner, Makromol. Chem. 178, 635 (1977).

[13] Z. Iqbal, R. R. Chance, and R. H. Baughman, J. Chem. Phys. 66, 5520 (1977).

[14] R. R. Chance, R. H. Baughman, H. Müller, and C. J. Eckhardt, J. Chem. Phys. 67, 3616 (1977).

[15] H. Müller, C. J. Eckhardt, R. R. Chance, and R. H. Baughman, Chem. Phys. Lett. 50, 22 (1977).

[16] D. Bloor and F. H. Preston, Phys. Status Solidi A 39, 607 (1977).

[17] D. Bloor and F. H. Preston, Phys. Status Solidi A 40, 279 (1977).

[18] H. Müller and C. J. Eckhardt, J. Chem. Phys. 67, 5386 (1977).

[19] B. Tieke, H. J. Graf, G. Wegner, B. Naegele, H. Ringsdorf, A. Banerkee, D. Day, and J. B. Lando, Colloid Polym. Sci. 255, 521 (1977).

[20] R. J. Hood, H. Müller, C. J. Eckhardt, R. R. Chance, and K. C. Yee, Chem. Phys. Lett. 54, 295 (1978).

[21] R. Jankowiak, J. Kalinowski, B. Reimer, and H. Bässler, Chem. Phys. Lett. 54, 483 (1978).

[22] A. Brillante, I. Pickrand, M. R. Philpott, and J. D. Swalen, Chem. Phys. Lett. 57, 395 (1978).

[23] G. C. Stevens, D. Bloor, and P. M. Williams, Chem. Phys. 28, 399 (1978).

[24] D. Bloor and C. L. Hubble, Chem. Phys. Lett. 56, 89 (1978).

[25] L. Sebastian and G. Weiser, Chem. Phys. Lett. 64, 396 (1979).

[26] G. N. Patel, R. R. Chance, and J. D. Witt, J. Chem. Phys. 70, 4397 (1979).

[27] H. Eckhardt, C. J. Eckhardt, and K. C. Yee, J. Chem. Phys. 70, 5498 (1979).

[28] R. R. Chance, G. N. Patel, and J. D. Witt, J. Chem. Phys. 71, 206 (1979).

[29] M. L. Shand, R. R. Chance, and R. Silbey, Chem. Phys. Lett. 64, 448 (1979).

[30] K. Lochner, H. Bässler, H. Sowa, and H. Ahsbahs, Chem. Phys. 52, 179 (1980).

[31] R. J. Kennedy, I. F. Chalmers, and D. Bloor, Macromol. Chem. 1, 357 (1980).

[32] R. R. Chance, K. C. Yee, R. H. Baughman, H. Eckhardt, and C. J. Eckhardt, J. Polym. Sci. Polym. Phys. Ed. 18, 1651 (1980).

[33] R. R. Chance, Macromolecules 13, 396 (1980).

[34] R. R. Chance, M. L. Shand, C. Hogg, and R. Silbey, Phys. Rev. B 22, 3540 (1980).

[35] G. N. Patel, J. D. Witt, and Y. P. Khawna, J. Polym. Sci. Polym. Phys. Ed. 18, 1383 (1980).

[36] D. Bloor, D. N. Batchelder, D. J. Ando, R. T. Read, and R. J. Young, J. Polym. Sci. Polym. Phys. Ed. 19, 321 (1981).

[37] D. N. Batchelder, R. J. Kennedy, and D. Bloor, J. Polym. Sci. Polym. Phys. Ed. 19, 677 (1981).

[38] L. Sebastian and G. Weiser, Phys. Rev. Lett. 46, 1156 (1981).

[39] L. Sebastian and G. Weiser, Chem. Phys. 62, 447 (1981).

[40] A. A. Murashov, E. A. Silinsh, and H. Bässler, Chem. Phys. Lett. 93, 1481 (1982).

[41] M. R. Philpott, Chem. Phys. Lett. 50, 18 (1977).

[42] N. A. Cade, Chem. Phys. Lett. 53, 45 (1978).

[43] D. R. Yarkony, Chem. Phys. 33, 171 (1978).

[44] K. Balasubramanian and D. R. Yarkony, Chem. Phys. Lett. 70, 374 (1980).

[45] G. Wegner, Z. Naturforsch. 24B, 824 (1969).

[46] E. Hädicke, E. C. Mez, C. H. Krauch, G. Wegner, and J. Kaiser, Angew. Chem. Int. Ed. Engl. 10, 266 (1971).

[47] J. Kaiser, G. Wegner, and E. W. Fischer, Isr. J. Chem. 10, 157 (1972).

[48] W. Schermann and G. Wegner, Makromol. Chem. 175, 407 (1974).

[49] R. H. Baughman and R. R. Chance, Ann. Acad. Sci. (N.Y.) 313, 705 (1978).

[50] G. Wegner, in Molecular Metals, edited by W. E. Hatfiled (Plenum, New York, 1979), p. 209.

[51] V. Enkelmann, in Recent Advances in the Quantum Theory of

    Polymers, edited by J.-M. André, J.-L. Brédas, J. Delhalle, J. Ladik, G. Leroy, and C. Moser (Springer, Berlin, 1980), p. 1.

[52]D. Bloor, in *Recent Advances in the Quantum Theory of Polymers,* edited by J.-M. André, J.-L. Brédas, J. Delhalle, J. Ladik, G. Leroy, and C. Moser (Springer, Berlin, 1980), p. 14.

[53]D. Kobelt and E. F. Paulus, Acta Crystallogr. Sect. B 30, 232 (1973).

[54]V. Enkelmann and B. J. Lando, Acta Crystallogr. Sect. B 34, 2352 (1978).

[55]R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).

[56]Y. Takeuti, Prog. Theor. Phys. 18, 421 (1957); Suppl. 12, 75 (1959).

[57]M. Lax, Phys. Rev. 94, 1391 (1954).

[58]G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).

[59]M. Altarelli and B. F. Bassani, J. Phys. C 4, L328 (1971).

[60]M. Kertész, Chem. Phys. 44, 349 (1979).

[61]A. L. Fetter and J. D. Valecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[62]H. Haken, *Quantenfeldtheorie des Festkörpers* (Teubner, Stuttgart, 1973).

[63]S. Suhai, Chem. Phys. 54, 91 (1980); Solid State Commun. (to be published).

[64]S. Suhai, J. Chem. Phys. (to be published).

[65]E. I. Blount, Solid State Phys. 13, 305 (1969).

[66]J. Des Cloizeaux, Phys. Rev. 135, A685 (1964); 135, A698 (1964).

[67]M. Kertész and G. Biczó, Phys. Status Solidi B 60, 249 (1973).

[68]S. Suhai (unpublished).

[69]A. B. Kunz, Phys. Rev. B 6, 606 (1972).

[70]J. T. Devreese, A. B. Kunz, and T. C. Collins, Solid State Commun. 11, 670 (1972).

[71]D. J. Mickish, A. B. Kunz, and T. C. Collins, Phys. Rev. B 9, 4461 (1974).

[72]S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B 10, 2602 (1974).

[73]S. Suhai, Int. J. Quantum. Chem. 23, 1239 (1983).

[74]S. Suhai, Phys. Rev. B 27, 3506 (1982).

[75]S. Suhai, Chem. Phys. Lett. 96, 619 (1983).

[76]Y. Toyozawa, Prog. Theor. Phys. 12, 422 (1954).

[77]W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969).

[78]R. Ditchfield, J. W. Hehre, and J. A. Pople, J. Chem. Phys. 54, 726 (1971).

[79]To calculate atomic integrals over Gaussians we make use of subroutines and the basis function library of the GAUSSIAN 76 program system developed by J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, and J. A. Pople, Quantum Chemistry Program Exchange (Bloomington, Indiana), program No. 368 (unpublished).

[80]A, Karpfen, J. Phys. C 13, 5673 (1980).

[81]W. Kohn, Phys. Rev. 110, 857 (1958).

[82]H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

[83]S. L. Adler, Phys. Rev. 126, 413 (1962).

[84]N. Wiser, Phys. Rev. 129, 62 (1963).

[85]D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1964), p. 146.

[86]J. Hermanson and J. C. Phillips, Phys. Rev. 150, 652 (1966).

[87]J. Hermanson, Phys. Rev. 150, 660 (1966).

[88]See, for example, V. R. Saunders, in *Computational Techniques in Quantum Chemistry and Molecular Physics,* edited by G. H. F. Diercksen, B. T. Sutcliffe, and A. Veillard (Reidel, Dordrecht, 1975), p. 347.

[89]E. G. Wilson, J. Phys. C 8, 727 (1975).

[90]D. E. Perry, Chem. Phys. Lett. 43, 597 (1976).

[91]C. Cojan, A. P. Agarwal, and C. Flytanis, Phys. Rev. B 15, 909 (1977).

[92]D. S. Boudreaux, Chem. Phys. Lett. 38, 341 (1976).

[93]M. Kertész, J. Koller, and A. Azman, Chem. Phys. 27, 273 (1978).

[94]J.-L. Brédas, R. R. Chance, R. Silbey, G. Nicolas, and Ph. Durand, J. Chem. Phys. 75, 255 (1981).

[95]B. Reimer and H. Bässler, Phys. Status Solidi B 85, 145 (1978).

[96]K. Lochner, H. Bassler, B. Tieke, and G. Wegner, Phys. Status Solidi B 88, 653 (1978).

[97]A. S. Siddiqui and E. G. Wilson, J. Phys. C 12, 4237 (1979).

[98]K. J. Donovan and E. G. Wilson, J. Phys. C 12, 4857 (1979).

[99]A. S. Siddiqui, J. Phys. C 13, L1079 (1980).

[100]A. S. Siddiqui, J. Phys. C 13, 2147 (1980).

[101]E. G. Wilson, Chem. Phys. Lett. 90, 221 (1981).

[102]D. N. Batchelder and D. Bloor, J. Phys. C 11, L629 (1978).

[103]A. C. Cottle, W. F. Lewis, and D. N. Batchelder, J. Phys. C 11, 605 (1978).

[104]D. Bloor, D. N. Batchelder, and D. J. Ando, J. Polym. Sci. Polym. Phys. Ed. 19, 321 (1981).

[105]D. N. Batchelder, R. J. Kennedy, and D. Bloor, J. Polym. Sci. Polym. Phys. Ed. 19, 677 (1981).