Quasiparticle energy-band structures in semiconducting polymers: Correlation effects on the band gap in polyacetylene

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Single- and many-particle effects contributing to the formation of energy-band gaps in semiconducting polymers are investigated using exact-exchange Hartree-Fock (HF) theory and Toyozawa's electronic-polaron model. The electron correlation is calculated by Møller-Plesset perturbation theory including explicitly all significant matrix elements in second order. Their efficient calculation is facilitated by the use of optimally localized Wannier functions. The importance of both short- and long-range contributions, of extended atomic basis sets, and of the use of the full virtual space is exhibited in the case of *trans*-polyacetylene (PA) as a model system. Correlation effects are shown to reduce the single-particle energy-band gap first by diminishing the bond alternation in PA. On the other hand, due to the self-energy corrections, the HF energy-band states are transformed to quasiparticle (electronic-polaron) states, the valence band is shifted upward, and the conduction band is shifted downward. The original HF energy-band gap of 5 eV is reduced to 3 eV at an estimated level of 70—75 % of valence-shell correlation. Its extrapolated value for full correlation is found to be 2.5 eV. The remaining 0.5-eV difference between theory and experiment is assigned to phonon-polaron and relaxation effects.

I. INTRODUCTION

During the past few years, considerable progress has been made in obtaining highly accurate wave functions for insulating and metallic polymers by the solution of the Hartree-Fock (HF) equations with nonlocal exchange.[1] Calculations of this type also confirmed, among other polymers, in the case of polyacetylenes[2] the expectations that the HF value of the fundamental energy-band gap would be larger than the experimental band gap by several electron volts. This fact is in agreement with similar observations made for other nonmetallic solids[3] and corroborates the previous theoretical results obtained by Kunz and co-workers.[4]

It is well established that the considerable errors introduced into the optical band gap are related to the principal deficiency of the HF point of view that neglects the correlation between the motions of electrons with opposite spin. Conduction-band electrons and valence-band holes are regarded as "bare" particles moving in the average periodic self-consistent potential produced by the nuclei and the other electrons that do not respond to the presence of the extra particle. It is evident that this picture cannot be physically correct, and there have been several early efforts to improve upon it.[5-7] The first quantum-

mechanical treatment of this problem was provided by Toyozawa,[8] who considered the interaction of an extra particle with the rest of the electrons by introducing the concept of the electronic polaron—an extra electron (or hole) dressed with virtual longitudinal excitons. The excitons are restricted to one band without dispersion in his model, and they are coupled to the electrons by a Fröhlich-type interaction, which requires that the extra charge be screened by the static dielectric constant at large distances. No requirement is imposed, however, for the short-range behavior. The formalism of Toyozawa's method closely resembles the lattice polaron problem, with the virtual excitons replacing the virtual optical phonons. Using the intermediate-coupling method of polaron theory,[9,10] Toyozawa studied the effect of electronic polarization on the state of a low-momentum conduction electron in the effective-mass approximation.

Haken and Schottky generalized Toyozawa's theory for the interaction of an electron and a hole via electronic polarization including both an $\vec{r}$-dependent dielectric function and self-energy corrections.[11] Inoue *et al.* calculated by the electronic-polaron model correlation corrections at the bottom of the conduction band of several alkali-halide crystals using both the Green-function and perturbation

methods to the Toyozawa Hamiltonian.[12] In Hermanson's approach[13] the collective excitations of the valence-electron system are represented by a plasmon field whose dispersion $\omega(\vec{q})$ is defined with the help of the longitudinal dielectric function $\epsilon(\vec{q},\omega)$, and the electron-plasmon interaction reflects the detailed $\vec{q}$ dependence of the dielectric response.

Kunz and co-workers extended the electronic-polaron model for the case an electron in a filled band as well and studied several nonmetallic crystals.[14–16] Pantelides et al.[17] also included metallic systems into the analysis and estimated the contribution of short-range effects. Finally, Toyozawa's model was applied to estimate correlation effects in organic molecular crystals of the tetracyano-quinolenium (TCNQ) type[18] and in deoxyribose nucleic acid (DNA) models.[19]

All the above-mentioned applications of the electronic-polaron model[12–19] gave interesting qualitative estimates about the effect of electron correlation in different solids. It is evident, however, that for quantitative predictions the two fundamental approximations, inherent in the previous calculations, must be removed: (i) the assumption of a single, dispersionless exciton band and (ii) the phenomenological estimation of the electron-exciton coupling matrix element. These improvements of the theory seem to be absolutely necessary if we consider that even in a relatively simple solid such as polyacetylene the conduction bands are spread over a region of about 60 eV, and, as we shall see later, excitations to higher-lying bands also give non-negligible contributions to the correlation energy. On the other hand, the interaction matrix elements strongly depend on the details of the excitonic wave function; therefore they must be calculated with the same accuracy that is achieved in solving the HF problem itself.

The aim of this work is to combine the electronic-polaron model with the theoretical methods worked out to calculate correlation effects in atomic and molecular systems from first principles (without empirical parameters or phenomenological approximations). The configuration-interaction (CI) method can be applied only after truncation to larger systems (restricted usually to single and double excitations). However, in this form it is not "size consistent," i.e., its application even to an ensemble of isolated units leads to nonadditive results. This feature makes it inapplicable to infinite solids.

On the other hand, many-body perturbation theoretical (MBPT) methods based on Rayleigh-Schrödinger (RS) PT define their total energy by the linked-cluster expansion,[20] ensuring proper size dependence for each order of PT.[21,22] Their efficien-

cy depends heavily on the choice of the zeroth-order Hamiltonian $\hat{H}_0$. Various possibilities for the choice of $\hat{H}_0$ for correlation-energy calculations will be discussed elsewhere.[23] In this paper we apply the Møller-Plesset (MP) partitioning scheme,[24] which treats the full Hamiltonian $\hat{H}$ as a perturbed spin-restricted HF (RHF) $\hat{H}_0$. A similar scheme based on a spin-unrestricted HF (UHF) zeroth-order Hamiltonian has recently been successful when applied to a larger number of molecules.[25,26]

As a physical system, we shall investigate the electronic structure of pure *trans*-polyacetylene (PA). This interesting polymer has been the subject of both theoretical and experimental investigations for many decades,[27] and the recent discovery of enormous changes in its conductivity upon doping[28] stimulated a great number of measurements and calculations to understand the mechanism of electrical conduction in this material. One of the basic quantities governing the electrical properties of PA is, of course, the fundamental energy gap whose origin has been the subject of dispute for a long time. Using the first-principles version of the electronic-polaron method, we shall therefore calculate this important quantity, including electron correlation.

The outline of the paper is as follows: In Sec. II the MP scheme for infinite periodic solids is introduced through the use of *ab initio* linear combination of atomic orbitals (LCAO) one-particle Bloch orbitals, and an expression for the ground-state correlation energy (E_{corr}) of the N-particle system is derived in terms of pair correlations. The electronic-polaron model is introduced in Sec. III using the previously discussed pair-correlation energies. Various factors (size of the atomic basis, number of included conduction bands, etc.) influencing the value of E_{corr} are investigated, and electron and hole self-energy corrections are calculated for *trans*-PA in Sec. IV. Finally, the summary and the conclusions are presented in Sec. V.

II. MØLLER-PLESSET SCHEME FOR INFINITE PERIODIC SOLIDS

The zeroth-order approximation to the true many-electron wave function Ψ is taken as a HF determinant

$$\Phi_{HF}=(N!)^{-1/2}\det[\cdots \phi_m^{\vec{k}}(\vec{r}_i)\alpha(\sigma_i)$$
$$\times\phi_m^{\vec{k}}(\vec{r}_{i+1})\beta(\sigma_{i+1})\cdots] .$$

$$(2.1)$$

The N electrons are assigned to doubly occupied Bloch orbitals (with band index m and quasimomentum index $\vec{k}$) for which a tight-binding LCAO expansion is used:

$$\phi_m^{\vec{k}}(\vec{r}) = G^{-1/2} \sum_{h=1}^{G} \exp(i\vec{k}\cdot\vec{R}_h)\Lambda_m^{\vec{k}}(\vec{r}-\vec{R}_h) \ , \qquad (2.2)$$

$$\Lambda_m^{\vec{k}}(\vec{r}-\vec{R}_h) = \sum_{p=1}^{n} c_{pm}^{\vec{k}} \chi_p(\vec{r}-\vec{R}_h) \ . \qquad (2.3)$$

G and n stand for the number of cells and for the number of basis orbitals per cell, respectively. The atomic functions χ_p are fixed linear combinations of Gaussian-type atomic orbitals (GTO), which have been optimized for atomic and molecular calculations.[29,30] The size of these atomic basis sets plays an important role both in the HF and correlation studies of solids; therefore we shall specify later in more detail the different sets used in our calculations. From the set of orthonormal occupied Bloch functions defined in Eq. (2.2) we can construct the first-order density matrix of the crystal

$$\rho(\vec{r},\vec{r}') = \sum_m \sum_{\vec{k}} \phi_m^{\vec{k}}(\vec{r})[\phi_m^{\vec{k}}(\vec{r}')]^* \ , \qquad (2.4)$$

which in turn defines the Fock operator (in atomic units)

$$\hat{F}(\vec{r}) = -\tfrac{1}{2}\nabla^2 - \sum_{h=1}^{G}\sum_{a=1}^{n_A} \frac{z_a}{|\vec{r}-\vec{R}_h-\vec{R}_a|}$$

$$+ \int d\vec{r}' \frac{\rho(\vec{r}',\vec{r}')}{|\vec{r}-\vec{r}'|}$$

$$- \int d\vec{r}' \frac{\rho(\vec{r},\vec{r}')}{|\vec{r}-\vec{r}'|}\hat{P}(\vec{r},\vec{r}') \ . \qquad (2.5)$$

n_A is the number of atoms per cell and $\hat{P}$ is the permutation operator interchanging the variables before integration. The self-consistent $\rho(\vec{r},\vec{r}')$ is obtained by the iterative solution of the Fock equation[1]

$$\hat{F}(\vec{r})\phi_m^{\vec{k}}(\vec{r}) = \epsilon_m^{\vec{k}}\phi_m^{\vec{k}}(\vec{r}) \ , \qquad (2.6)$$

which defines the one-electron energy-band structure $\epsilon_m^{\vec{k}}$. In calculating the matrix elements of $\hat{F}$, special attention must be paid to the proper truncation of the infinite lattice sums, arising from the potentials in Eq. (2.5), to avoid numerical instabilities that may lead to nonphysical solutions in the case of extended atomic basis sets.[31-33]

Following Møller and Plesset[24] we now choose the unperturbed Hamiltonian $\hat{H}_0$ as sum of the Fock operators. Besides Φ_{HF}, we can construct further eigenfunctions of $\hat{H}_0$ by replacing some of the occupied orbitals in Φ_{HF} by virtual orbitals, which we also obtain from Eq. (2.6). Introducing the fermion creation and annihilation operators $c_I^\dagger$ and c_I, respectively (with the compound index $I \equiv \{i,\vec{k}\}$), and labeling the states such that $I,J,\ldots$ stand for

occupied levels in the ground-state configuration, while $A,B,\ldots$ refer to virtual levels, we can classify the eigenfunctions of $\hat{H}_0$ as singly, doubly, etc., excited configurations:

$$\Phi_0 = \Phi_{\text{HF}} \ , \qquad (2.7)$$

$$\Phi_I^A = c_A^\dagger c_I \Phi_{\text{HF}} \ , \qquad (2.8)$$

$$\Phi_{IJ}^{AB} = c_A^\dagger c_B^\dagger c_I c_J \Phi_{\text{HF}} \ , \qquad (2.9)$$

$$\cdots \ .$$

The corresponding eigenvalues of $\hat{H}_0$ are

$$E_0 = \sum_K^{(\text{occ})} \epsilon_K \ , \qquad (2.10)$$

$$E_I^A = \sum_{K\neq I}^{(\text{occ})} \epsilon_K + \epsilon_A \ , \qquad (2.11)$$

$$E_{IJ}^{AB} = \sum_{\substack{K\neq I \\ K\neq J}}^{(\text{occ})} \epsilon_K + \epsilon_A + \epsilon_B \ , \qquad (2.12)$$

$$\cdots \ .$$

Expanding the eigenfunction Ψ^λ and the corresponding eigenvalue E^λ of $\hat{H}^\lambda = \hat{H}_0 + \lambda\hat{Q}$ (where $\hat{Q} = \hat{H} - \hat{H}_0$ is the perturbation operator) according[20] to the RS PT in the form

$$\Psi^\lambda = \Phi_0 + \lambda\Psi_1 + \lambda^2\Psi_2 + \cdots \ , \qquad (2.13)$$

$$E^\lambda = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots \ , \qquad (2.14)$$

and terminating these series at second order, we observe that the only matrix elements of $\hat{Q}$ that must be calculated, are of the type $\langle\Phi_0|\hat{Q}|\Phi_{IJ}^{AB}\rangle$ (due to Brillouin's theorem and of the fact that $\hat{Q}$ contains only two-electron operators). Setting $\lambda=1$, we obtain in first order the term missing from E_0 to the HF energy, i.e.,

$$E_{\text{HF}} = E_0 + E_1 = E_0 + \langle\Phi_0|\hat{Q}|\Phi_0\rangle \ , \qquad (2.15)$$

while in higher orders we get correlation corrections to it. The full correlation energy is defined as $E_{\text{corr}} = E - E_{\text{HF}}$. Its value in second order is obtained as

$$E_2 = \sum_I \sum_J \sum_A \sum_B{}' \frac{\langle\Phi_0|\hat{Q}|\Phi_{IJ}^{AB}\rangle\langle\Phi_{IJ}^{AB}|\hat{Q}|\Phi_0\rangle}{E_0 - E_{IJ}^{AB}}$$

$$(2.16)$$

(the prime on the summations ensures that each double substitution is counted only once). Using the Slater-Condon rules to expand the matrix elements in Bloch functions, we get

$$E_2 = \sum_I \sum_J \sum_A \sum_B{}' \frac{|\langle \phi_I(1)\phi_J(2) | (1-\hat{P}_{12})r_{12}^{-1} | \phi_A(1)\phi_B(2) \rangle|^2}{\epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B} . \tag{2.17}$$

One of the major advantages of second-order PT in correlation studies is the fact that in this case only matrix elements between the ground-state and doubly excited configurations must be computed. In the next order, however, the knowledge of the elements $\langle \Phi_{IJ}^{AB} | \hat{Q} | \Phi_{KL}^{CD} \rangle$ is also required, whose list may exceed that of the former elements by orders of magnitude, since even with the use of basis sets of moderate size the virtual orbitals are much more numerous than the occupied ones. It seems, therefore, that even applying sophisticated techniques for the evaluation of the above-mentioned matrix elements the determination of the higher-order correlation corrections will not be an easy task for medium-sized elementary cells. In order to get an estimate of the importance of these terms, MP calculations up to fourth order are in progress in the case of simple monatomic linear chains.

Two other possibilities of improving E_{corr} seem to be, however, more promising in the case of solids. On one hand, the use of the virtual orbitals obtained from Eq. (2.6) for the construction of excited configurations is only a convenient, but not necessarily the most efficient choice. Modified HF virtuals[34-37] as well as other sets of orbitals orthogonal to the occupied space could be used here as well [but trivial generalizations of the molecular methods do not work for solids since the operator added to $\hat{F}$ to obtain proper virtual orbitals that correspond to an $(N-1)$-particle potential[34] goes to zero in infinite systems]. On the other hand, one can utilize the fact that there is no natural expansion parameter λ to be used in Eqs. (2.13) and (2.14) for the correlation problem. This makes the definition of the order of the perturbation contributions ambiguous and permits the modification of E_2 in Eq. (2.16) in order to get closer to E in second order. Various partitioning schemes have been proposed to achieve this goal,[38] but their common feature is that they finally arrive at the "shifted denominator" of the Epstein-Nesbet PT.[39] Work along these lines is in progress in our laboratory.

Another important feature that makes second-order PT especially attractive for solid-state applications is the fact that E_2 can be thought of as a sum of separate electron-pair contributions if it is written in the form

$$E_2 = \sum_I \sum_J{}' \epsilon_{IJ} , \tag{2.18}$$

where the pair-correlation energies ϵ_{IJ} are defined by the comparison of Eqs. (2.16) and (2.18). In this way, the particle concept can also be preserved beyond the HF theory, and one can define quasiparticle states (and energy bands) that incorporate correlation effects at the given level of approximation. Together with the corresponding wavefunction corrections obtained from

$$\Psi_1 = \sum_I \sum_J \sum_A \sum_B{}' \frac{\langle \Phi_{IJ}^{AB} | \hat{Q} | \Phi_0 \rangle}{E_0 - E_{IJ}^{AB}} \Phi_{IJ}^{AB} , \tag{2.19}$$

these quasiparticle bands play an important role in the calculation of optical and transport properties in polymers.[40] As it is well known, furthermore, the energy is invariant in all orders of MPPT with respect to unitary transformations among the occupied spin orbitals in Φ_{HF} (since $\hat{H}_0$ itself is invariant in the same sense). The individual terms ϵ_{IJ} in E_2, on the other hand, are not invariant and they may turn out to be quite different for, e.g., canonical (Bloch) orbitals or for localized ones. This degree of freedom permits us to transform the Bloch basis [by the appropriate choice of the free phase of the ϕ's as obtained from Eq. (2.6)] to a set of Wannier functions for which the intraorbital contributions are maximized. The same procedure also helps to compute ϵ_{IJ}'s that are transferable between related polymers and to facilitate the inclusion of correlation effects in aperiodic polymers.[40]

The calculation of the matrix elements appearing in Eq. (2.17) is somewhat tedious but requires only simple algebra. Substituting the Bloch functions (2.2) and using their transformational properties, we obtain for the pair-correlation energies

$$\epsilon_{IJ} = \sum_a \sum_b \sum_{\vec{q}}{}' G^{-2} \frac{|A(i,j,a,b,\vec{k}_i,\vec{k}_j,\vec{q})|^2}{\epsilon_{k_i}{}^i + \epsilon_j{}^j - \epsilon_a{}^{\vec{k}_i+\vec{q}} - \epsilon_b{}^{\vec{k}_j-\vec{q}}} \tag{2.20}$$

with

$$A(i,j,a,b,\vec{k}_i,\vec{k}_j,\vec{q}) = \sum_{\vec{R}} \sum_{\vec{R}_i} \sum_{\vec{R}_j} [\exp[i(\vec{q}\cdot\vec{R} - \vec{k}_i\cdot\vec{R}_i - \vec{k}_j\cdot\vec{R}_j)]$$

$$\times \langle \Lambda_i^{\vec{k}_i}(\vec{r}_1)\Lambda_j^{\vec{k}_j}(\vec{r}_2 - (\vec{R}_j - \vec{R}_i - \vec{R})) | r_{12}^{-1} | \Lambda_a^{\vec{k}_i + \vec{q}}(\vec{r}_1 - (-\vec{R}_i))\Lambda_b^{\vec{k}_j - \vec{q}}(\vec{r}_2 - (-\vec{R}_i - \vec{R})) \rangle$$

$$-\exp\{i[(\vec{k}_j - \vec{k}_i - \vec{q})\cdot\vec{R} - \vec{k}_i\cdot\vec{R}_i - \vec{k}_j\cdot\vec{R}_j]\}$$

$$\times \langle \Lambda_i^{\vec{k}_i}(\vec{r}_1)\Lambda_j^{\vec{k}_j}(\vec{r}_2 - (\vec{R}_j - \vec{R}_i - \vec{R})) | r_{12}^{-1} | \Lambda_b^{\vec{k}_j - \vec{q}}(\vec{r}_1 - (-\vec{R}_i))\Lambda_a^{\vec{k}_i + \vec{q}}(\vec{r}_2 - (-\vec{R}_i - \vec{R})) \rangle] .$$

$$(2.21)$$

The physically meaningful correlation energy per elementary cell is given by

$$e_{\text{corr}} = \frac{E_2}{G} = \sum_i \sum_j \sum_a \sum_b \sum_{\vec{k}_i} \sum_{\vec{k}_j} \sum_{\vec{q}} G^{-3} \frac{|A(i,j,a,b,\vec{k}_i,\vec{k}_j,\vec{q})|^2}{\epsilon_k^{\vec{k}_i} + \epsilon_j^{\vec{k}_j} - \epsilon_a^{\vec{k}_i + \vec{q}} - \epsilon_b^{\vec{k}_j - \vec{q}}} . \qquad (2.22)$$

Since there are G values of $\vec{k}$ in the first Brillouin zone, the three summations in reciprocal space give a contribution proportional to G^3, i.e., e_{corr} is independent of G as G goes to infinity. (One reciprocal space sum is saved due to momentum conservation: This fact underlines the importance of the proper use of translational symmetry in correlation studies on solids.)

III. QUASIPARTICLE ENERGY BANDS: THE ELECTRONIC-POLARON FORMALISM

The physical content of the HF energy bands is given by Koopmans's theorem,[41] which states that the orbital energies calculated by Eq. (2.6) for the conduction and valence bands, respectively, are equal to the corresponding electron affinities and ionization potentials:

$$\epsilon_c^{\vec{k}\,c}(\text{HF}) = E_{\text{HF}}^{(N+1)} - E_{\text{HF}}^{(N)} , \qquad (3.1)$$

$$\epsilon_l^{\vec{k}\,l}(\text{HF}) = E_{\text{HF}}^{(N)} - E_{\text{HF}}^{(N-1)} . \qquad (3.2)$$

If we make the assumption that during the excitation of an electron from the state $\phi_l^{\vec{k}\,l}$ to $\phi_c^{\vec{k}\,c}$ the distribution of the other electrons is not changed, i.e., no relaxation takes place (which is quite a reasonable assumption for an infinite system) and, furthermore, if the excited electron and the remaining hole are infinitely separated, then the excitation is a simple one-electron transition over the *single-particle* energy-band gap:

$$\Delta\epsilon_g(\text{HF}) = \epsilon_c^{\vec{k}\,c}(\text{HF}) - \epsilon_l^{\vec{k}\,l}(\text{HF}) . \qquad (3.3)$$

Following Toyozawa's suggestion,[8] as further developed by Kunz and co-workers,[14-17] we can also retain the above picture if we go beyond the HF model. By analogy to Eqs. (3.1) and (3.2) we define *quasiparticle* (QP) states using, instead of the HF total energies, the correlated energies from the preceding section:

$$\epsilon_c^{\vec{k}\,c}(\text{QP}) = E^{(N+1)} - E^{(N)} , \qquad (3.4)$$

$$\epsilon_l^{\vec{k}\,l}(\text{QP}) = E^{(N)} - E^{(N-1)} . \qquad (3.5)$$

By writing for the total energy $E = E_{\text{HF}} + E_2$, we obtain

$$\epsilon_c^{\vec{k}\,c}(\text{QP}) = \epsilon_c^{\vec{k}\,c}(\text{HF}) + E_2^{(N+1)} - E_2^{(N)} , \qquad (3.6)$$

$$\epsilon_l^{\vec{k}\,l}(\text{QP}) = \epsilon_l^{\vec{k}\,l}(\text{HF}) + E_2^{(N)} - E_2^{(N-1)} . \qquad (3.7)$$

In order to interpret these expressions we use the decomposition of E_2 into the sum of independent pair correlations. We note that the application of the results obtained for the N-particle system in Sec. II involves a further approximation here since the $(N+1)$- and $(N-1)$-particle states are not closed-shell configurations. Thus Brillouin's theorem does not exactly apply and, therefore, also single-particle excitations should be included in PT. It can be shown,[12,14] however, that the contribution of these singly excited configurations is negligible as compared to the doubly excited ones, which are included here. A further problem should be also mentioned, though it is a general problem in band-structure theory: Namely, the ϕ's used to construct the $(N+1)$- and $(N-1)$-particle states are eigenfunctions of the N-particle Fock operator instead of belonging to the $(N+1)$- or $(N-1)$-particle Fock operators, respectively. In principle, one should use again an open-shell formalism for their determination, but it can be hoped (and the overall success of band theory supports this view) for the infinite system that the error made is not a serious one.

Using the convention that, e.g., $E_2^{(N-1)_L}$ denotes the correlation energy of the $(N-1)$-particle state, which we obtain by removing an electron from the valence-band state L, we obtain from Eq. (2.18)

$$E_2^{(N)} = \sum_I \sum_J{}' \epsilon_{IJ}^{(N)} = \sum_{I\neq L} \sum_{J\neq L}{}' \epsilon_{IJ}^{(N)} + \sum_{I\neq L} \epsilon_{IL}^{(N)} ,$$

$$(3.8)$$

$$E_2^{(N-1)L} = \sum_{I \neq L} \sum_{J \neq L} {}' \epsilon_{IJ}^{(N-1)L} , \tag{3.9}$$

$$E_2^{(N+1)C} = \sum_I \sum_J {}' \epsilon_{IJ}^{(N+1)C}$$
$$\phantom{E_2^{(N+1)C}} _{(C)\,(C)}$$
$$= \sum_I \sum_J {}' \epsilon_{IJ}^{(N+1)C} + \sum_I \epsilon_{IC}^{(N+1)C} . \tag{3.10}$$

[The first two summations in Eq. (3.10) involve also the extra occupied conduction-band state C.] Substituting these expressions into Eqs. (3.6) and (3.7), we get for the quasiparticle energies

$$\epsilon_C(\text{QP}) = \epsilon_C(\text{HF}) + \sum_I \epsilon_{IC}^{(N+1)C}$$
$$+ \sum_I \sum_J (\epsilon_{IJ}^{(N+1)C} - \epsilon_{IJ}^{(N)}) , \tag{3.11}$$

$$\epsilon_L(\text{QP}) = \epsilon_L(\text{HF}) + \sum_{I \neq L} \epsilon_{IL}^{(N)}$$
$$+ \sum_{I \neq L} \sum_{J \neq L} (\epsilon_{IJ}^{(N)} - \epsilon_{IJ}^{(N-1)L}) . \tag{3.12}$$

Following the suggestion of Pantelides et al.,[17] we can interpret the correction terms appearing in addition to the HF band energies in these equations as electron and hole self-energies [$\Sigma(e)$ and $\Sigma(h)$, respectively]. For this purpose we introduce the notation

$$\epsilon_C(\text{QP}) = \epsilon_C(\text{HF}) + \Sigma_C^{(N+1)}(e) + \Sigma_C^{(N+1)}(h) ,$$
$$\tag{3.13}$$

$$\epsilon_L(\text{QP}) = \epsilon_L(\text{HF}) + \Sigma_L^{(N)}(e) + \Sigma_L^{(N)}(h) . \tag{3.14}$$

Recalling Toyozawa's electronic-polaron model, we can identify the origin of these self-energy corrections as a cloud of virtual excitons dressing the "bare" HF particles (in complete analogy to the lattice polaron problem, where virtual optical phonons accompany the polarizing particle). As shown by Eq. (2.20), each "correlation bond" between two HF particles consists of a sum of momentum-conserving virtual scattering pairs $(\phi_i^{\vec{k}_i} \rightarrow \phi_a^{\vec{k}_i + \vec{q}}$ and $\phi_j^{\vec{k}_j} \rightarrow \phi_b^{\vec{k}_j - \vec{q}}$, respectively).

With this physical model in mind we can visualize the formation of an electronic polaron according to Eqs. (3.11) and (3.13) in two steps. At first, the extra particle put into the HF conduction-band state $\phi_c^{\vec{k}_c}$ must establish its new correlation bonds with the other N particles present in the $(N+1)$-particle system $\Phi^{(N+1)C}$, giving rise to the electronic self-energy correction $\Sigma_C^{(N+1)}(e)$. At the same time, owing to the occupation of the previously empty state $\Phi_c^{\vec{k}_c}$, the pair correlations ϵ_{IJ} ($I \neq C$, $J \neq C$) are re-

duced in $\Phi^{(N+1)C}$ as compared to $\Phi^{(N)}$, since scatterings to $\phi_c^{\vec{k}_c}$ are excluded. From the point of view of $\Phi^{(N+1)}$, the terms $\epsilon_{IJ}^{(N+1)C} - \epsilon_{IJ}^{(N)}$ in Eq. (3.13) destabilize the hole in $\phi_c^{\vec{k}_c}$ (before its occupation with the extra electron); their sum results, therefore, in a hole self-energy $\Sigma_C^{(N+1)}(h)$. The formal analysis of these self-energies can be made more transparent if we denote the contribution of each double excitation to the correlation energy by τ_{IJ}^{AB}, i.e., we write Eq. (2.17) in the form

$$E_2 = \sum_I \sum_J \sum_A \sum_B {}' \tau_{IJ}^{AB} . \tag{3.15}$$

In terms of these τ's the self-energies are obtained as

$$\Sigma_C^{(N+1)}(e) = \sum_I \epsilon_{IC}^{(N+1)C} = \sum_I \sum_{A \neq C} \sum_{B \neq C} {}' \tau_{IC}^{AB} ,$$
$$\tag{3.16}$$

$$\Sigma_C^{(N+1)}(h) = \sum_I \sum_J {}' \left[\sum_{A \neq C} \sum_{B \neq C} {}' \tau_{IJ}^{AB} - \sum_A \sum_B {}' \tau_{IJ}^{AB} \right]$$
$$= - \sum_I \sum_J \sum_A {}' \tau_{IJ}^{AC} . \tag{3.17}$$

Before explicitly calculating these quantities we can observe some qualitative trends for them.[17] For the bottom of the conduction band the denominators of τ_{IC}^{AB} in Eq. (3.16) are always negative (see Fig. 1); therefore, the electron self-energy shifts this state downward. Also, since the τ_{IJ}^{AC}'s in Eq. (3.17) are negative, the hole self-energy produces a positive (upward) shift. [Note that in the calculation of $\Sigma_C^{(N+1)}(h)$, C is regarded as an empty state that will be occupied only as a second step after the correlation stabilization of the corresponding "hole state."] Furthermore, we can expect that $|\Sigma_C^{(N+1)}(e)|$ will be usually larger than $|\Sigma_C^{(N+1)}(h)|$ since in the latter case both scattering events occur across the gap and, therefore, as a net
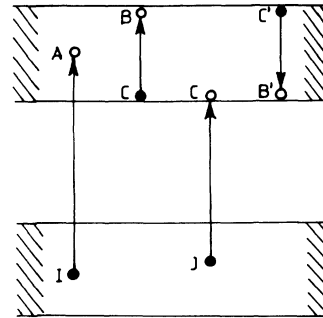

FIG. 1. Virtual excitations contributing to the formation of electron and hole self-energy corrections in the $(N+1)$-particle state.

result the bottom of the conduction band will move downward due to polaron formation. It must be mentioned, however, that this comparison is very approximate since in most cases the symmetry of the wave functions entering the calculation of the τ's (which can be different for different conduction bands) may strongly modify this picture or even reverse it (higher-lying conduction bands may have larger correlation contributions than the lowest conduction band, despite the larger denominators).

A further difficulty may arise if we calculate polaron states belonging to the upper part of the conduction band. As we can see from Fig. 1 for the state C' the self-energy correction is larger than that for C since the energy differences for the scatterings $I \rightarrow A$ and $C' \rightarrow B$, respectively, have opposite sign [and at the same time the denominators of the $J \rightarrow C$ scatterings increase in Eq. (3.17)]. This situation results in a stronger shift for the upper conduction-band states than for the lower states, i.e., in an effective band narrowing (in analogy to the Franck-Condon factor appearing in phonon-polaron theory). We have to keep in mind, however, that if the width of the HF conduction band is equal to or larger than the forbidden gap, second-order MPPT breaks down for the top of the band, and one must either sum up to higher orders or choose another partitioning scheme. For the same reason, higher-lying conduction bands cannot be corrected by the scheme applied previously.

To calculate polaron corrections to valence-band states we decompose the self-energies defined by Eqs. (3.12) and (3.14) as

$$\Sigma_L^{(N)}(e) = \sum_{I \neq L} \epsilon_{IL}^{(N)} = \sum_{I \neq L} \sum_A \sum_B {}' \tau_{IL}^{AB} , \qquad (3.18)$$

$$\Sigma_L^{(N)}(h) = \sum_{I \neq L} \sum_{J \neq L} {}' \left[\sum_A \sum_B {}' \tau_{IJ}^{AB} - \sum_A \sum_B \tau_{IJ}^{(AB)L} \right]$$
$$\phantom{\Sigma_L^{(N)}(h) = } {}_{(L) (L)}$$

$$= - \sum_{I \neq L} \sum_{J \neq L} \sum_A {}' \tau_{IJ}^{AL} . \qquad (3.19)$$

Looking at Fig. 2, with the same reasoning used before, we conclude that at the top of the valence band $\Sigma_L^{(N)}(e)$ produces a negative shift, while $\Sigma_L^{(N)}(h)$ a positive shift; in this case the latter should be generally larger in magnitude. The same caution as discussed above applies again using MP partitioning.

IV. CORRELATION EFFECTS IN trans-POLYACETYLENE

Pure PA may be crystallized into two isomers having cis and trans single-chain structures. The
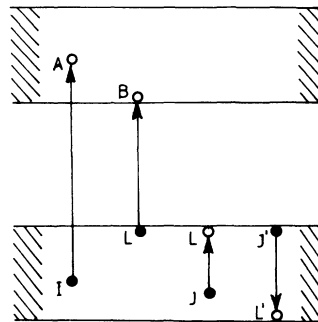

FIG. 2. Virtual excitations contributing to the formation of electron and hole self-energy corrections in the N-particle state.

former is thermodynamically unstable, and it is transformed upon heat treating or doping to the latter structure. The lack of single crystals and the fibrous morphology of PA preclude the determination of the geometrical structure by traditional crystallographic methods, and therefore, the "existence and magnitude of bond alternation has been the crucial and fundamental issue remaining to be resolved."[42] The closely related second important question is, of course, the origin of the energy-band gap observed in the excitation spectrum of PA.[43]

Since no precise structural parameters of PA can be obtained experimentally, the theoretical investigations optimizing the single-chain bond lengths and bond angles from first-principles calculations (without empirical input) are of interest. They predict at the one-electron (HF) level the trans form to be more stable, independent of the atomic basis sets applied.[44-46] Inclusion of interchain interactions as well as electron correlation effects does not qualitatively change this picture.[46]

Before applying the previously discussed electronic-polaron scheme to the energy-band gap problem of PA, we shortly summarize the results of MP correlation calculations performed for the N-particle ground-state problem. Since it is well known from molecular physics that the extension of the atomic basis set plays a crucial role in correlation studies, we applied in this work five different sets starting from a minimal one (STO-3G, Ref. 29), extending it to double-ζ set in the valence shell [4-31G, 6-31G (Ref. 30)], and including also d-type polarization functions on carbon (6-31G*) and a p set on hydrogen (6-31G**, Ref. 47). The specifications of these sets are collected in Table I. The systematically increasing quality of these basis sets allows one to observe the influence of the size of the atomic basis on the one hand, and it permits one also to draw, by extrapolation, basis-set—independent conclusions. In the course of the PT calculations we

TABLE I. Atomic basis functions used in the LCAO expansion of the Bloch orbitals. The convention $\mu s\,vp/\bar{\mu}s\,\bar{v}p$, etc., means that on each atom μ s-type, v p-type, etc., Gaussians are centered and are divided into $\bar{\mu}$, $\bar{v}$, etc., groups (contractions).

	Notation	Carbon atomic set	Hydrogen atomic set
a:	STO-3G	$6s\,3p/2s\,1p$	$3s/1s$
b:	4-31G	$8s\,4p/3s\,2p$	$4s/2s$
c:	6-31G	$10s\,4p/3s\,2p$	$4s/2s$
d:	6-31G*	$10s\,4p\,1d/3s\,2p\,1d$	$4s/2s$
e:	6-31G**	$10s\,4p\,1d/3s\,2p\,1d$	$4s\,1p/2s\,1p$

did not include excitations from core orbitals, since we found in a preliminary calculation that they contribute only 1–2 % to E_2 (on the other hand, an unpolarized core is a certainly good approximation in the case of the physical effects that we are looking for).

The major computational effort in PT is the transformation of the bielectronic integrals, which are calculated for the HF problem in terms of the AO basis (X's), into the Bloch basis (ϕ's). In second order, not considering $\vec{k}$ dependence, this would be a relatively simple task since the number of operations needed would be proportional only to n^4v (where v is the number of filled bands). The difficulty arises, however, from the fact that the matrix elements in Eq. (2.21) must be calculated in a momentum-dependent manner, i.e., one would have to perform the above transformation for a larger number of representative points in the Brillouin zone (BZ), which would be an impractical time-consuming procedure for PA (especially for larger atomic sets). We can see, on the other hand, that the problem is not the entire $\vec{k}$ dependence in Eqs. (2.20) and (2.21), but only the part entering through the LCAO coefficients $c_{pm}^{\vec{k}}$ into the fourfold summation over the AO indices [see Eq. (2.3)] when we form integrals of the type $\langle \Lambda_i\Lambda_j \,|\, r_{12}^{-1} \,|\, \Lambda_a\Lambda_b \rangle$. Thus we can avoid those difficulties by expanding the Bloch orbitals in terms of Wannier functions (WF's)

$$\phi_m^{\vec{k}}(\vec{r})=G^{-1/2}\sum_{\vec{R}}\exp(i\vec{k}\cdot\vec{R})w_m(\vec{r}-\vec{R})\ . \quad (4.1)$$

The WF $w_m(\vec{r}-\vec{R})$, localized around the cell $\vec{R}$, belongs to band m; it is obtained by a unitary transformation of the corresponding ϕ's:

$$w_m(\vec{r}-\vec{R})=G^{-1/2}\sum_{\vec{k}}\exp(-i\vec{k}\cdot\vec{R})\phi_m^{\vec{k}}(\vec{r})\ .$$

$$(4.2)$$

The WF's solve the previously discussed problem only if they are well localized in real space, i.e., in their LCAO expansion

$$w_m(\vec{r}-\vec{R})=\sum_h\sum_p d_{pm}^h\,X_p(\vec{r}-\vec{R}-\vec{R}_h)\ , \quad (4.3)$$

the overwhelming contribution comes from the central cell and its closest neighbors. This can be achieved in PA if before performing the transformation in Eq. (4.2) we make use of the fact that the phase of the ϕ's, as obtained from Eq. (2.6), is undetermined, i.e., any Bloch function of the form $\widetilde{\phi}_m^{\vec{k}}=\phi_m^{\vec{k}}\exp(i\lambda_m^{\vec{k}})$ is also an eigenfunction of the same Fock operator (with the same eigenvalue). This degree of freedom can be used to influence various properties of the WF's as obtained from Eq. (4.2) (symmetry, localization, real or complex nature).[48-51] Comparing different methods,[51] we found that in PA the most efficient localization can be obtained by optimizing the integral proposed by Blount[48]:

$$I(\lambda_m^{\vec{k}})=\int_\Omega w_m^*(\vec{r})z^2 w_m(\vec{r})d\vec{r}\ , \quad (4.4)$$

where the z axis is identical with the polymer axis and the integration is restricted to the unit cell at $\vec{R}=0$. This variational procedure of determining $\lambda_m^{\vec{k}}$ in the entire BZ allows for one further degree of freedom that can be used to calculate either real or symmetry-adapted WF's. From the point of view of the PT calculation, the former property turned out to be more advantageous.[51]

Substituting the Bloch functions as given by Eq. (4.1) into Eq. (2.17), we arrive at the same expression for the matrix elements A as before [Eq. (2.21)], with the only difference being that the $\vec{k}$-dependent Λ's are substituted by the $\vec{R}$-dependent w's. The computational problem has been further reduced in our calculations by an effective selection procedure applied *before* the actual transformation of the integrals from the AO basis to the WF's. To estimate the order of magnitude of whole groups of integrals proved to be especially important in systems such as PA, where the majority of the contributions is very small due to symmetry reasons.

Turning to the results, we present first in Table II the HF and correlated ($E=E_{HF}+E_2$) total energies per elementary cell of trans-PA as obtained for the optimum of the bond alternation ΔR (the four independent structural parameters shown in Fig. 3 had been optimized previously using the same basis

TABLE II. Optimized single-double bond-length difference ΔR in *trans*-PA as obtained with the HF approximation and using second-order MPPT $(E = E_{HF} + E_2)$. The total energies per elementary C_2H_2 units E_{HF} and E belong to the optimum bond alternation for a given basis set.

Basis set	ΔR_{HF} (Å)	E_{HF} (a.u.)	ΔR_E (Å)	E (a.u.)
STO-3G	0.156	$-75.947\,121$	0.122	$-76.065\,389$
4-31G	0.112	$-76.776\,843$	0.091	$-76.955\,733$
6-31G	0.109	$-76.859\,247$	0.085	$-77.036\,179$
6-31G^*	0.103	$-76.886\,912$	0.084	$-77.137\,486$
6-31G^{**}	0.103	$-76.892\,675$	0.084	$-77.168\,100$

sets[52]). We can see that the value of ΔR is well converged at both levels of approximation with respect to the basis-set extension, and its correlated value (if projected on the polymer axis) is in good agreement with the experimental one published recently.[41] We can observe at the same time that, though E_{HF} has reasonably converged, a considerable part of E_2 is still missing. This is physically understandable since our *spd* sets still do not have enough oscillations to make it possible for the electrons to avoid each other efficiently. For this purpose further basis functions with higher angular momenta would be required that could increase (through their nodes) the kinetic energy and thus result in a larger correlation contribution by virtue of the virial theorem. The comparison of the influence of the atomic basis for E_{HF} and E_2 is facilitated by Fig. 4. We can see that the magnitude of the slope for the E_2-vs-E_{HF} curve gets larger and larger in the region of better basis sets.

Another question, especially interesting from the point of view of electronic-polaron theory, is the role of short-range correlation effects missing from the Toyozawa model. These effects are associated with larger exciton momentum, i.e., thinking in an extended zone scheme, they involve excitations to high-lying conduction bands. We therefore introduced in a test calculation thresholds for the max-
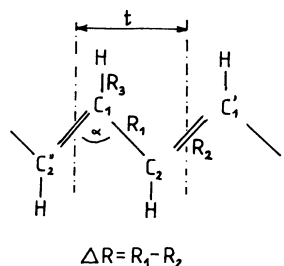
imum exciton energy in calculating E_2. The results, presented in Table III, show that high-energy excitations give, despite the larger energy denominators associated with them, substantial contributions to the correlation energy. It is interesting to observe, furthermore, that energy differences are also strongly influenced by these effects. As we can see from the table, the prediction of the correlation contribution to the alternating-to-equidistant phase transition energy in PA would be in considerable error on the basis of low-lying excitations. The extension of the virtual space is, of course, closely related to the previously discussed basis-set problem and underlines again the need for f, g, etc., orbitals to obtain proper short-range correlations.

One would like to know, of course, the percent of the full valence-shell correlation energy included in E_2 with the best *spd* basis used. We can get an approximate answer for this question if we recall that the valence-shell correlation energy of an acetylene unit was estimated to be ~ -10 eV (Ref. 53); there-

FIG. 3. Geometrical structure of *trans*-PA showing the bond alternation $\Delta R = R_1 - R_2$.
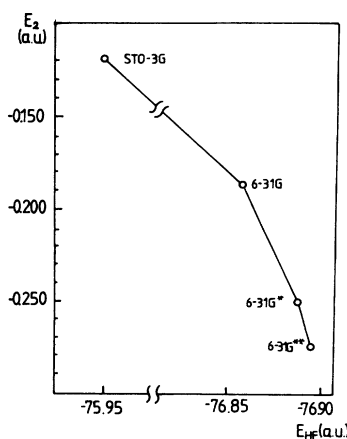

FIG. 4. Correlation energy per C_2H_2 formula unit vs HF energy per C_2H_2 formula unit in alternating *trans*-PA using different basis sets (second-order Møller-Plesset PT, RHF scheme).

TABLE III. Dependence of the correlation energy (E_2) in alternating and equidistant *trans*-PA on the number of conduction bands included in the second-order MPPT calculation. $E_{exc,max}$ is the upper energy limit for conduction-band states that are used to form virtual exciton pairs (results obtained with a 4-31G basis set).

$E_{exc,max}$ (a.u.)	Number of conduction bands included	E_2^{alt} (a.u.)	E_2^{equid} (a.u.)	$E_2^{alt} - E_2^{equid}$ (kcal/mol)
0.51	4	$-0.035\,851$	$-0.040\,146$	2.695
0.88	6	$-0.069\,262$	$-0.072\,908$	2.324
1.05	8	$-0.104\,408$	$-0.107\,464$	1.921
1.26	11	$-0.151\,770$	$-0.154\,257$	1.561
1.95	15	$-0.178\,890$	$-0.181\,135$	1.409

fore our best energy (~ -7.5 eV) should cover 70—75 % of the total value. Nearly the same result was also obtained recently for an infinite atomic-hydrogen model chain.[54]

Since various π-electron Hamiltonians have been very extensively applied in the past to the polyene problem,[27] it is also of interest to ask what part of the correlation originates from purely π-electron interactions. (Both the highest filled and lowest unfilled bands have π symmetry. This question is, therefore, decisive for doping and for conductive properties.) Since, due to symmetry, the σ- and π-type Bloch functions can be completely separated, we can evaluate the π-π, σ-σ, and π-σ contributions to E_2 individually. Almost independently of the atomic basis set, we found that $E_2^{\pi,\pi}$ contributes only 15—20 %, showing that for this kind of polymers the whole valence shell must be treated as an entity; a simple model separating bands with π-type symmetry would not work.

The central part of this work is the evaluation of

the self-energy corrections to the HF band energies using Eqs. (3.11) and (3.12). These quantities are collected in Table IV for basis sets a, c, and e (the results obtained for b and d are very similar to c and e, respectively; therefore, they are not shown here). The Σ_c's are calculated at the bottom of the lowest conduction band, while the Σ_v's refer to the top of the highest valence band. These results substantiate for all basis sets the conclusions of the previous formal analysis, though the quantitative details are different. We can see that the shifts result for both bands from a positive and a negative term, but as a net effect the conduction band is shifted downward while the valence band is shifted upward.

We can follow the formation of the polyene energy-band gap in four consecutive steps as shown in Fig. 5. The uppermost curve is obtained at the HF level using the fixed geometry obtained for the
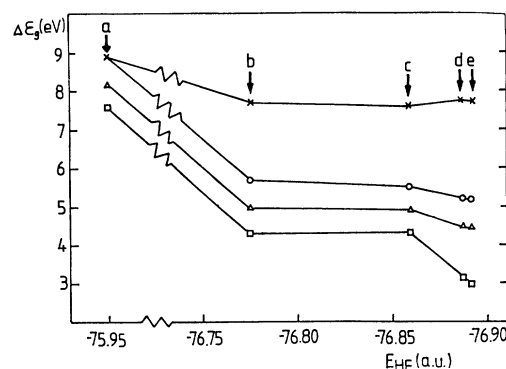
TABLE IV. Different physical quantities contributing to the formation of the quasiparticle energy-band gap in the alternating *trans*-PA: one-particle energies ϵ(HF), electron and hole self-energies, $\Sigma(e)$ and $\Sigma(h)$, respectively, and quasiparticle energies ϵ(QP). All quantities are given in eV.

Quantity	STO-3G	6-31G	6-31G^{**}
$\epsilon_{cond,min}$(HF)	3.719	-0.806	-1.322
$\Sigma_{cond,min}^{(N+1)}(h)$	0.112	0.193	0.274
$\Sigma_{cond,min}^{(N+1)}(e)$	-0.452	-0.623	-0.938
$\epsilon_{cond,min}$(QP)	3.379	-1.236	-1.996
$\epsilon_{val,max}$(HF)	-4.563	-5.732	-5.749
$\Sigma_{val,max}^{(N)}(h)$	0.583	0.896	1.497
$\Sigma_{val,max}^{(N)}(e)$	-0.312	-0.436	-0.724
$\epsilon_{val,max}$(QP)	-4.293	-5.361	-4.976

FIG. 5. Energy-band gap of *trans*-PA vs the HF energy per C_2H_2 formula unit obtained with the five different basis sets $(a-e)$ defined in Table I. $\times$: HF calculation with fixed bond alterntion. $\bigcirc$: HF calculation with optimized bond alternation. $\triangle$: HF + MP calculation with optimized bond alternation but using $\Delta\epsilon_g$ $= \epsilon_{cond,min}$(HF) $- \epsilon_{val,max}$(HF). $\square$: electronic polaron model: $\Delta\epsilon_g = \epsilon_{cond,min}$(QP) $- \epsilon_{val,max}$(QP).
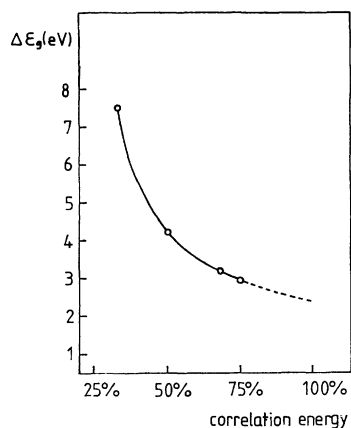
FIG. 6. Extrapolation of the energy-band gap in *trans*-PA obtained by the electronic-polaron method using different basis sets.

minimal basis (a). The extension of the atomic basis does not influence significantly in this case the value of $\Delta\epsilon_g$(HF). On the other hand, it is reduced by ~ 4 eV if the bond alternation is optimized (at the HF level) with each basis set (second curve from the top). Nearly ~ 0.7 eV further reduction is obtained if the structural optimization is performed with the correlated wave function (third curve from the top). The lowest curve shows the energy-band gap values after polaron formation [$\Delta\epsilon_g$(QP)]. It can be seen here that the amount of correlation, included at this stage, plays a predominant role: The polaron effect is more than 2 times larger in the case of the extended *spd* basis than for the minimal one. The best value obtained with this method is $\Delta\epsilon_g = 2.98$ eV. For the ionization potential we get at the same time 4.976 eV, which can be reasonably compared with the experimental value of 4.6 eV.[43]

Since even our best wave function contains only $\sim 75\%$ of the total valence-shell correlation, it would be interesting to extrapolate the obtained value of $\Delta\epsilon_g$(QP) for the case of full correlation. Figure 6 shows that the estimated theoretical value would lie at ~ 2.5 eV, i.e., about half an electron volt higher than the position of the first peak in the absorption spectrum of pure *trans*-PA.[43] The tail of the experimental spectrum reaches to 1.4–1.5 eV probably due to structural disorder present in PA. This tail is, of course, not represented in the above fully periodic calculation, for which the one-dimensional density of states curve has a sharp maximum at the band edge. Our theoretical result must be compared, therefore, with the position of the corresponding peak in experiment, which lies about ~ 2 eV.[43]

V. SUMMARY AND CONCLUSIONS

The role of various single- and many-particle effects in the formation of the band gap in polyenes has been the subject of a number of previous theoretical investigations.[55−67] In these calculations the π-electron system of polyene has been treated independently of the other valence (and core) electrons, and it has been described by model Hamiltonians of the Hubbard[68] or Pariser-Parr-Pople[69] type. Different instabilities of the one-particle (HF) model have been also identified, and their possible contribution to the energy-band gap in polyene has been established (for a recent review and systematization of these instabilities we refer to Ref. 66).

Following the discovery of highly conducting PA samples, the electronic structure of different PA models has also been calculated by semiempirical all-valence electron methods like extended Hückel theory[70] and complete neglect of differential overlap[71] as well as using *ab initio* HF procedures.[72,44−46] No effort has been undertaken, however, until now to correct the unrealistically large HF energy-band gap values obtained in these calculations.

The main objective of our present study was the separation of the one- and many-particle effects to clear up their individual contribution to the energy-band gap. We optimized, therefore, the structural parameters of polyene first at the HF level, using more and more extended atomic basis sets. We found that the bond alternation converges with respect to basis set size at the *spd* level but the energy-band gap at the estimated HF limit is still ~ 5 eV (the corresponding bond alternation is 0.103 Å).

As a second step we included many-particle (correlation) effects in the ground state by second-order PT, which reduced the bond alternation to 0.084 Å and the gap to ~ 4.4 eV. Contrary to the one-particle level, we found the *spd* basis still not completely satisfactory. Further polarization functions as well as higher orders of PT are needed to cover the missing 25–30 % of correlation energy in this system. The short- and long-range parts of the correlation proved to be equally important; therefore, the high-lying conduction bands must be included without doubt in such calculations on solids. Since, however, the bond alternation practically converged at the estimated level of 70–75 % correlation, the single-particle energy-band gap would probably also not change by improving our wave function.

A further substantial reduction of the energy-band gap is observed if correlation is included not only in the ground state but also during the band-

to-band excitation process. The charge carriers produced in this way are no longer "bare" electrons and holes, but quasiparticles consisting of a HF particle and a polarization cloud. The energy-band gap for this quasiparticle excitation process is ~ 3 eV at our 70–75 % correlation level. Extrapolation of our results to the case of full correlation reduces this value to ~ 2.5 eV, lying still half an electron volt above the experimental result. One could think that the difference comes mainly from the binding of the created quasielectron to the remaining quasihole. Our calculations[51] have shown, however, that this excitonic binding is very small in polyene due to screening effects (the exciton, which is bound for a HF electron-hole pair, is nearly dissociated if correlation is included). We think, therefore, that other polarization processes (including high-frequency lattice vibrations) should be also included in the polaron calculations to find the origin of the above discrepance.

On the other hand, the approximate procedure used in this work to construct the $(N \pm 1)$-particle many-electron states from the self-consistent N-particle ground state should be also improved by applying truly self-consistent open-shell wave functions for these ionized states. Work along these lines is in progress in our laboratory.

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