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Correlation effects on bond alternation in polyacetylene

Peter Horsch
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80,
Federal Republic of Germany

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The influence of the electronic interactions on bond alternation in *trans*-polyacetylene is examined on the basis of the Pariser-Parr-Pople Hamiltonian. The ground state of the dimerized chain is studied within a recently developed local approach to the computation of electronic correlation energies. For a Hubbard-type interaction it is shown that electronic correlations are the principle driving mechanism for the dimerization. When the long-range part of the Coulomb interaction is included, the correlations turn out to stabilize the undimerized structure. A rather weak static screening due to σ electrons, however, is sufficient to recover the instability found for the Hubbard interaction.

I. INTRODUCTION

Bond alternation in long polyenes has been a subject of discussions for many years. The backbone structure of the polyene molecules is determined by the sp_2 hybridization of the valence orbitals. Three of the four carbon valence electrons fill the σ orbitals formed by these hybrids. The remaining electron occupies the π band, which is formed by orbitals of $2p_z$ symmetry. The π band is half-filled.

The energy of the lowest excitation in short polyenes scales with the inverse chain length,[1] in good agreement with early results obtained from the molecular orbital (MO) theory by Lennard-Jones[2] and Coulson.[3] However, MO theory predicted a vanishing gap for the long polyenes, whereas experiments tend to a finite gap of about 2 eV. Later Kuhn[4] proposed that bond alternation should persist in the long polyenes. This was confirmed by Longuet-Higgins and Salem,[5] who proved within the linear combination of atomic orbitals (LCAO) theory, by using rather general arguments, that the infinite polyene is unstable with respect to dimerization. This result is reminiscent of the Peierls instability[6,7] in one-dimensional metals. Here the instability results from the half-filled band of π electrons. This explains the optical gap qualitatively and, provided the bond alternation is large enough, even quantitatively.[8,9] There is, however, no experimental data which measures the degree of bond alternation in polyacetylene directly.

A different explanation for the origin of the optical gap was suggested by Ovchinnikov,[10] who argued that the gap results from electronic correlations and not from bond alternation. Estimating the relevant physical parameters for polyacetylene from substances such as benzene, ethylene, and graphite, he found that the bond alternation was too small to explain the experimental gap. The Peierls gap obtained was only of the order $0.1-0.3$ eV. The influence of the electronic interaction on bond alternation was investigated by Harris and Falicov[11] in cyclic polyenes $C_{4N+2}H_{4N+2}$ within the unrestricted Hartree-Fock theory. They compared the normal Hückel solution which exhibits bond alternation with a spin-density-wave (SDW) ground state. The SDW state turned out to be most stable without bond alternation and to have a much lower energy than the bond-alternating state. However, their result that bond alternation is not very likely is not conclusive, since they compare ground states on different levels of sophistication. The SDW state due to the broken spin symmetry includes correlation whereas the normal state does not. But their results certainly reveal that correlation effects are important. We will show below that the bond-alternation ground state does, in fact, have a lower energy than the SDW state when correlations are taken into account.

There are indications from two different sources that electronic interactions could favor bond alternation in polyacetylene. Chui[12] *et al.* showed for the one-dimensional interacting electron gas model[13,14] that the transition temperature for the Peirerls instability T_P is higher for the interacting case than for the noninteracting case. Kondo[15] considered a half-filled Hubbard model for the π electrons, with an effective intrasite Coulomb energy U and alternating transfer integrals $t_0 \pm t_1$. In the strong correlation limit, i.e., $U >> t_0$, this model can be mapped on a spin-$\frac{1}{2}$ Heisenberg chain model.[16] This model was shown to undergo a spin-Peierls transition[17]; that is, even in the range of large U a tendency towards dimerization persists. This is in contradiction to the result obtained within the unrestricted Hartree-Fock scheme, which predicts a complete suppression of the dimerization. The latter model applies to $(CH)_x$ but the strong coupling condition for the parameters may not be fulfilled in polyacetylene.[18]

In this paper we study the influence of electronic correlations on bond alternation in polyacetylene. The π-electron system is represented by a tight-binding model of the Pariser-Parr-Pople type.[19] Two different model interactions are considered, (i) Hubbard and (ii) long-range Coulomb interaction. We use a local approach[20] to the electronic correlation problem. By means of a specific set of local operators the mean-field ground state is modified in order to allow for a correlated motion of electrons. The ground-state energy is determined by variation. The approximations made in the present work apply to the case where the Hubbard U is smaller or equal to the π bandwidth W. Up to now this method has been applied to various systems, including small atoms and molecules,[20,21] the homogenous electron gas,[22] and the ground state of diamond.[23] For the molecules[21] it was shown that this method yields approximately 95% of the correlation energy which is obtainable within a given basis set.

The paper is organized as follows. In Sec. II we introduce the Pariser-Parr-Pople model Hamiltonian. In Sec. III we consider the characteristic features of the bond-alternation ground state within the independent electron picture. In Sec. IV we discuss the variational method used for the computation of correlation energies. Section V contains the results obtained for the correlation energies for the Hubbard and the long-range interactions and a discussion of the implications for the Peierls transition in polyacetylene. The results are summarized in Sec. VI.

II. THE π-ELECTRON HAMILTONIAN

The π-electron system of the conjugated hydrocarbon chain can be represented by a tight-binding Hamiltonian of the Pariser-Parr-Pople (PPP) type[19]

$$
\begin{aligned}
H &= H_0 + H'_{ra} + H'_{er} , \qquad (2.1)\\
H_0 &= -\sum_{n,\sigma} t_{n+1,n}(c^{\dagger}_{n+1\sigma}c_{n\sigma} + H.c.)\\
&\quad + \tfrac{1}{2}\sum_{n} K(u_{n+1} - u_n)^2 ,\\
H'_{ra} &= U\sum_{n} n_{n\uparrow}n_{\downarrow} - I\sum_{n\sigma} n_{n\sigma} ,\\
H'_{er} &= \tfrac{1}{2}\sum_{m,n;\sigma,\sigma'}{}' V_{mn}n_{n\sigma}n_{m\sigma'}\\
&\quad - \sum_{m,n;\sigma}{}' V_{mn}n_{n\sigma} + \tfrac{1}{2}\sum_{m,n}{}' V_{mn} .
\end{aligned}
$$

Here $c^{\dagger}_{n\sigma}$ and $c_{n\sigma}$ are fermion creation and annihilation operators, respectively referring to the mutually orthogonal atomic $2p_z$ orbitals at site n and with spin σ. The π-electron number operator is denoted by $n_{n\sigma} = c^{\dagger}_{n\sigma}c_{n\sigma}$. The Hamiltonian is subdivided into three parts; H_0 represents the kinetic energy of the π electrons and includes an elastic contribution due to the σ electrons as well, while H'_{ra} and H'_{er} represent the intra-atomic and interatomic interaction, respectively.

The Hamiltonian H_0 is equivalent to that used by Su *et al.*[24,25] The resonance integrals $t_{n+1,n}$ are changed when the atoms and consequently the $2p_z$ orbitals are displaced by u_n from their positions in the undimerized state. Here the u_n's are projections of the real displacments onto the chain axis. To first order in the displacements $t_{n+1,n}$ is given by

$$t_{n+1,n} = t_0 - \alpha(u_{n+1} - u_n) , \qquad (2.2)$$

where α is the electron-lattice coupling constant. The elastic contribution in H_0 stabilizes the undimerized geometry. K is the σ-bond stretching force constant.

The intra-atomic interaction Hamiltonian H'_{ra} consists of a Hubbard term U and a term which guarantees a correct ionization potential I in the atomic limit. Changes of U due to the displacements of the atoms are assumed to be small and will be neglected.

The interatomic interaction Hamiltonian H'_{er} consists of three terms arising from electron-electron repulsion, electron-ion attraction, and ion-ion repulsion. The prime on the sum indicates that interactions are excluded between electrons at the same site, i.e., $m \neq n$. For the interaction integrals V_{mn} various empirical parametrizations have been proposed.[19] Here we employ the Mataga-Nishimoto formula for V_{mn},[26] which is given by

$$V_{mn}=\frac{14.397}{14.397/U+r_{mn}}\ , \tag{2.3}$$

where r_{mn} is the interatomic distance in Å and U is put equal to 11.13 eV.

Neglecting the interatomic Hamiltonian H_{er} altogether and taking $t_{n+1,n}=t_0$, the Hamiltonian H reduces to the one-dimensional Hubbard model.[27,28] Note that for the half-filled case this model has a gap in the excitation spectrum for any value of U.

III. INDEPENDENT PARTICLE SOLUTION FOR THE PERFECTLY DIMERIZED CHAIN

We begin by considering the kinetic energy Hamiltonian H_0 in the Born-Oppenheimer approximation. For the perfectly dimerized trans-polyacetylene the displacements are given by

$$u_n=(-1)^n u_0\ . \tag{3.1}$$

There are two different resonance integrals $T=t_0+t_1$ and $t=t_0-t_1$ according to Eq. (2.2). Since there are two sites per unit cell, the general solution for the valence- and conduction-band Bloch functions can be written as

$$\psi_k(\underline{r})=\frac{1}{\sqrt{N_c}}\sum_{n=\text{even}} e^{ikan}[\alpha_k\phi_n(\underline{r})+\beta_k\phi_{n+1}(\underline{r})]\ ,$$

where ϕ_n and ϕ_{n+1} represent the $2p_z$ orbitals at the n'th and $(n+1)$'th atom. The projection of the interatomic distance $r_0=1.397$ Å is denoted by $a=(\sqrt{3}/2)r_0$. Assuming the orthogonality of the basis functions ϕ_n, i.e., $(\phi_n\,|\,\phi_m)=\delta_{nm}$, the secular equations turn out as

$$\begin{gathered}\beta_k(T+te^{-ik2a})=\alpha_k E_k\ ,\\ \alpha_k(T+te^{+ik2a})=\beta_k E_k\ .\end{gathered} \tag{3.3}$$

The energy eigenvalues are given by

$$E_k=\pm[T^2+2Tt\cos(2ka)+t^2]^{1/2}\ . \tag{3.4}$$

Here the negative and positive signs refer to valence and conduction bands, respectively. The expansion coefficients α_k and β_k are complex quantities. For the valence (b) band

$$\alpha_k^b=\frac{1}{\sqrt{2}}e^{i\psi_k/2},\ \ \beta_k^b=\frac{1}{\sqrt{2}}e^{-1\psi_k/2}\ , \tag{3.5a}$$

and for the conduction (a) band

$$\alpha_k^a=\frac{1}{\sqrt{2}}e^{i\psi_k/2},\ \ \beta_k^a=-\frac{1}{\sqrt{2}}e^{-i\psi_k/2}\ . \tag{3.5b}$$

The phase ψ_k is defined by

$$tg\psi_k=-t\sin(2ka)/[T+t\cos(2ka)]\ . \tag{3.6}$$

In the undimerized limit, i.e., $T=t$, the phase is $\psi_k=-ka$, whereas in the limit of independent dimers, i.e., $t=0$, one finds $\psi_k=0$.

The total kinetic energy E_{kin} can be computed from the dispersion (3.4) (Refs. 5 and 25)

$$E_{\text{kin}}=-\frac{4}{\pi}t_0E(1-y^2)\ , \tag{3.7}$$

where E is the complete elliptic integral of the second kind and $y=t_1/t_0=2\alpha u_0/t_0$. For small distortions, the asymptotic behavior of Eq. (3.7) is

$$E_{\text{kin}}=-\frac{4}{\pi}t_0\left\{1+\frac{y^2}{4}\left[2\ln\left[\frac{4}{y}\right]-1\right]\right\}\ . \tag{3.8}$$

Here the logarithimic contribution $y^2\ln y$ is the driving term of the Peierls instability, since it overcompensates the increase of elastic energy in Eq. (2.1) for small distortions.

The annihilation operators related to valence and conduction bands are given according to (3.2) and (3.5) by

$$a_{k\sigma}^b=\frac{1}{\sqrt{N}}\sum_{n=\text{even}} e^{ikan}(e^{i\psi_k/2}c_{n\sigma}+e^{-i\psi_k/2}c_{n+1,\sigma})\ , \tag{3.9a}$$

$$a_{k\sigma}^a=\frac{1}{\sqrt{N}}\sum_{n=\text{even}} e^{ikan}(e^{i\psi_k/2}c_{n\sigma}-e^{-i\psi_k/2}c_{n+1,\sigma})\ . \tag{3.9b}$$

In order to obtain a better understanding of the character of the above solution and also for later use we consider the electronic density and density matrix. The density is given by

$$\rho(\underline{r})=2\sum_{mn}P_{mn}\phi_m^*(\underline{r})\phi_n(\underline{r})\ , \tag{3.10}$$

where the factor 2 results from the spin summation. The single-particle density matrix P_{mn} is defined by

$$P_{mn}=\langle c_{m\sigma}^\dagger c_{n\sigma}\rangle\ . \tag{3.11}$$

The expectation value is taken with respect to the ground state $|\,\phi_0\rangle$ evaluated within the independent electron picture,

$$|\,\phi_0\rangle=\prod_k a_{k\uparrow}^{b\dagger}a_{k\downarrow}^{b\dagger}\,|\,0\rangle\ . \tag{3.12}$$

The P_{mn} (3.11) can be computed easily from the inverse of transformation (3.9). For even values of

m and n, one finds

$$P_{mn}=P_{m+1,n+1}=\begin{cases}\frac{1}{2} \text{ for } m=n\\ 0 \text{ otherwise}\end{cases}, \tag{3.13a}$$

$$P_{m+1,n}=\frac{1}{N}\sum_k \cos[\psi_k-ka(m-n)] . \tag{3.13b}$$

It is convenient to introduce bond orders[1,29]

$$p_d=2P_{10},\ p_s=2P_{-10} , \tag{3.14}$$

referring to double and single bonds, respectively. The kinetic energy is completely characterized by the two bond orders

$$E_{\mathrm{kin}}=-N[(t_0+t_1)p_d+(t_0-t_1)p_s] . \tag{3.15}$$

In the undimerized limit $p_d=p_s=2/\pi$ while in the limit of independent dimers, i.e., $t=0$, $p_d=1$, and $p_s=0$. See Fig. 1 for illustration. The ground state can therefore be visualized as a wave of alternating bond orders or a bond-order wave (BOW) state.

From Eq. (3.13a) it follows that the electronic charge at an atomic site remains unchanged when dimerization takes place, i.e., $\langle n_{n\sigma}\rangle=P_{nn}=\frac{1}{2}$ independent of dimerization. This result has an important consequence when one includes the Hubbard interaction from H'_{ra}. The expectation value of the Hubbard interaction in the ground state (3.12) of the independent electron picture

$$\langle H'_H\rangle=N\frac{U}{4} \tag{3.16}$$

does not depend on dimerization. Therefore, within mean-field approximation the Hubbard interaction has no effect on bond alternation.[30] The contribution of the Hubbard interaction to the total Hamiltonian in the mean-field approximation reads

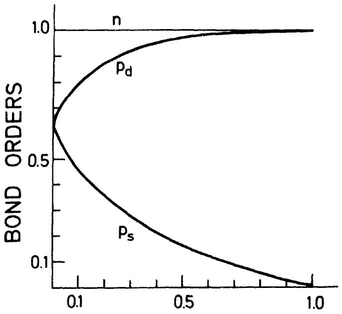

FIG. 1. Bond orders of double p_d and single p_s bonds, respectively, are shown as function of the relative change of the resonance integrals t_1/t_0.

$$\tilde{H}'_H=U\sum_n(\langle n_{n\uparrow}\rangle n_{n\downarrow}+n_{n\uparrow}\langle n_{n\downarrow}\rangle-\langle n_{n\uparrow}\rangle\langle n_{n\downarrow}\rangle) . \tag{3.17}$$

Here the last term prevents double counting of the interactions. One can show that ψ_k as given by (3.2) together with (3.5) are still solutions of the Hamiltonian $\tilde{H}_0+\tilde{H}'_H$. The only change is a rigid upward shift of the single-particle bands E_k by $U/2$.

This result of the tight-binding model is in contrast to the interacting electron gas model. For this model one would expect a reduction of the Peierls transition temperature T_P, when the interaction is treated within mean-field approximation.[31,32] Up to this point we have not mentioned charge-density waves (CDW). Obviously there is more charge within a double bond than within a single bond; however, the change of interaction energy due to the CDW arises from the interatomic interaction Hamiltonian H'_{er} (2.1) and not via the Hubbard interaction. We will come back to this point in Sec. V where we treat the interatomic interactions.

In the next section we will consider the correlation energy. Usually the correlation energy is only a small fraction of the total interaction energy. But even small changes of the correlation energy are expected to be significant for bond alternation, when, as was shown above for the Hubbard model, the interaction energy in mean-field approximation does not change when the system dimerizes.

IV. CORRELATION ENERGY

The most important correlations are those which prevent two electrons with opposite spins being on the same site. This occurs with a probability of $\frac{1}{4}$ in the mean-field ground state $|\phi_0\rangle$ and gives rise to the energy contribution (3.16). For the Hubbard model one expects this probability to go to zero in the infinite U limit.

Here we employ a variational method[20-22] to study the correlation problem. The correlated ground state $|\psi\rangle$ is constructed from the ground state within the independent particle picture (3.12) by means of a certain set of local operators S, i.e.,

$$|\psi\rangle=\exp(S)\,|\phi_0\rangle . \tag{4.1}$$

The two particle-hole operator S consists of local density and spin-density operators. Hence the method can be considered as a local approach to the correlation problem. Here we will only use density-density operators for S. It is convenient to split S into two parts:

$$S_1 = \sum_n \eta_0 n_{n\uparrow} n_{n\downarrow} , \tag{4.2a}$$

$$S_2 = \sum_{n \neq m;\sigma,\sigma'} \eta_{nm} n_{n\sigma} n_{m\sigma'} . \tag{4.2b}$$

Spin-density operators cannot be neglected generally, for instance they are responsible for the Hunds rule in atoms. However, in the model considered here, i.e., with one orbital per site, the additional inclusion of spin correlations yields only a small gain of correlation energy. The reason is that here the local charge fluctuations and spin fluctuations are not independent. The operator S_1 allows for the reduction of double occupancies of atomic $2p_z$ orbitals as described above and yields the largest part of the correlation energy in the case of the Hubbard model. S_2 allows for long-range correlations and therefore it is of particular importance when the interaction is also long ranged. For the homogeneous electron gas[22] it is possible to obtain the random-phase approximation (RPA) result for the ground-state energy by using S_2 which is an exact description of the long-range correlation effects.

The variational parameters η are determined by minimization of the funcional for the ground-state energy

$$E(\eta) = \langle e^{S(\eta)} H e^{S(\eta)} \rangle_c . \tag{4.3}$$

Here the expectation value has to be taken with respect to the mean-field ground state (3.12), and it can be evaluated by using Wick's theorem. The expression (4.3) is correctly normalized when only connected diagrams are taken into account as indicated by $\langle \cdots \rangle_c$.[22]

The functional for the ground-state energy (4.3) cannot, in general, be computed without further approximations. Here we will make use of the "linear" approximation[20,21] where exp(S) is replaced by $(1+S)$. This approximation applies to the weak and intermediate correlation case and gives good results for intra-atomic[21] as well as for long-range correlations.[22] Equation (4.3) becomes:

$$E(\eta) = \langle H \rangle + 2\langle SH' \rangle_c + \langle SH_0 S \rangle_c + \langle SH'S \rangle_c . \tag{4.4}$$

The first term on the right-hand side (rhs) $\langle H \rangle$ represents the mean-field ground-state energy. The remaining terms contribute to the correlation energy E_{corr}, defined as the difference between the exact ground-state energy and the mean-field ground-state energy, i.e.,

$$E(\eta) = \langle H \rangle + E_{\text{corr}}(\eta) . \tag{4.5}$$

The first two terms of the correlation energy according to (4.4) and (4.5) are proportional to U^2, while the last term on the rhs of Eq. (4.4) is proportional to U^3. Note that the variational parameters η in S turn out to be proportional to U when U is small compared to the bandwidth W.

V. NUMERICAL RESULTS

A. Hubbard interaction

For the Hubbard interaction the largest part of the correlation energy can be obtained from the single-site operator S_1 (4.2a),

$$S_1 = \eta_0 O \text{ where } O = \sum_n n_{n\uparrow} n_{n\downarrow} . \tag{5.1}$$

For illustration we want to consider this simple case first. Minimizing Eq. (4.4) we find

$$\eta_0 = -\langle OH' \rangle_c / \langle OH_0 O \rangle_c , \tag{5.2}$$

$$E_{\text{corr}} = -\langle OH' \rangle_c^2 / \langle OH_0 O \rangle_c . \tag{5.3}$$

Note that for the half-filled Hubbard chain the term $\langle OH'O \rangle_c$, as well as $\langle O^2 H' \rangle_c$ and $\langle H' O^2 \rangle_c$ which appear in (4.3) but have been dropped in (4.4), are equal to zero and consequently there is no third-order contribution in U, in agreement with the exact solution by Lieb and Wu.[27] The matrix elements for Eqs. (5.2) and (5.3) are given in the Appendix. The only information from the single-particle solution we need for their evaluation is the density matrix P_{mn} [(3.13a) and (3.13b)].

The correlation energy is shown in Fig. 2. The

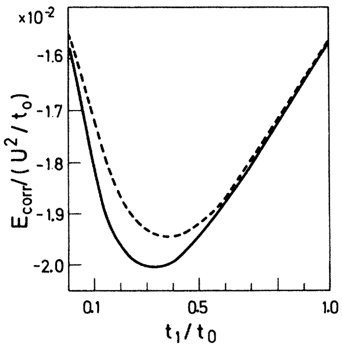

FIG. 2. Correlation energy per electron for the Hubbard interaction. Dashed curve: single-site operator (5.1) only; solid line: includes long-range correlation (4.2b).

absolute value of the correlation energy shows a nearly linear increase in the region $y=t_1/t_0=0-0.2$. Therefore, within the Hubbard model correlation energy favors bond alternation. This has to be seen in contrast to the lowering of the kinetic energy due to the $y^2\ln y$ term in Eq. (3.8). The inclusion of long-range correlation (4.2b) gives only a minor additional gain of less than 4% of the correlation energy.

The minimum of the correlation energy can be understood from the dependence of the quantities $\langle OH'\rangle_c$ and $\langle OH_0O\rangle_c$ on t_1, see Fig. 3. The increase of the absolute value of E_{corr} for small t_1 follows from the increase of $\langle OH'\rangle_c$ in this region. The decrease of $|E_{\text{corr}}|$ for large t_1, however, results from the increase of $\langle OH_0O\rangle_c$, while $\langle OH'\rangle_c$ is nearly constant in that region. The matrix element $\langle OH_0O\rangle_c$ represents the average kinetic energy of the virtual excitations from the valence to the conduction band. Its increase with increasing t_1 results from the opening of the gap, i.e., $E_g=4t_1$. The reduced value of $\langle OH'\rangle_c$ for small t_1 cannot be explained so easily, but it can be traced back to the change of the bond orders p_s and p_d (Fig. 1). Physically the reduced value of $\langle OH'\rangle_c$ reflects the stiffness of the ground-state wave function in the undimerized case, i.e., small t_1. Namely a local modification of the pair-correlation function requires a change of the wave function over many dimers in the small t_1 limit, whereas in the opposite limit a local change is restricted to one dimer only.

The accuracy of the method can be tested in the two limits, i.e., $t_1=0$ and $t_1=t_0$, where accurate results for the model under investigation exist. Expanding the exact result of Lieb and Wu[27] for the half-filled Hubbard chain in the limit $U/t_0\rightarrow 0$ yields for the leading U^2-term of the correlation energy $E_{\text{corr}}=\kappa U^2/t_0$ with $\kappa=0.01695$.[33] Within the local approach we obtain $\kappa=0.01552$ for the single-site operator S_1 (4.2a) and $\kappa=0.01577$ when also long-range correlations are included (4.2b). These are 91.7% and 92.6% of the correlation energy, respectively. In the limit of independent dimers κ turns out to be identical to the expansion coefficient of the exact result for a dimer, i.e., $\kappa=\frac{1}{64}$. For $U/W\simeq 1$, where $W=4\,t_0$ is the bandwidth, more than 80% of the correlation energy is obtained.

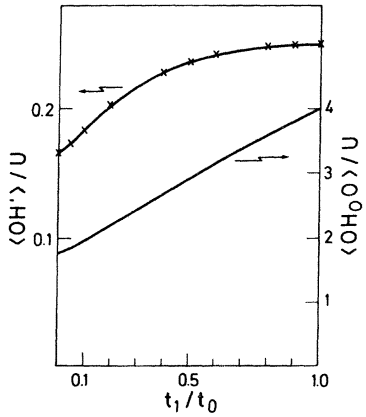

FIG. 3. Matrix elements $\langle OH'\rangle_c$ and $\langle OH_0\rangle_c$ as used for the evaluation of the correlation energy (5.3) for the Hubbard interaction model (solid lines). An approximative result for $\langle OH'\rangle_c$ where the density matrix P_{mn} has been truncated at next-nearest neighbors is denoted by crosses.

For the total energy we make use of the parametrization used by Harris and Falicov,[11] in order to compare our results with their SDW ground-state energy. The resonance integrals are now assumed to have an exponential dependence

$$\begin{aligned} T&=t_0\exp(y)\ , \\ t&=t_0\exp(-y)\ . \end{aligned} \tag{5.4}$$

The distortion coordinate y, which enters here as an independent variable, can be related to the change d of the bond length via the Coulson-Golebiewski[1] rule:

$$y=d/0.3727\ \text{Å}\ . \tag{5.5}$$

The resonance integral $t_0=1.597$ eV is smaller than the now accepted value of about 2.5 eV.[19,24] The elastic energy per carbon atom is assumed to be $E_{el}=4.282y^2$ eV. This parametrization corresponds to $\alpha=3.7$ eV/Å and $K=35$ eV/Å^2 in Eq. (2.1). These values are close to those given by Kakitani[34]; however, his value for t_0 is 2.95 eV.

The total energy for the Hubbard model is shown in Fig. 4. The topmost curve, i.e., the $U=0$ curve, includes kinetic and elastic energies only. There is a weak minimum for finite distortion $y=0.06$, where the total energy is lowered by 0.002 eV with respect to the undimerized case. The $U\neq 0$ curves are lowered by the correlation energy with respect to the $U=0$ curve. The correlation energy not only reduces the total energy it also yields an increase of condensation energy of the dimerized state

$$E_{\text{cond}}=E_{\text{tot}}(0)-E_{\text{tot}}(y)\ . \tag{5.6}$$

For $U=8$ eV the condensation energy is larger by a factor of about 40 compared with that of uncorrelated electrons. The distortion is found to be much larger when correlations are taken into account and the screened spring constant K_T (Ref. 35) is also modified. A comparison with the SDW state of Harris and Falicov is given in Fig. 5. The correlated ground states with and without distortion are found to have a much lower energy than the SDW state.

We should mention here that although we start out from a paramagnetic ground state (3.12) the pair-correlation function of the correlated ground state (4.1) has antiferromagnetic short-range order.

These results change the picture for the Peierls instability substantially. For the Hubbard interaction it is found that bond alternation is stabilized by the gain of correlation energy, while the gain of kinetic energy due to the opening of a gap at the Fermi level, is an order of magnitude smaller. Hence one may conclude that the gain of correlation energy is the principle driving mechanism of the Peierls instability in the present model.

B. Long-range interaction

The interaction energy $V_{nn'}$ of two electrons at sites n and n', respectively, is parametrized according to the Mataga-Nishimoto formula (2.3). The intra-atomic interaction U is assumed to be independent on the dimerization, while the nearest-neighbor interaction within double or single bonds increases or decreases, respectively, due to the changes in the bond length. The bond length changes by an amount of d

$$d=\frac{2}{\sqrt{3}}2u_0=\frac{2}{\sqrt{3}}t_1/\alpha=0.35\frac{t_1}{t_0}\ \text{Å}\ , \qquad (5.7)$$

according to Eq. (2.2). Here we used $\alpha=8.0$ eV/Å^2 (Ref. 35) and $t_0=2.43$ eV (Ref. 19).

First we will consider the mean-field approximation for the interatomic interaction Hamiltonian H'_{er}:

$$\begin{aligned}\tilde{H}'_{er}=\tfrac{1}{2}\sum_{m,n;\sigma,\sigma'}{}' V_{mn}\{ &\langle n_{m\sigma}\rangle n_{n\sigma'}+n_{m\sigma}\langle n_{n\sigma'}\rangle-\langle n_{m\sigma}\rangle\langle n_{n\sigma'}\rangle \\ &-\delta_{\sigma\sigma'}(\langle c^\dagger_{m\sigma}c_{n\sigma}\rangle c^\dagger_{n\sigma}c_{m\sigma}+c^\dagger_{m\sigma}c_{n\sigma}\langle c^\dagger_{n\sigma}c_{m\sigma}\rangle-\langle c^\dagger_{m\sigma}c_{n\sigma}\rangle\langle c^\dagger_{n\sigma}c_{m\sigma}\rangle)\} \\ -\sum_{m,n;\sigma}{}' V_{mn}n_{n\sigma}+\tfrac{1}{2}\sum_{m,n}{}' V_{mn}\ . \qquad (5.8)\end{aligned}$$

Since $\langle n_{m\sigma}\rangle=\frac{1}{2}$ (3.13a), the first line in the above expression is exactly canceled by the last two terms, i.e., by the electron-ion and ion-ion interaction. Making use of the definition of the density matrix P_{mn} (3.11), we obtain for $\tilde{H}'_{er}$

$$\begin{aligned}\tilde{H}'_{er}=&-\tfrac{1}{2}\sum_{m,n\sigma}{}' V_{mn}P_{mn}(c^\dagger_{m\sigma}c_{n\sigma}+H.c.) \\ &+\sum_{m,n}{}' V_{mn}P^2_{mn}\ . \qquad (5.9)\end{aligned}$$

Here the first term on the rhs has exactly the same from as the kinetic energy in H_0 (2.1) if we neglect hopping terms beyond nearest neighbors. It is na-

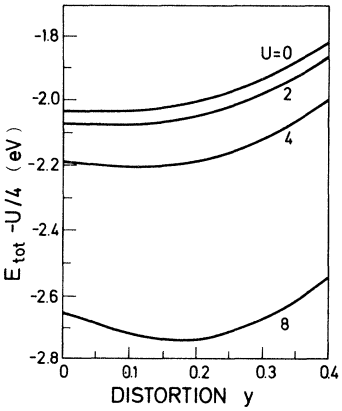

FIG. 4. Total energies for the Hubbard interaction model are given as function of the distortion coordinate y for various values of U. The $U=2$-, 4-, and 8-eV curves are lowered with respect to the $U=0$ curve by the amount of correlation energy. The mean-field contribution of the interaction (3.17) has been subtracted out.

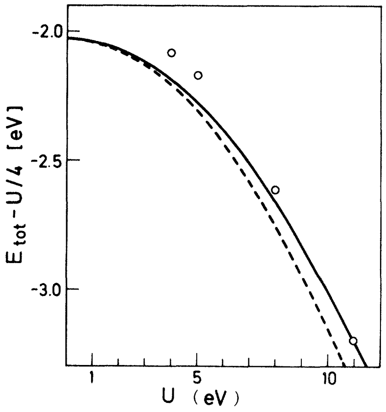

FIG. 5. Total energies for the Hubbard interaction in comparison with the spin-density wave ground state of Ref. 11 (open circles). Solid curve: ground-state energy without bond alternations; dashed curve: ground-state with dimerization.

tural in the spirit of the parametrized PPP-Hamiltonian to assume that this term is incorporated in H_0 in terms of an effective resonance integral

$$t^{\mathrm{eff}}_{n+1,n}=t_{n+1,n}+\tfrac{1}{2}V_{n+1,n}P_{n+1,n} \; . \tag{5.10}$$

The second term on the rhs of Eq. (5.9) changes proportionally to u_0^2 when the structure undergoes a dimerization, therefore it can be absorbed in H_0 via a renormalized force constant K^{eff}. Thus within the mean-field approximation we can start again from the ground-state solution found for H_0.

In the case of the Mataga-Nishimoto interaction (2.3) long-range correlations play a much more important role than for the Hubbard interaction. As can be seen from Fig. 6(a) the π-electron system can gain additional correlation energy due to long-range correlations in the region where the system is weakly dimerized, i.e., for small t_1. Whereas in the region where the system separates into almost independent dimers, there is clearly no additional gain of ground-state energy arising from long-range correlations. Therefore, in contrast to our findings for the Hubbard interaction where correlation effects strongly favor the dimerized structure, in the long-range interaction case the undimerized structure is stabilized.

The situation changes again when the Mataga-Nishimoto interaction is screened by a static dielectric constant ϵ_0, i.e.,

$$\widetilde{V}_{mn}=V_{mn}/\epsilon_0 \; , \tag{5.11}$$

while the intra-atomic interaction U remains unscreened. In the case of $(\mathrm{CH})_x$ the static dielectric constant ϵ_0 is assumed to arise from the polarizability of the σ electrons, which are not included in the π-electron Hamiltonian (2.1). It turns out that even a rather small screening of about $\epsilon_0=2$ of the interatomic interaction is sufficient to recover results for E_{corr} [see Fig. (6b)] similar to those found for the Hubbard interaction.

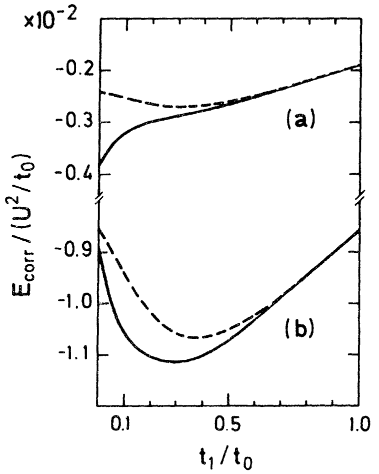

FIG. 6. Correlation energies for a long-range interaction as function of t_1/t_0. (a) Mataga-Nishimoto interaction, (b) same as (a) but screened by $\epsilon_0=3$. Dashed curves: single-site operator (4.2a) only: solid curves: includes long-range correlation (4.2b).

Here we want to comment on our treatment of long-range correlations in the limit of vanishingly small dimerization, i.e., when the single-particle gap approaches zero. From the three-dimensional homogeneous electron gas it is known that perturbation theory diverges in the $q\rightarrow 0$ limit; however, for the present approach it was found earlier[22] that even the second-order functional in η (4.4) used here together with (4.2) removes this divergence. The results obtained are close to the RPA result for small q. The same can be shown to be the case here. In momentum representation the correlation energy can be written as

$$E_{\mathrm{corr}}=\int_0^{\infty} dq\, q^{d-1}E_q \; . \tag{5.12}$$

In the one-dimensional case, i.e., $d=1$, the Fourier transform of the Mataga-Nishimoto interaction (2.3) has a singular behavior like $\ln q$, whereas $E_q \propto q\ln q$ is nondivergent for small q. Therefore, the computation of the correlation energy in the long-range limit poses no problems. Actually the minimum of the correlation energy at $t_1=0$ in Fig. 6(a) is not a particular feature due to the long-range nature of the Mataga-Nishimoto interaction (2.3). It is also present when the interaction is truncated at nearest or next nearest neighbors, respectively, provided that the nearest-neighbor interaction is large enough compared to U.

VI. SUMMARY AND CONCLUSIONS

We have studied the influence of the electronic interaction on the bond alternation in polyacetylene. The above calculations were done within a Pariser-Parr-Pople tight-binding model for the π electrons. The ground state of the dimerized trans-polyacetylene has been studied using a recently developed variational approach to the computation of electronic correlation energies.

For the Hubbard type of interaction it was found that there is a gain of correlation energy when the chain undergoes a dimerization. The gain of correlation energy is approximately a linear function of the dimerization coordinate y, therefore correlations strongly favor bond alternation. This has to be seen in contrast to the lowering of the kinetic energy, being proportional to $y^2 \ln y$, which is considered as the driving force for the Peierls transition in the independent particle picture. The gain of correlation energy can be much larger than the gain of kinetic energy depending on the values of the parameters U/t_0 and α^2/Kt_0. These results imply a significant change in the accepted picture of a Peierls transition and it clearly shows that electronic correlation effects have to be taken fully into account.

There have been recent investigations[36,37] along the steps of Harris and Falicov[11] using the unrestricted Hartree-Fock approximation. The bond-alternation ground state is found to be stable for U smaller than 4.66 eV, when using the parameters of Su *et al.*,[24] while above this threshold the SDW ground state is found to be more stable. These results imply a complete suppression of bond alternation above $U = 4.66$ eV. Our results, however, imply an increase of bond alternation with increasing U and predict the bond-alternation ground state to be more stable than the SDW ground state (Fig. 5) in the range where our approximations are valid, i.e., $U/t_0 < 4$. However, if U is increased further we are in the regime of the spin-Peierls transition,[15,17,18] there the dimerization should persist but its magnitude should decrease again.

These results are strongly modified if we consider a slowly decreasing long-range interaction. In this case long-range correlation effects turn out to stabilize the undimerized structure. However, a rather small static screening of the interatomic interaction, turns out to be sufficient to recover the results found for the Hubbard interaction. In the case of polyacetylene the static screening is argued to be due to the polarizability of the σ electrons. This finding should be of particular importance for those quasi-one-dimensional systems in which the chains are formed by large molecules[38] and where these complex molecules can have a rather high polarizability.

An extension of this work to excited states is planned. Further work should be undertaken to bridge the gap between the two extreme theoretical models, i.e., the interacting electron gas model and the tight-binding model used in this work.

Note added in proof. After this paper EPC had been completed direct experimental evidence of dimerization in trans-$(CH)_x$ from x-ray scattering has been reported by C. Fincher, C. E. Chen, A. J. Heeger, and A. G. MacDiarmid at the International Conference on Low-Dimensional Conductors, Boulder, 1981.

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APPENDIX: COMPUTATIONS OF THE EXPECTATION VALUES $\langle SH' \rangle_c$, $\langle SH_0S \rangle_c$, AND $\langle SH'S \rangle_c$

The operator S (4.2) is defined in terms of the density-density operator $O_{nn'}$,

$$S = \sum_{nn'} \eta_{nn'} O_{nn'} , \tag{A1}$$

$$O_{nn'} = \sum_{\sigma\sigma'} n_{n\sigma} n_{n'\sigma'} . \tag{A2}$$

Note that this definition of $O_{nn'}$ also applies to the operator S_1 in (4.2a), since all terms with $\sigma = \sigma'$ exactly cancel for this case. The expectation values with respect to $O_{nn'}$ can be decomposed by using Wicks theorem and expressed in terms of the matrices

$$P_{mn} = \langle c_{m\sigma}^{\dagger} c_{n\sigma} \rangle , \tag{A3}$$

$$Q_{mn} = \langle c_{m\sigma} c_{n\sigma}^{\dagger} \rangle = \delta_{mn} - P_{mn} . \tag{A4}$$

The only contribution arising from the kinetic energy H_0 up to second order is given by

$$\begin{aligned} &\langle O_{nn'} H_0 O_{mm'} \rangle_c \\ &\qquad -P_{nm} H_{n'm'} (2Q_{nm} Q_{n'm'} \\ &\qquad -Q_{nm'} Q_{n'm})] , \end{aligned} \tag{A5}$$

where

$$G_{n'm'} = \sum_{i,j} Q_{in'} t_{ij} Q_{jm'} , \tag{A6}$$

$$H_{n'm'} = \sum_{i,j} P_{in'} t_{in} P_{jm'} . \tag{A7}$$

In order to compute the expectation values for a general two-particle interaction V_{ijkl} we introduce the following four auxiliary matrices:

$$\begin{aligned} U_{mm'nn'} &= \sum_{ijkl} P_{jm} Q_{im'} P_{kn} Q_{ln'} V_{ijkl} , \\ W_{mm'nn'} &= \sum_{ijkl} P_{jm} P_{im'} Q_{kn} Q_{ln'} V_{ijkl} , \\ S_{mm'nn'} &= \sum_{ijkl} Q_{jm} Q_{im'} Q_{kn} Q_{ln'} V_{ijkl} , \\ P_{mm'nn'} &= \sum_{ijkl} P_{jm} P_{im'} P_{kn} P_{ln'} V_{ijkl} . \end{aligned} \tag{A8}$$

Note in our case (2.3) $V_{ijkl}=\delta_{ij}\delta_{kl}V_{lk}$. Finally one obtains

$$\langle O_{nn'}H'\rangle_c=2(2U_{nnn'n'}-U_{nn'n'n})\ , \tag{A9}$$

and

$$\begin{aligned}\langle O_{nn'}H'O_{mm'}\rangle_c=4[&4P_{n'm'}Q_{n'm'}(2U_{nnmm}-W_{nmnm})-2P_{n'm'}Q_{n'm}(2U_{mmnn'}-W_{nmnn'})\\&-2P_{m'n'}Q_{nm'}(2U_{nn'mm}-W_{mnmn'})+2P_{n'm}Q_{nm'}(U_{nn'm'm}-2W_{nm'n'm})\\&+P_{n'm}P_{nm'}(2S_{n'mnm'}-S_{n'm'mn})+Q_{n'm}Q_{nm'}(2P_{n'mnm'}-P_{n'm'nm})]\ .\end{aligned} \tag{A10}$$

In order to present the above formulas in compact form we have tabulated them here without translational invariance being taken into account. Further matrix elements including spin-density operators can be found in Ref. 21.

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