PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

Electron correlations in polyacetylene

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(Received 25 September 1984)

The influence of electronic correlations on structural and electronic properties of polyacetylene is studied by adding a Hubbard term (on-site Coulomb coupling U) to the Su-Schrieffer-Heeger Hamiltonian. We use the Gutzwiller wave function as an ansatz for the electronic ground state. For weak electron-phonon coupling ($\lambda \ll 1$) and $U/(4t_0) \ll 1$ (where $4t_0$ is the π bandwidth) we obtain analytical results for the ground-state energy, the amplitude of bond alternation, the effective force constant for the bond-stretching mode, and a mean-field gap parameter Δ. For intermediate couplings the energy is minimalized numerically. Our results are applicable for $U/(4t_0) \lesssim 1$ where they agree surprisingly well with the Monte Carlo calculations of Hirsch. We find strong indications that everywhere in this region the ground state is dimerized if $\lambda > 0$. For larger U we expect a smooth crossover to the spin-Peierls phase. For $\lambda < 0.37$ the Hubbard term initially enhances bond alternation and the dimerization amplitude exhibits a maximum at a finite value of U. For larger values of λ the maximum occurs at $U = 0$ and electronic correlations decrease bond alternation. Using single-particle parameters as deduced from properties of small organic molecules we compare our results with empirical data on polyacetylene. Our analysis consistently reproduces the measured properties if U is chosen between 7 and 9 eV.

I. INTRODUCTION

Despite the remarkable success of single-particle models[1,2] in describing electrical, magnetic, and optical properties of conducting polymers,[3] there is now accumulating experimental evidence that electron-electron interactions cannot be neglected. For example, Coulomb correlations appear to be relevant for interpreting triple-magnetic-resonance experiments[4] if the observed spin densities are related to neutral solitons. Similar conclusions have been drawn on the basis of optical measurements in the infrared, in particular from photoluminescence,[5] photo-induced optical absorption,[6] and photothermal deflection spectroscopy.[7] Nevertheless the importance of Coulomb correlations has not yet been fully established in the case of conducting polymers. This is in contrast to the case of short polyenes, where the relevance of correlation effects seems to be generally accepted.[8]

Ovchinnikov and co-workers argued theoretically many years ago that the Coulomb correlation (and not the bond alternation) was at the origin of the optical gap in long polyenes.[9] They proposed that the appropriate model for these systems was the Hubbard Hamiltonian (with on-site Coulomb coupling U) and not the Hückel description, where the gap is produced by the electron-phonon interaction (characterized by the parameter λ). However, using variational calculations, Ukrainskii[10] and Horsch[11] showed that the Peierls instability, which gives rise to bond alternation, and electron correlation, which produces localization and antiferromagnetic ordering, are not competing effects. Instead correlation was found to enhance bond alternation. This at first sight surprising result disagrees with mean-field theory,[12-14] according to which the amplitude of bond alternation is independent of U for $U/4t_0 \lesssim \pi\lambda/(1+2\lambda)$, $4t_0$ being the π-electron bandwidth. For larger values of U the mean-field ground state has a different symmetry: bond alternation vanishes and a spin-density wave appears. The enhancement of dimerization due to correlation effects as predicted by variational calculations[10,11] has been confirmed by various methods. Kivelson and Heim used a perturbation expansion relative to the mean-field state which is limited to small values of U.[15] Hirsch performed Monte Carlo calculations both for small and intermediate values of U.[16] He found that, after an initial increase of bond alternation as a function of U, there is a maximum for $U/4t_0 \sim 1$. Similar results were obtained by Mazumdar and Dixit using exact finite-ring calculations together with an analysis of valence-bond diagrams.[17]

In this paper we examine the ground-state properties of a one-dimensional π-electron system as a function of λ and U. We choose the Gutzwiller ansatz as variational ground state, which has been already used by Horsch.[11] However, in our approach three parameters are varied: the correlation parameter η, the dimerization amplitude Δ_0, and the gap parameter Δ. The latter is responsible for the exponential decay of the correlation functions. Horsch assumed the relation $\Delta = \Delta_0$ (which holds for $U = 0$) to remain valid for $U > 0$ (which is an unnecessary restriction). We find that, except for very small values of λ, our variational state with alternating bond order $\Delta_0 \neq 0$ has lower energy than the exact result obtained by Lieb and Wu[18] for $\Delta_0 = 0$. For $\lambda \lesssim 0.37$ the bond alternation increases first as a function of U and passes through a maximum at a U value which depends on λ. For $\lambda=0.1$ the maximum occurs at $U/4t_0 \sim 1$. With increasing λ it moves to lower values of U. For the particular case $\lambda=0.29$ where Monte Carlo data are available[16] our results are in good agreement with the numerical simulations in the region $U/4t_0 \lesssim 1$. For larger values of U our expansion in powers of η breaks down. On the other hand, in the limit $U/4t_0 \gg 1$ it is known that the ground state exhibits a spin-Peierls distortion which has exactly the same symmetry as the bond alternation induced by the Peierls instability in the region $U/4t_0 \lesssim 1$. This indicates strongly that for $\lambda \neq 0$ the ground state is always a bond-ordered state and that no phase transition to a spin-density-wave state takes place, in contrast to the predictions of mean-field theory.

The paper is organized as follows. The variational procedure is outlined in Sec. II. In Sec. III analytical results are derived which are valid for $U/4t_0 \ll 1$. Numerical results are presented in Sec. IV and shown to compare favorably with Monte Carlo data in the region $U/4t_0 \lesssim 1$. The effective force constant related to the bond-stretching mode is derived in Sec. V. It is found that electron correlation produces a stiffening of the lattice. In Sec. VI it is shown that an "unbiased" choice of single-particle parameters leads to a consistent modeling of polyacetylene if U is taken to be of the order of 7—9 eV. Part of this material has been summarized elsewhere.[19]

II. VARIATIONAL APPROACH

We consider the following π-electron Hamiltonian:

$$H=-\sum_{i\alpha} t_i(c_{i\alpha}^\dagger c_{i+1\alpha}+c_{i+1\alpha}^\dagger c_{i\alpha})+U\sum_i n_{i\uparrow}n_{i\downarrow}\ , \tag{1}$$

where $c_{i\alpha}^\dagger$ creates a π electron at site i with spin projection α and $n_{i\alpha}=c_{i\alpha}^\dagger c_{i\alpha}$. The resonance integrals are assumed to be alternating

$$t_i=t_0-\tfrac{1}{2}(-1)^i\Delta_0\ , \tag{2}$$

Δ_0 being proportional to the dimerization amplitude of the lattice, as explained in Table I for both the Hückel description[1] and the Su-Schrieffer-Heeger (SSH) convention.[2] The second term in Eq. (1) is the on-site Coulomb interaction. In principle the long-range part

$$\tfrac{1}{2}\sum_{i\neq j} V_{ij}n_i n_j$$

should also be taken into account, but for simplicity we assume that these terms are included within an "effective U." We construct the ground state using the variational ansatz

$$|\psi\rangle=e^S|0\rangle\ , \tag{3}$$

where

$$S=-\tfrac{1}{2}\eta\sum_i n_{i\uparrow}n_{i\downarrow} \tag{4}$$

and $|0\rangle$ is the ground state of an effective single-particle (mean-field-type) Hamiltonian

$$H_0=-\sum_{i\alpha}[t_0-\tfrac{1}{2}(-1)^i\Delta] \times(c_{i\alpha}^\dagger c_{i+1\alpha}+c_{i+1\alpha}^\dagger c_{i\alpha})\ . \tag{5}$$

With this ansatz we have introduced two electronic parameters: the correlation parameter η and the "gap parameter" Δ. The latter would be the true gap parameter for $U=0$; for $U>0$ the connection of Δ to the quasiparticle excitation spectrum remains to be clarified. In order to determine the two electronic parameters η,Δ together with the lattice parameter Δ_0, we have to minimalize the total energy (per site)

$$\epsilon(\eta,\Delta_0,\Delta)=\Delta_0^2/(4\pi\lambda t_0)+N^{-1}\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle\ , \tag{6}$$

where the first term is the elastic energy associated with σ-bond compression (cf. Table I) and N is the number of sites. A similar procedure has been used by Horsch,[11] but he assumed the relation $\Delta=\Delta_0$ to hold and thus disposed

TABLE I. Characteristic quantities of a dimerized $(\mathrm{CH})_x$ chain for the Hückel and SSH models. The lattice coordinates of the Hückel model are the bond lengths r_i. The SSH parametrization in terms of displacements u_i in chain direction corresponds to the geometry of trans polyacetylene.

	Hückel	SSH	Connection
Dimerization amplitude	$y=(-1)^i(r_i-r)$	$u=(-1)^i u_i$	$u=-y/\sqrt{3}$
Elastic energy	$\frac{1}{2}\left[\frac{d^2E_\sigma}{dr^2}\right]y^2$	$2K_0u^2$	$K_0=\frac{3}{4}\frac{d^2E_\sigma}{dr^2}$
Δ_0	$2\left[\frac{dt}{dr}\right]y$	$-4\alpha u$	$\alpha=\left[\frac{3}{4}\right]^{1/2}\frac{dt}{dr}$
λ	$\dfrac{2\left[\frac{dt}{dr}\right]^2}{\pi t_0\left[\frac{d^2E_\sigma}{dr^2}\right]}$	$\dfrac{2\alpha^2}{\pi t_0 K_0}$	

only of two parameters. By varying Δ_0 and Δ independently, one can lower the energy further. Moreover, it appears that this allows one to produce consistent results even for the region $U/4t_0 \sim 1$ where both the method of Horsch[11] and the perturbation expansion of Kivelson and Heim[15] are no longer valid. Using the linked-cluster theorem[20] and expanding e^S to second order in η, we rewrite the electronic energy as

$$\begin{aligned}\langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle &= \langle \psi | H | \psi \rangle_c \\ &= \langle 0 | H | 0 \rangle - \tfrac{1}{2}\eta \langle 0 | \{ W,H \} | 0 \rangle_c \\ &\quad + \tfrac{1}{8}\eta^2 \langle 0 | \{ W, \{ W,H \} \} | 0 \rangle_c \,,\end{aligned} \tag{7}$$

where $\{ A,B \} = AB + BA$ and $W = \sum_i n_{i\uparrow} n_{i\downarrow}$. The subscript c means that only the connected diagrams have to be taken into account. Following Horsch we introduce the correlation functions

$$P_{ij} = \langle 0 | c_{i\alpha}^{\dagger} c_{j\alpha} | 0 \rangle \,. \tag{8}$$

Explicit expressions for these functions are derived in Appendix A, in particular

$$P_{n,n+2m} = \tfrac{1}{2}\delta_{m,0} \,, \tag{9}$$

$$P_{n,n+1} = [E - \delta^2 K + (-1)^n \delta (E - K)] / [\pi (1 - \delta^2)] \,, \tag{10}$$

where $\delta = \Delta/(2t_0)$ and E,K are the complete elliptic integrals with argument $k = (1 - \delta^2)^{1/2}$. The functions $P_{n,n+2m+1}$ decrease as $\exp(-2|m|\delta)$ for large m and $\delta \neq 0$. Using Wick's theorem the electronic energy, Eq. (7), is expressed in terms of P_{ij} as

$$\langle \psi | H | \psi \rangle_c = -4t_0 \sum_i [1 - (-1)^i \delta_0] \left[P_{i,i+1} + \tfrac{1}{2}\eta^2 \left[\sum_j P_{ij}^3 P_{j,i+1} - 2 \sum_{nm} P_{nm}^3 P_{in} P_{mi+1} \right] \right] + U \left[\tfrac{1}{4}N - \eta \sum_{ij} P_{ij}^4 \right] , \tag{11}$$

where we have introduced the parameter $\delta_0 = \Delta_0/(2t_0)$. Equation (11) is derived in Appendix B. The fact that only equal-time functions P_{ij} and not time-dependent propagators are involved originates from our static treatment of the lattice. It amounts to assume that quantum fluctuations due to phonons are negligible. This is expected to be true if the phonon energies are small with respect to the "gap" 2Δ.

III. THE SMALL-U LIMIT

A. The Hubbard model ($\Delta_0 = 0$)

In order to compare our approximate ground state with the exact result for the Hubbard model,[18] we first evaluate the expression (11) for $\Delta_0 = \Delta = 0$. In this limit the functions $P_{n,n+2m+1}$ have the simple form (see Appendix A)

$$P_{n,n+2m+1} = (-1)^m \pi^{-1}/(2m+1) \,. \tag{12}$$

The summations can be carried out explicitly and we find

$$\epsilon(\eta,0,0) = -4t_0/\pi + \tfrac{1}{4}U + \epsilon_{\text{corr}} \,, \tag{13}$$

where the correlation energy is given by

$$\epsilon_{\text{corr}} = -\tfrac{1}{12}U\eta + \pi^{-1}(\tfrac{1}{4} + \pi^{-2}) t_0 \eta^2 \,. \tag{14}$$

Minimalizing with respect to η yields

$$\epsilon_{\text{corr}}/t_0 = -\kappa (U/4t_0)^2 \,, \tag{15}$$

where $\kappa = \pi^3/[9(\pi^2+4)] = 0.2484$. The exact result has the same functional form with $\kappa = 0.2719$.[21] Therefore our variational ground state can account for more than 90% of the correlation energy in the limit $U \to 0$. For comparison we mention the variational calculation of Ukrainskii[10] who finds again Eq. (15) but with $\kappa = 0.1744$, a considerably smaller value than the exact result.

B. Bond alternation for weak couplings ($\lambda \ll 1$, $U \ll 4t_0$)

In the presence of bond alternation ($\Delta_0 \neq 0$) we are not able to carry out the summations in Eq. (11) analytically. Therefore we truncate the series by assuming that $P_{ij} = 0$ for $|i-j| \geq 3$. In the case of the simple Hubbard model this procedure yields a correlation energy as in Eq. (15) with

$$\kappa = \pi(1 + 32/\pi^4)^2/[16(1 + 48/\pi^4)] = 0.2321 \,.$$

This corresponds to a reduction in correlation energy of only 7% relative to the value obtained by performing the complete summations. This error is expected to diminish with increasing gap parameter Δ since these functions decrease exponentially with the coherence length $2t_0/\Delta = \delta^{-1}$. For $\delta \ll 1$ the correlation function $P_{n,n+1}$ given in Eq. (10) can be approximated as

$$P_{n,n+1} \sim \pi^{-1}[1 - \tfrac{1}{2}\delta^2(\Lambda - \tfrac{3}{2}) + (-1)^n \delta (1 - \Lambda)] \,, \tag{16}$$

where $\Lambda = \ln(4/\delta)$. With this form the truncated summations yield the following expression for the energy (including terms up to order δ^2).

$$\begin{aligned}\epsilon(\eta,\delta_0,\delta)/t_0 = {} & \delta_0^2/(\pi\lambda) - (4/\pi)\{ 1 - \tfrac{1}{2}\delta^2(\Lambda - \tfrac{3}{2}) + \delta_0\delta(\Lambda - 1) - \tfrac{1}{2}\eta^2[a_0 + a_1\delta^2(\Lambda-1)^2 - a_2\delta^2(\Lambda - \tfrac{3}{2}) + a_3\delta_0\delta(\Lambda - 1)] \} \\ & + (U/4t_0)\{ 1 - \eta[b_0 + b_1\delta^2(\Lambda-1)^2 - b_2\delta^2(\Lambda - \tfrac{3}{2})] \}\end{aligned} \tag{17}$$

with coefficients $a_0=\frac{1}{8}+6/\pi^4$, $a_1=28/\pi^4$, $a_2=\frac{1}{16}+15/\pi^4$, $a_3=\frac{1}{8}-2/\pi^4$, $b_0=\frac{1}{4}+8/\pi^4$, $b_1=48/\pi^4$, $b_2=16/\pi^4$. An alternative approach which may yield a better approximation for very small δ, in particular for $\delta^{-1}\gg 3$, is to sum over the long-range correlations using the form of Eq. (12) for $|i-j|\geq 3$. This yields the same expression, Eq. (17), for the energy with $a_0=\frac{1}{8}+1/2\pi^2$, $b_0=\frac{1}{3}$, the other coefficients remaining the same as previously.

The minimalization of the energy with respect to the three parameters η,δ_0,δ is carried out in Appendix C. We find

$$\eta=c_0U/4t_0\equiv\hat{U}\ , \tag{18}$$

$$\delta=4\exp(-1-1/2\tilde{\lambda})\ , \tag{19}$$

$$\delta_0=\delta(1-c_1\hat{U}^2)\lambda/\tilde{\lambda}\ , \tag{20}$$

where the renormalized coupling $\tilde{\lambda}$ is given by

$$\tilde{\lambda}=[\lambda(1-c_1\hat{U}^2)^2+c_2\hat{U}^2]/(1-2c_3\hat{U}^2) \tag{21}$$

with coefficients $c_0=1.398$, $c_1=0.052$, $c_2=0.133$, $c_3=0.016$. These results are valid if $\eta\ll 1$, $\delta_0\ll 1$, $\delta\ll 1$ which requires that $U/4t_0\ll 1$ and $\lambda\ll 1$. The gap parameter δ satisfies the same BCS-type equation as for $U=0$ except that λ is replaced by an effective coupling $\tilde{\lambda}$ which increases with U. It is also worthwhile noticing that $\delta>\delta_0$ for $U>0$. Nevertheless, also the bond-alternation amplitude δ_0 increases with U and this effect becomes more pronounced for smaller λ. The energy is found to be

$$\epsilon_{\min}/t_0=-4/\pi+U/4t_0-2\pi^{-1}a_0\hat{U}^2-\pi^{-1}(1-2c_3\hat{U}^2)\delta^2 \tag{22}$$

where the third term corresponds to the correlation energy for $\delta=0$ and the last term is the condensation energy due to bond alternation. As a consequence of the U dependence of $\tilde{\lambda}$ the condensation energy is strongly enhanced by correlation effects. In the region where Eq. (22) is valid there is always a gain in energy due to bond alternation. Furthermore it turns out that our variational energy for $\Delta_0\neq 0$ is lower than the exact result of Lieb and Wu[18] for $\Delta_0=0$ (at least if λ is not too small; otherwise the failure of the Gutzwiller ansatz to reproduce the exact correlation energy for $\lambda=0$ becomes relevant). This indicates strongly that the Lieb-Wu ground state is unstable against bond alternation in the presence of electron-phonon coupling, at least for $U/4t_0\lesssim 1$. This presents a completely different picture from what is predicted by mean-field theory, according to which a phase transition to a spin-density-wave state occurs.[12-14] For $U/4t_0\lesssim 1$, there is bond alternation, but no spin-density wave. From the numerical analysis (below) as well as the large U results we will conclude that in the whole region of parameter space ($\lambda>0$, $U>0$) the system exhibits bond alternation and there is no phase transition to a spin-density-wave state.

IV. NUMERICAL ANALYSIS

So far we have assumed that all three parameters η, δ_0, and δ are much smaller than unity. However our approximation (i.e., the expansion in powers of η) requires only η to be small. Therefore it is worthwhile to examine Eq. (11) without requiring δ and δ_0 to be much smaller than 1. We truncate again the summations in Eq. (11) by retaining only correlation functions P_{ij} with $|i-j|<3$. The total energy becomes

$$\begin{aligned}\epsilon(\eta,\delta_0,\delta)/t_0=\ &\delta_0^2/(\pi\lambda)-4\{P_1+\delta_0\delta P_2-\eta^2[P_1(\tfrac{1}{16}+3P_1^4+14\delta^2P_1^2P_2^2-\delta^4P_2^4)\\&+\delta_0\delta P_2(\tfrac{1}{16}-P_1^4+14\delta^2P_1^2P_2^2+3\delta^4P_2^4)]\}\\&+(U/4t_0)\{1-\eta[\tfrac{1}{4}+8(P_1^4+6\delta^2P_1^2P_2^2+\delta^4P_2^4)]\}\ ,\end{aligned} \tag{23}$$

where

$$P_1=[\pi(1-\delta^2)]^{-1}(E-\delta^2K),\quad P_2=[\pi(1-\delta^2)]^{-1}(K-E) \tag{24}$$

and E,K are the complete elliptic integrals with $k=(1-\delta^2)^{1/2}$. The minimalization with respect to η is easily done analytically, but subsequently the parameters δ_0 and δ have to be optimized numerically. The resulting parameters δ_0, δ, and η are shown in Figs. 1–3 for various values of λ. Both the bond-alternation parameter δ_0 (Fig. 1) and the gap parameter δ (Fig. 2) increase with U for small U. However, while δ increases monotonically to the maximum value 1 (the completely localized limit) δ_0 reaches a maximum at $U/4t_0\sim 1$ and subsequently decreases rapidly. One notices that δ_0 remains small (with respect to unity) for all three values of λ. Within our approximation scheme δ_0 would cross zero for $U/4t_0\sim\sqrt{2}$, but this is an artifact of our expansion in powers of η. Indeed, as shown in Fig. 3, η is larger than 1 in this region. We believe that after passing the maximum the order parameter decays like $U^{-3/2}$ due to the spin-Peierls mechanism.[22-24] In Fig. 1 the Monte Carlo data are also included. It is seen that our results are in surprisingly good agreement with the numerical simulation even in the region of the maximum. The small discrepancy at $U=0$ originates from quantum fluctuations[25,26] which have been neglected in our approach. Quantum effects are expected to become less important with increasing U due to the increase of the gap parameter Δ.

In Fig. 4 our result for the ground-state energy is compared with the Lieb-Wu solution,[18,27] which represents the

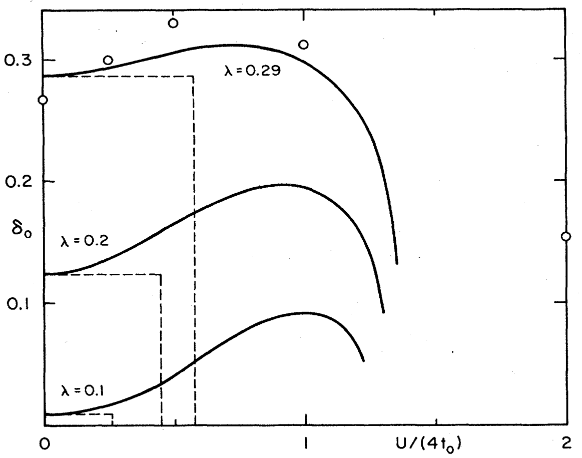

FIG. 1. Amplitude of bond alternation $\delta_0=\Delta_0/(2t_0)$ as a function of U for three different values of λ. Dashed lines indicate the corresponding mean-field (unrestricted Hartree-Fock) solutions. The circles represent the Monte Carlo result of Hirsch (Ref. 16) (who used $\lambda=0.29$).

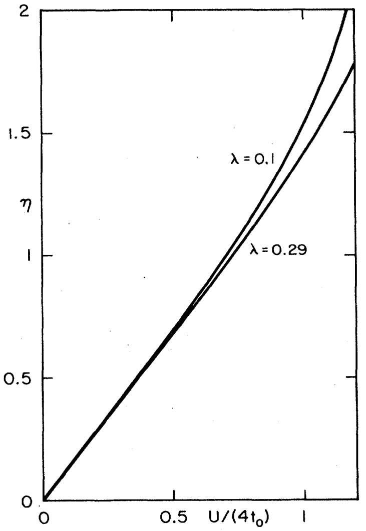

FIG. 3. Correlation parameter η as a function of U.

exact ground state of the Hamiltonian (1) for $\Delta_0=0$. Our variational result (with $\Delta_0\neq 0$) is seen to have lower energy than the exact $\Delta_0=0$ solution if λ is not too small. For very small values of λ the condensation energy due to bond alternation is too small to compensate for our approximate treatment of the correlation energy (cf. Sec. III A). Therefore we conclude that the system does exhibit bond alternation in the whole region where the present approximation is applicable, namely, for $U/4t_0 \lesssim 1$. For $U\rightarrow\infty$ the ground state will be of the spin-Peierls type, i.e., of the same symmetry as the dimerization due to bond alternation. This strongly indicates that there is no phase transition for finite U and that the system always remains dimerized.

It is worthwhile to emphasize that the analytical results derived in the preceding section are in close agreement with the numerical results represented in Figs. 1—4 up to $U/(4t_0)\sim 1$. In particular the analytical treatment yields also a maximum for the bond alternation. According to Eq. (20) the maximum originates from two competing effects: on the one hand from the increase in δ which is dominating for small U, on the other hand from the decrease in $\lambda/\tilde{\lambda}$ which becomes dominant when δ approaches saturation. With increasing λ the former effect weakens and the maximum shifts towards lower values of U. For $\lambda \gtrsim 0.37$ the maximum occurs at $U=0$ which means that U decreases bond alternation for large enough electron-phonon coupling.

V. SCREENED FORCE CONSTANT

The second derivative of the total energy with respect to the dimerization parameter yields the effective force constant associated with the bond stretching mode which includes the screening effect due to π electrons. The ratio between screened and unscreened force constants is given by (cf. Table I)

$$\Omega_0^2/\omega_0^2=\tfrac{1}{2}\pi\lambda d^2(\epsilon/t_0)/d\delta_0^2\ . \tag{25}$$

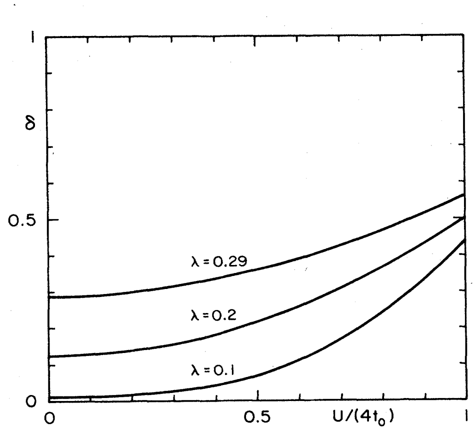

FIG. 2. Gap parameter $\delta=\Delta/2t_0$ as a function of U for three different values of λ.

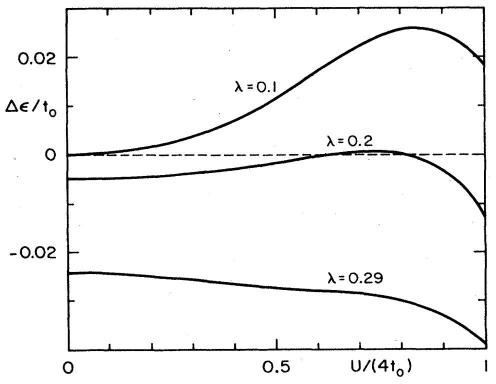

FIG. 4. Energy difference $\Delta\epsilon=\epsilon(\eta,\delta_0,\delta)-\epsilon(\mathrm{LW})$ between the variational result $\epsilon(\eta,\delta_0,\delta)$ for finite bond alternation and the exact result $\epsilon(\mathrm{LW})$ for vanishing bond alternation.

For noninteracting electrons ($U=0$, $\eta=0$, $\delta=\delta_0$), one obtains from Eq. (17) the usual result

$$\Omega_0^2/\omega_0^2=2\lambda\ , \tag{26}$$

which has been used sometimes to determine the unscreened phonon frequency ω_0 (by taking Ω_0 from the observed Raman lines and adjusting λ to reproduce the observed electronic gap[28]). For $U>0$ we have to find out how the two electronic parameters η and δ change when δ_0 is modified. According to the adiabatic approximation this is accomplished by minimalizing $\epsilon(\eta,\delta_0,\delta)$ with respect to η and δ for fixed δ_0. This procedure is carried out in Appendix D for the limit $\lambda \ll 1$, $U/4t_0 \ll 1$ with the following result:

$$\Omega_0^2/\omega_0^2=2\tilde{\lambda}\frac{1-2c_3\hat{U}^2}{1-(2c_2-2c_3+c_2/\tilde{\lambda})\hat{U}^2}\ . \tag{27}$$

It implies that the screening effect is reduced by electron correlation. This picture is fully confirmed by numerical calculations based on Eq. (23). The resulting curves for three different values of λ are shown in Fig. 5. It is seen that Ω_0^2/ω_0^2 comes close to 1 when $U/(4t_0)$ is of the order of 1. Above this point the screening factor passes through a maximum and starts to decrease when U is further enhanced. This looks like an artifact of our approximation which is no more valid for $U/4t_0>1$. Nevertheless, in the spin-Peierls limit ($U\rightarrow\infty$) we find $\Omega_0^2/\omega_0^2=\frac{2}{3}$ when using the expressions for the ground-state energy as given by Nakano and Fukuyama[24] or, more recently, by Dassen and de Moura[29] who include logarithmic corrections.

VI. DISCUSSION AND CONCLUSIONS

The present analysis shows that the Hubbard term strongly affects the ground-state properties of conjugated polymers. For $U/(4t_0)\lesssim 1$ (and $\lambda\lesssim 0.37$) U enhances bond alternation and reduces the screening of elastic forces. In order to estimate these effects for polyacetylene we use the parameters of Kakitani[30,31] shown in Table II.

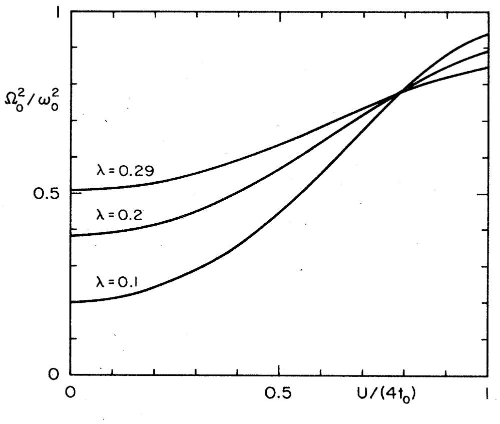

FIG. 5. Screening factor for the force constant of the bond-stretching mode.

TABLE II. Parameters for polyacetylene as derived from properties of small molecules.

Hückel model	SSH model
$t_0=2.9$ eV	$t_0=2.9$ eV
$\dfrac{dt}{dr}=4.5$ eV Å^{-1}	$\alpha=3.9$ eV Å^{-1}
$\dfrac{d^2E_\sigma}{dr^2}=46$ eV Å^{-2}	$K_0=35$ eV Å^{-2}

They give a parameter $\lambda\sim 0.1$. It has to be noticed that these parameters are determined from properties of organic molecules, for instance the frequency of the fully symmetric vibrational mode in benzene which does not involve the π electrons. The measured bond alternation y in polyacetylene is of the order of 0.04 to 0.05 Å (Refs. 32–34) which corresponds to $\delta_0=(dt/dr)y/t_0\sim 0.06$ to 0.08. The effective force constant $d^2\epsilon/dy^2$ is related to the frequency of the bond-stretching mode Ω_0 as $d^2\epsilon/dy^2=\frac{1}{3}M\Omega_0^2$ (in the case of the trans isomer), where M is the mass of a CH unit. If we associate this mode with the 1470-cm^{-1} Raman line we find $d^2\epsilon/dy^2=34.5$ eV Å^{-1}. This gives a screening factor $\Omega_0^2/\omega_0^2\sim 0.75$. A slightly different factor is obtained from the lattice-dynamical calculations of Mele and Rice[35] if we compare the observed frequency with their value for the bare frequency $\omega_0=1900$ cm^{-1}. In this case we find $\Omega_0^2/\omega_0^2\sim 0.6$. These empirical values for δ_0 and Ω_0^2/ω_0^2 are compared with our predictions in Fig. 6. The width of the hatched

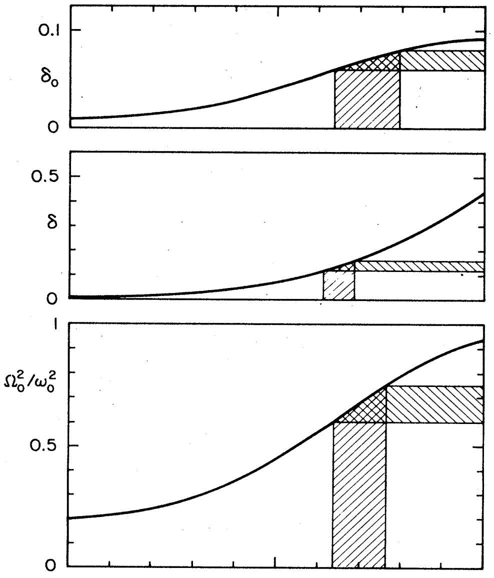

FIG. 6. Comparison of the variational results for the bond-alternation amplitude $\delta_0=\Delta_0/(2t_0)$, the gap parameter $\delta=\Delta/(2t_0)$ and the screening factor Ω_0^2/ω_0^2 with the corresponding experimental data. Thereby the parameters of Kakitani (Ref. 30) were used ($t_0=2.9$ eV, $\lambda=0.1$). The width of the hatched areas reflects experimental uncertainties.

area reflects the variations in available data. Additional uncertainty which has not been taken into account comes from the choice of basic parameters.

The empirical data for δ_0 and Ω_0^2/ω_0^2 are reproduced by our theory using essentially the same values of U, namely, $U/(4t_0)\sim 0.6$ to 0.8. This consistency is indeed very encouraging. With $t_0=2.9$ eV we have to conclude that the effective U in polyacetylene is of the order of 7 to 9 eV. A similar conclusion has been previously reached by Horsch,[36] but his variational result is no more reliable quantitatively for these U values. On the other hand our rather large U values disagree with estimates given by Kivelson and Heim on the basis of their perturbation expansion.[15] Our result is not too far from the "bare U" of 11.13 eV. This effective U is reduced from its bare value due to the nonlocal part of the Coulomb interaction. However, it is not accurately known how to model this nonlocal part nor is it well established how to incorporate this part within an effective Hubbard term. Therefore it seems to be rather difficult to get a reliable estimate for U "from first principles."

Empirical values for the optical gap 2Δ vary between 1.4 and 1.9 eV. With $t_0=2.9$ eV this gives a parameter δ between 0.12 and 0.16 which corresponds to $U/(4t_0)\sim 0.6$ to 0.7 in our theory (cf. Fig. 6). The connection between the optical gap and our mean-field parameter δ is of course somewhat problematic since, on the one hand, the optical threshold may be dominated by excitonic effects, on the other hand the link between δ and the quasiparticle excitation spectrum has to be clarified. A study of excited states within the present approach, in particular singlet and triplet excitons, would be highly desirable.

Note added in proof. Recently we have included the nearest-neighbor term $V\sum_i n_i n_{i+1}$ in our analysis. We find that Eq. (18) is modified to $\eta=c_0 U_{\text{eff}}/4t_0$ where $U_{\text{eff}}=U-1.216$ V. However the effects on δ and δ_0 cannot be simply represented in terms of U_{eff}.

ACKNOWLEDGMENTS

One of the authors (D.B.) would like to thank the University of Southern California for support during the initial stage of this work. We have both benefited from the hospitality of the University of Geneva. This work was supported in part by the National Science Foundation under Grant No. DMR-82-14525.

APPENDIX A: EVALUATION OF THE CORRELATION FUNCTIONS P_{nm}

The mean-field Hamiltonian, Eq. (5), is diagonalized by the canonical transformation

$$c_{n\alpha}=N^{-1/2}\sum_k \exp\{i[kn+(-1)^n\vartheta_k]\} \times[b_{k\alpha}+(-1)^n a_{k\alpha}] , \tag{A1}$$

where $-\pi/2<k\leq\pi/2$ and the phase ϑ_k is determined as

$$\tan(2\vartheta_k)=-(\Delta/2t_0)\tan k . \tag{A2}$$

Equation (5) becomes

$$H_0=\sum_{k\alpha} E_k(a_{k\alpha}^\dagger a_{k\alpha}-b_{k\alpha}^\dagger b_{k\alpha}) , \tag{A3}$$

where the spectrum E_k is given by

$$E_k=[(2t_0)\cos^2 k+\Delta^2\sin^2 k]^{1/2} . \tag{A4}$$

In the ground state $|0\rangle$ the valence band is full, $\langle 0|b_{k\alpha}^\dagger b_{k\alpha}|0\rangle=1$, and the conduction band is empty, $\langle 0|a_{k\alpha}^\dagger a_{k\alpha}|0\rangle=0$. The correlation functions defined by Eq. (8) are then easily obtained as

$$P_{n,n+2m}=\frac{1}{2\pi}\int_{-\pi/2}^{\pi/2}dk\, e^{2ikm}=\tfrac{1}{2}\delta_{m,0} , \tag{A5}$$

$$P_{n,n+2m+1}=\frac{1}{2\pi}\int_{-\pi/2}^{\pi/2}dk\, e^{ik(2m+1)} \times[2t_0\cos k+i(-1)^n\Delta\sin k]/E_k , \tag{A6}$$

from which Eqs. (9), (10), and (12) follow.

APPENDIX B: EXPANSION OF THE ENERGY TO SECOND ORDER IN η

The correlation functions generated by the expansion in powers of η, Eq. (7), can be decomposed according to Wick's theorem in terms involving the functions P_{ij} [Eq. (8)] and

$$Q_{ij}=\langle 0|c_{i\alpha}c_{j\alpha}^\dagger|0\rangle=\delta_{ij}-P_{ij} . \tag{B1}$$

These functions are symmetric, $P_{ij}=P_{ji}$, $Q_{ij}=Q_{ji}$, and satisfy the sum rules

$$\sum_i P_{ij}P_{jk}=P_{ik} , \tag{B2}$$

$$\sum_i Q_{ij}Q_{jk}=Q_{ik} , \tag{B3}$$

$$\sum_i P_{ij}Q_{jk}=0 . \tag{B4}$$

Consider first the kinetic energy

$$\langle T\rangle=-\sum_{i\alpha} t_i\langle 0|e^S(c_{i\alpha}^\dagger c_{i+1\alpha}+c_{i+1\alpha}^\dagger c_{i\alpha})e^S|0\rangle_c . \tag{B5}$$

Expanding as in Eq. (7) we find

$$\begin{aligned}\langle 0|e^S c_{i\alpha}^\dagger c_{i+1\alpha}e^S|0\rangle_c &= P_{i,i+1}-\tfrac{1}{2}\eta\langle 0|\{W,c_{i\alpha}^\dagger c_{i+1\alpha}\}|0\rangle_c\\ &\quad+\tfrac{1}{8}\eta^2\langle 0|\{W,\{W,c_{i\alpha}^\dagger c_{i+1\alpha}\}\}|0\rangle_c .\end{aligned} \tag{B6}$$

The decomposition in terms of P_{ij} and Q_{ij} gives

$$\langle 0|\{W,c_{i\alpha}^\dagger c_{i+1\alpha}\}|0\rangle_c=\tfrac{1}{2}\sum_j(P_{j,i+1}Q_{ji}+P_{ij}Q_{i+1j})=0 , \tag{B7}$$

$$\begin{aligned}\langle 0|\{W,\{W,c_{i\alpha}^{\dagger}c_{i+1\alpha}\}\}|0\rangle_c=\sum_{nm}\{&4P_{nm}Q_{nm}P_{nn}(P_{mi+1}Q_{mi}+Q_{mi+1}P_{mi})\\&+P_{nn}P_{mm}[(Q_{ni}P_{mi+1}+P_{ni}Q_{mi+1})(Q_{nm}-P_{nm})\\&\qquad+2(Q_{mi}Q_{ni+1}P_{nm}-P_{mi}P_{ni+1}Q_{nm})]\\&+P_{nm}^2[(Q_{ni}P_{mi+1}+P_{ni}Q_{mi+1})(P_{nm}-Q_{nm})\\&\qquad+2(Q_{mi}Q_{ni+1}Q_{nm}-P_{mi}P_{ni+1}P_{nm})]\}\;. \qquad \text{(B8)}\end{aligned}$$

Equations (B7) and (B8) are represented by diagrams in Figs. 7(a) and 7(b), respectively. The sum rule (B4) implies that only the third diagram of Fig. 7(b) gives a finite contribution. Using Eqs. (A5) and (B1)—(B4) we find

$$\langle 0|\{W,\{W,c_{i\alpha}^{\dagger}c_{i+1\alpha}\}\}|0\rangle_c=\tfrac{1}{2}P_{ii+1}+2P_{ii+1}^3-8\sum_{nm}P_{nm}^3P_{mi}P_{ni+1}\;. \qquad \text{(B9)}$$

Collecting Eqs. (B5)—(B9) we obtain the kinetic energy as given in Eq. (11). The expansion of the potential energy in powers of η gives

$$\langle V\rangle=U[\langle 0|W|0\rangle-\eta\langle 0|W^2|0\rangle_c+\tfrac{1}{2}\eta^2\langle 0|W^3|0\rangle_c]\;, \qquad \text{(B10)}$$

where $W=\sum_i n_{i\uparrow}n_{i\downarrow}$. The individual terms are obtained as

$$\langle 0|W|0\rangle=\sum_i P_{ii}^2=\tfrac{1}{4}N\;, \qquad \text{(B11)}$$

$$\langle 0|W^2|0\rangle_c=\sum_{ij}(2P_{ii}P_{jj}P_{ij}Q_{ij}+P_{ij}^2Q_{ij}^2)=\sum_{ij}P_{ij}^4\;, \qquad \text{(B12)}$$

$$\begin{aligned}\langle 0|W^3|0\rangle_c=\sum_{ijk}\{&2P_{ii}P_{jj}P_{kk}(P_{ij}Q_{jk}Q_{ki}-Q_{ij}P_{jk}P_{ki})+6P_{jj}P_{kk}P_{ij}Q_{ij}P_{ik}Q_{ik}\\&+P_{jk}^2[Q_{ij}Q_{jk}(Q_{ik}-2P_{ik})-P_{ij}P_{jk}(P_{ik}-2Q_{ik})]+(Q_{ij}P_{jk}P_{ki}-P_{ij}Q_{jk}Q_{ki})^2\}\;. \qquad \text{(B13)}\end{aligned}$$

Equations (B12) and (B13) are represented diagrammatically in Figs. 8(a) and 8(b), respectively. The first diagram of Fig. 8(a) and the first three diagrams of Fig. 8(b) are easily seen to yield vanishing contributions by virtue of the sum rule (B4). But also the last term in Eq. (B13) is found to be 0. Therefore the potential energy has the form given in Eq. (11).

APPENDIX C: MINIMALIZATION OF THE ENERGY FOR $\lambda \ll 1$, $U/4t_0 \ll 1$

The η-dependent terms in Eq. (17) can be written as

$$\frac{2}{\pi}a_0A\eta^2-b_0B(U/4t_0)\eta\;, \qquad \text{(C1)}$$

where

$$A=1+a_0^{-1}[a_1\delta^2(\Lambda-1)^2-a_2\delta^2(\Lambda-\tfrac{3}{2})+a_3\delta_0\delta(\Lambda-1)]\;, \qquad \text{(C2)}$$

$$B=1+b_0^{-1}[b_1\delta^2(\Lambda-1)^2-b_2\delta^2(\Lambda-\tfrac{3}{2})]\;. \qquad \text{(C3)}$$

The term (C1) is easily minimalized with respect to η, giving

$$\eta=\hat{U}B/A\;, \qquad \text{(C4)}$$

where

$$\hat{U}=(\pi b_0/4a_0)(U/4t_0)\;. \qquad \text{(C5)}$$

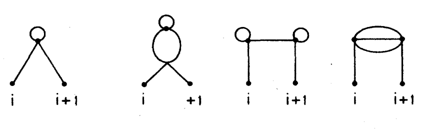

FIG. 7. Diagrammatic representation of the (a) first- and (b) second-order contributions to the kinetic energy.

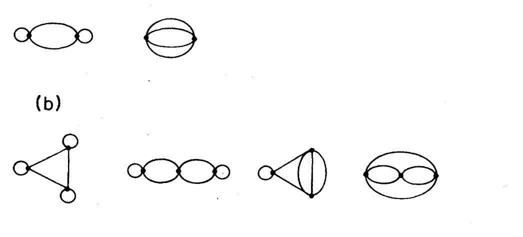

FIG. 8. Diagrammatic representation of the (a) first- and second-order contributions to the potential energy.

For $\delta \ll 1$ we obtain Eq. (18). Inserting Eq. (C4) into Eq. (17) we obtain the following expression for the energy:

$$\epsilon/t_0 = \delta_0^2/(\pi\lambda) - (4/\pi)[1 - \tfrac{1}{2}\delta^2(\Lambda - \tfrac{3}{2}) + \delta_0\delta(\Lambda - 1)] + (U/4t_0) - (2/\pi)a_0\hat{U}^2B^2/A \ . \tag{C6}$$

Expanding the last term to second order in δ and δ_0 we find

$$\epsilon/t_0 = \epsilon_0/t_0 + \delta_0^2/(\pi\lambda) - (4/\pi)[\,(1 - c_1\hat{U}^2)\delta_0\delta(\Lambda - 1) + c_2\hat{U}^2\delta^2(\Lambda - 1)^2 - (\tfrac{1}{2} - c_3\hat{U}^2)\delta^2(\Lambda - \tfrac{3}{2})] \ , \tag{C7}$$

where

$$\epsilon_0/t_0 = -(4/\pi) + U/4t_0 - (2/\pi)a_0\hat{U}^2 \ , \tag{C8}$$

and $c_1 = \frac{1}{2}a_3$, $c_2 = a_0 b_0^{-1} b_1 - \frac{1}{2}a_1$, $c_3 = -a_0 b_0^{-1} b_2 + \frac{1}{2}a_2$. The minimalization of Eq. (C7) with respect to δ_0 gives

$$\delta_0 = 2\lambda(1 - c_1\hat{U}^2)\delta(\Lambda - 1) \ . \tag{C9}$$

Inserting this result into Eq. (C7) we obtain

$$(\epsilon - \epsilon_0)/t_0 = -(4/\pi)\{\,[\lambda(1 - c_1\hat{U}^2)^2 + c_2\hat{U}^2]\delta^2(\Lambda - 1)^2 - (\tfrac{1}{2} - c_3\hat{U}^2)\delta^2(\Lambda - \tfrac{3}{2})\} \ . \tag{C10}$$

Minimalizing this expression with respect to δ we finally get

$$\Lambda \equiv \ln(4/\delta) = 1 + 1/(2\tilde{\lambda}) \ , \tag{C11}$$

where $\tilde{\lambda}$ is given by Eq. (21). Inserting Eq. (C11) into Eqs. (C9) and (C10), we obtain Eqs. (20) and (22).

APPENDIX D: SCREENED FORCE CONSTANT FOR $\lambda \ll 1$, $U/4t_0 \ll 1$

We have to minimalize the energy $\epsilon(\eta,\delta_0,\delta)$ with respect to η and δ for given δ_0. For $\delta_0 \ll 1$, $\delta \ll 1$, the variation with respect to η leads to Eq. (C7) of Appendix C. Differentiating with respect to δ we find

$$(1 - c_1\hat{U}^2)\delta_0 + 2c_2\hat{U}^2\delta(\Lambda - 1) - (1 - 2c_3\hat{U}^2)\delta = 0 \tag{D1}$$

which represents an implicit equation for the function $\delta = \delta(\delta_0)$. Differentiating Eq. (D1) with respect to δ_0 gives

$$\frac{d\delta}{d\delta_0} = (1 - c_1\hat{U}^2)/[1 - 2c_3\hat{U}^2 - 2c_2\hat{U}^2(\Lambda - 2)] \ . \tag{D2}$$

Considering Eq. (C7) as a function of δ and δ_0, i.e., $\epsilon/t_0 = f(\delta_0, \delta(\delta_0))$ we obtain for the second derivative of the energy with respect to δ_0

$$\frac{d^2(\epsilon/t_0)}{d\delta_0^2} = \frac{\partial^2 f}{\partial\delta_0^2} + 2\frac{\partial^2 f}{\partial\delta\partial\delta_0}\frac{d\delta}{d\delta_0} + \frac{\partial^2 f}{\partial\delta^2}\left[\frac{d\delta}{d\delta_0}\right]^2 , \tag{D3}$$

where we have used the fact that $\partial f/\partial\delta = 0$ at equilibrium. The individual terms are

$$\frac{\partial^2 f}{\partial\delta_0^2} = 2/\pi\lambda \ , \tag{D4}$$

$$\frac{\partial^2 f}{\partial\delta_0\partial\delta} = -4\pi^{-1}(1 - c_1\hat{U}^2)(\Lambda - 2) \ , \tag{D5}$$

$$\frac{\partial^2 f}{\partial\delta^2} = -4\pi^{-1}[2c_2\hat{U}^2(\Lambda - 2) - 1 + 2c_3\hat{U}^2](\Lambda - 2) \ . \tag{D6}$$

Combining Eqs. (D3)—(D6) and using Eqs. (C11) and (21), one obtains indeed the expression (27) for the screening factor.

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