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COULOMB CORRELATIONS AND OPTICAL GAP IN POLYACETYLENE

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ABSTRACT

A model including both electron-phonon coupling (as in the SSH Hamiltonian) and electron-electron interactions (on-site term U , nearest-neighbor term V) is treated within the variational scheme of Gutzwiller. It is shown that for weak electron-phonon coupling the primary effect is a bond-order wave induced by electronic correlation, whereas the lattice dimerisation is a secondary effect. Correspondingly the optical gap is mainly due to electronic correlation.

1. INTRODUCTION

Single-particle models such as the SSH Hamiltonian are very attractive since most relevant quantities can be calculated in a transparent way. This provides a good motivation for being reluctant to include many-body effects, the more since those are difficult to handle without uncontrollable approximations. It seems, however, to become increasingly clear that effective single-particle models can at most provide a qualitative description of conducting polymers. They even fail completely if specific questions are addressed, e.g. the optical absorption [1] and the spin densities [2] associated with neutral solitons or the optical absorption from photogenerated defects [3]. This is not surprising in view of the well-established role of electron-electron interactions in finite polyenes [4]. Importantly, an "unbiased" set of single-particle parameters as derived from properties of organic molecules [5] fails to predict those properties which can be reproduced by the single-particle model if the parameters are appropriately adjusted [6]. We have earlier shown that an intermediate value of the on-site electron-electron interaction (U) is needed in order to account for the ground-state properties of polyacetylene using unbiased single-particle parameters [7]. This agrees with recent conclusions reached on the basis of finite chain calculations for the low-lying electronic excitations [8].

In this contribution we extend our variational calculations (based on the Gutzwiller approach) in two directions. First, an analysis of the optical energy gap and the conductivity sum rule indicates that the optical absorption spectrum is mainly determined by correlation effects and not by the lattice dimerisation.

Second, the inclusion of a nearest-neighbor interaction (V) yields only minor modifications as long as the bond-order wave (BOW) state has lower energy than the competing charge-density wave (CDW) phase. The Gutzwiller approach extends slightly the stability region of the BOW state (at the expense of the CDW state) as compared to the mean-field prediction.

2. VARIATIONAL METHOD

We add both on-site and nearest-neighbor Coulomb interactions to the SSH model and consider the following electronic Hamiltonian

$$H = - \sum_{i\sigma} t_i (c_{i\sigma}^\dagger c_{i+1,\sigma} + c_{i+1,\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_i n_i n_{i+1} \quad (1)$$

where $t_i = t_0 - \frac{1}{2}(-1)^i \Delta_0$, $c_{i\sigma}^\dagger$ creates a π -electron at site i with spin projection σ , $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ and $n_i = \sum_\sigma n_{i\sigma}$. The parameter Δ_0 is proportional to the dimerisation amplitude. It is determined so as to minimise the total energy

$$E = N\Delta_0^2/(4\pi\lambda t_0) + \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle \quad (2)$$

where the first term represents the elastic energy, N is the number of sites, λ characterises the strength of the electron-phonon coupling and $|\psi\rangle$ is the ground state of H . We use the Gutzwiller ansatz

$$|\psi\rangle = e^S |\phi\rangle, \quad S = -\frac{1}{2}\eta \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3)$$

where η is a variational parameter and $|\phi\rangle$ is the ground state of an appropriately chosen single-particle Hamiltonian. We choose it to have the same form as the kinetic energy in Eq. (1) with Δ_0 replaced by the "gap parameter" Δ . Horsch [9] who was the first to apply the Gutzwiller approach to polyacetylene did not distinguish between Δ and Δ_0 . (In the absence of interactions these parameters are indeed identical.) The distinction between Δ and Δ_0 allows the interactions to act differently on the electronic states than on the lattice dimerisation and is therefore quite natural. It will require a thorough treatment of excited states to demonstrate that 2Δ is equal to the optical energy gap. On the other hand, this turns out to be very plausible, as will be discussed in Section 3.

Our ansatz for the ground state energy depends on the three parameters η , $\delta_0 = \Delta_0/(2t_0)$ and $\delta = \Delta/(2t_0)$. As in our earlier work [7] we expand the electronic part up to second order in η . This corresponds to a small U expansion. The energy is written in terms of the correlation functions $P_{ij} = \langle \phi | c_{i\sigma}^\dagger c_{j\sigma} | \phi \rangle$ which decrease exponentially with distance $|i - j|$, the correlation length being given by $1/\delta$. In order to get analytical results we have previously neglected all P_{ij} for $|i - j| \geq 3$. The results presented in the next section have been obtained by taking all P_{ij} into account. The corresponding modifications of our previous results are small (typically of the order of 5%).

3. DIMERIZATION AND OPTICAL GAP FOR $V = 0$

We have minimised numerically the energy, Eq. (2), by varying the three parameters η , δ_0 and δ . The correlation parameter η increases essentially linearly with U/t_0 and depends only weakly on λ . The dimerisation parameter δ_0 is shown in Fig. 1 as a function of λ for three different values of U . For $U = 0$ δ_0

Fig. 1. Dimerisation parameter as a function of λ for three different values of U .

is given by the usual BCS relation. For finite U it varies linearly with λ for small enough λ . The larger U the more pronounced is this linear relationship. In regions of parameter space where δ_0 is a linear function of λ the BOW is not induced by the Peierls instability. The lattice simply responds linearly to the BOW which is driven by the electron-electron interaction. We emphasize that this is a true correlation effect since in Hartree-Fock approximation the BOW state becomes unstable for large enough U .

It is not a priori clear that 2Δ can be identified with the optical gap E_g , but Fig. 2 suggests that we are allowed to do so. It shows the parameter $\delta = 2\Delta/(4t_0)$ for three different values of λ as against the exactly known quantity $E_g/(4t_0)$ for $\lambda = 0$ [10,11]. For $\lambda = 0.1$ our variational result lies only slightly above the optical gap of the Hubbard model and is dominated by correlation effects for $U/(4t_0) > 0.3$. An analysis of properties of organic molecules [5,6], in particular of benzene, gives $\lambda \approx 0.1$. The extrapolation from molecules to polymers appears reasonable in view of a recent analysis of Raman experiments on polyacetylene, which yields essentially the same bare force constant for the polymer as is known for benzene [12]. We have shown previously that with this value of λ one needs $U/(4t_0) \approx 0.7$ (and therefore $U \approx 8\text{eV}$) in order to reproduce the experimentally observed values of the dimerisation amplitude, the optical gap and the effective force constant [7]. A recent discussion of photogeneration experiments yields essentially the same value [13]. For these values of λ and U the optical gap originates mainly from correlation effects.

Additional support for this conclusion comes from the conductivity sum rule which is proportional to the kinetic energy. Our variational result for the sum rule for $U/(4t_0) \approx 0.7$ is practically independent of λ

Fig. 2. Gap parameter as a function of U for three different values of λ (full lines) compared with the exact solution for the Hubbard chain (broken line).

4. NEAREST-NEIGHBOR COULOMB INTERACTION

The restriction to an on-site Coulomb interaction represents quite a drastic assumption since it is widely believed (in particular in the chemical literature) that the long-range terms are not negligible for conjugated polymers. Therefore it is important to study at least the effect of the nearest-neighbor term (V). We have calculated the modifications due to V using the truncation procedure described in Section 2. Here we quote only the essential results obtained analytically for $\eta \ll 1$, $\delta_0 \ll 1$, $\delta \ll 1$. Details will be published elsewhere. The correlation parameter η is found to increase linearly with $(U - 1.22V)$. The other properties are not simply functions of η and cannot be represented in terms of an effective U . In particular we find

$$\delta \approx 4 \exp \left[- \left(1 + \frac{1}{2\lambda} \right) \right] \quad (4)$$

$$\delta_0 \approx \frac{\lambda}{\tilde{\lambda}} \delta \quad (5)$$

$$\tilde{\lambda} \approx \lambda + 0.64v + 0.26(u - 1.22v)(u - 0.39v) \quad (6)$$

where $u = U/(4t_0)$, $v = V/(4t_0)$. For $\lambda = 0.1$ and small values of U ($u < 0.8$) both the dimerisation parameter δ_0 and the gap parameter δ increase with V . For larger values of U the gap decreases as a function of V whereas the dimerisation remains practically constant. For the specific parameter values which we believe to be appropriate for polyacetylene ($\lambda = 0.1$, $u = 0.7$) the effects of V are very small. This is of course only true as long as V is small enough, namely $V < U/2$. For larger values the CDW state has lower energy than the BOW phase and thus $\delta_- = 0$. We have studied the CDW instability again using the Gutzwiller ansatz

Eq. (3), with a mean-field state $|\phi\rangle$ of the appropriate symmetry. In the CDW phase the gap parameter can be written as in Eq. (4) with $\tilde{\lambda}$ given by

$$\tilde{\lambda} \approx 0.93v - 0.04u + 1.59(v - 0.57u)(v - 0.07u). \quad (7)$$

The correlation effects are much stronger in the CDW phase than in the BOW phase. In fact, the Hartree-Fock approximation [6] predicts $\tilde{\lambda} \approx \lambda + 2\pi^{-1}v$ for the BOW phase, in agreement with Eq. (6) to linear order in the interaction parameters, but $\tilde{\lambda} \approx \pi^{-1}(4v - u)$ for the CDW phase which disagrees with Eq. (7). This result is not surprising in view of the fact that the electron density at a given site is changed due to the formation of a CDW but remains unchanged in the case of a BOW. Comparing the energies of the two possible ground states we find that the correlation effects enlarge the BOW phase at the expense of the CDW phase. For small λ we obtain a phase diagram (in the U, V plane) which is in good agreement with general considerations about the effects of long-range Coulomb interactions [15].

A glance at Eqs. (4) to (6) confirms our conclusion at the end of the previous section. In the presence of interactions $\tilde{\lambda}$ remains finite for $\lambda \rightarrow 0$. Therefore the gap remains finite even if the dimerisation vanishes.

5. CONCLUDING REMARKS

Various techniques such as valence bond theory [16], numerical computations for finite chains [8,17,18], perturbation expansions [19] and variational methods [7,9] have consistently shown that, at least for $\lambda < 0.4$, dimerisation is enhanced by the Hubbard term as long as $U \neq 4t_0$. From our variational results for $\lambda \approx 0.1$ and $U/(4t_0) \approx 0.7$ we conclude that the electron-electron interactions have a more profound effect: it is due to electronic correlation that the ground state exhibits a BOW and not due to the Peierls effect. This conclusion is based on the following three observations. First the gap does not vanish for $\lambda \rightarrow 0$. For $\lambda = 0.1$ it is already very close to the exact optical gap for $\lambda = 0$. Second the conductivity sum rule is reduced by correlation effects from its value in the absence of interactions. The reduction factor is practically unchanged when λ is included. Third in this region of parameter space the dimerisation is a linear function of the gap parameter. This confirms that the correlation-induced BOW-instability is the primary effect. The dimerization represents the linear response of the lattice to the already existing BOW and in this sense is a secondary effect.

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