Molecular Crystals and Liquid Crystals

Correlation Effects in Conducting Polymers

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CORRELATION EFFECTS IN CONDUCTING POLYMERS

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Abstract The influence of on-site Coulomb interaction on the
amount of bond alternation is studied by adding a Hubbard
term (U) to the Hückel model. Using the Gutzwiller ansatz
for the electronic ground state the bond alternation is found
to increase as a function of U and to reach a maximum at
$U \approx 4t_o$.

1. INTRODUCTION

The single-particle description (Hückel model, SSH Hamilto-
nian) has been quite successful in describing the bond alternation,
the vibrational modes and the electronic gap in conjugated poly-
mers. Extensive studies on finite polymers, however, have shown
that electronic correlation effects are essential for describing
excited states. Furthermore, recent experiments on polyacetylene
such as ENDOR, optical absorption and luminescence have indicated
that the single-particle model is not sufficient for describing
the data. Theoretically the relevance of interaction effects has
been frequently emphasized, in particular by Ovchinnikov and co-

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workers[1] who argued that the electronic gap was due to correlation
and not due to bond alternation. The combined effects of correla-
tion and bond alternation have been studied by Ukrainskii[2] and
Horsch[3] who concluded that these are not competing effects but
that bond alternation was even enhanced by Coulomb correlation.
This result has recently been confirmed by Monte Carlo calcula-
tions[4] and numerical studies on finite rings[5]. Therefore, the ob-
served bond alternation in polyacetylene[6] cannot be taken as guar-
anty for the validity of the single-particle description. In this
note we present analytical results on the ground state properties
of a Hamiltonian including both electron-phonon and on-site elec-
tron-electron interactions. The correlation effects are derived
using the Gutzwiller ansatz. Our results agree surprisingly well
with Monte Carlo data; in particular bond alternation is enhanced
by a small on-site Coulomb term U and reaches a maximum for
$U \approx 4t_o$. For small values of U this enhancement can be under-
stood in terms of an effective single-particle picture with re-
normalized electron-phonon coupling $\tilde{\lambda}$. In the following our
procedure together with the main results for the ground state are
briefly outlined; more details will be published elsewhere[7].

2.   APPROACH

We consider the following π-electron Hamiltonian

$$H = -\sum_{ns} t_n (c^+_{ns} c_{n+1s} + c^+_{n+1s} c_{ns}) + U \sum_n c^+_{n\uparrow} c_{n\uparrow} c^+_{n\downarrow} c_{n\downarrow} \tag{1}$$

where the resonance integrals t_n are alternating between long
and short bonds, $t_n = t_o - (-1)^n \Delta_o/2$, Δ_o being proportional to
the amplitude of bond alternation. The total energy is given by

$$E = N\Delta_o^2/(4\pi\lambda t_o) + \langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle \tag{2}$$

where the first term is the elastic energy due to σ-bond compression, N is the number of sites, λ the dimensionless electron-phonon coupling constant and $|\psi\rangle$ the electronic ground state. We use the Gutzwiller wavefunction[3]

$$|\psi\rangle = e^{S}|0\rangle, \quad S = -\frac{1}{2}\eta \sum_{n} c_{n\uparrow}^{+} c_{n\uparrow} c_{n\downarrow}^{+} c_{n\downarrow} \quad , \tag{3}$$

where $|0\rangle$ is the ground state of the mean-field Hamiltonian

$$H_{o} = -\sum_{ns} [t_{o} - (-1)^{n}\Delta/2](c_{ns}^{+} c_{n+1s} + c_{n+1s}^{+} c_{ns}) \quad . \tag{4}$$

The three parameters η, Δ_{o} and Δ are determined by minimalizing the energy, Eq. (2). Using the linked-cluster theorem and expanding up to second order in η we find

$$\langle\psi|H|\psi\rangle/\langle\psi|\psi\rangle = \langle 0|e^{S}He^{S}|0\rangle_{c}$$

$$= -4\sum_{n} t_{n}[P_{n,n+1} + \frac{1}{2}\eta^{2}(\sum_{i} P_{in}^{3} P_{in+1} - 2\sum_{ij} P_{ij}^{3} P_{in} P_{jn+1})]$$

$$+ U(\frac{1}{4}N - \eta \sum_{ij} P_{ij}^{4}) + O(\eta^{3}) \tag{5}$$

where $P_{nm} = \langle 0|c_{ns}^{+} c_{ms}|0\rangle$. The correlation functions P_{nm} are easily calculated, in particular

$$P_{n,n+2m} = \frac{1}{2}\delta_{m,o}$$

$$\tag{6}$$

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

where $\delta = \Delta/(2t_{o})$ and $E = E(k^{2} = 1 - \delta^{2})$, $K = K(k^{2} = 1 - \delta^{2})$ are the complete elliptic integrals. The functions $P_{n,n+2m+1}$ decrease exponentially for $|m| \to \infty$ with a correlation length δ^{-1}.

3. RESULTS

In order to obtain simple analytical expressions for the energy we have neglected correlation functions P_{nm} with $|n-m| \geq 3$. For $\Delta = 0$

where $P_{n,n+2\ell+1} = (-1)^{\ell}(2\ell+1)^{-1}/\pi$

this approximation yields a reduction in correlation energy of less than 10%; for $\Delta \neq 0$ where the correlation functions P_{nm} decrease exponentially it should become even better. In the weak-coupling limit where $\delta \ll 1$ we have

$$P_{n,n+1} \approx [1 + \tfrac{1}{2}\delta^2(\tfrac{3}{2} - \Lambda) + (-1)^n\delta(1 - \Lambda)]/\pi \tag{7}$$

where $\Lambda = \ell n(4/\delta)$. Using this form and truncating the summation as described above we obtain an explicit expression for the energy. Its minimalization with respect to the three parameters η, Δ_o, Δ yields the "gap equation"

$$\Delta = 8t_o/\exp(1 + \frac{1}{2\widetilde{\lambda}}) \tag{8}$$

where $\widetilde{\lambda} \approx \lambda + 0.26 (U/4t_o)^2$ is an effective coupling constant which increases with U. The bond alternation amplitude Δ_o is related to Δ as

$$\Delta_o \approx \Delta[1 - 0.10(U/4t_o)^2]\lambda/\widetilde{\lambda} \tag{9}$$

which is also an increasing function of U. If the electron-phonon coupling is dominating, i.e. for $(U/4t_o)^2 \ll \lambda \ll 1$, Eqs (8) and (9) give
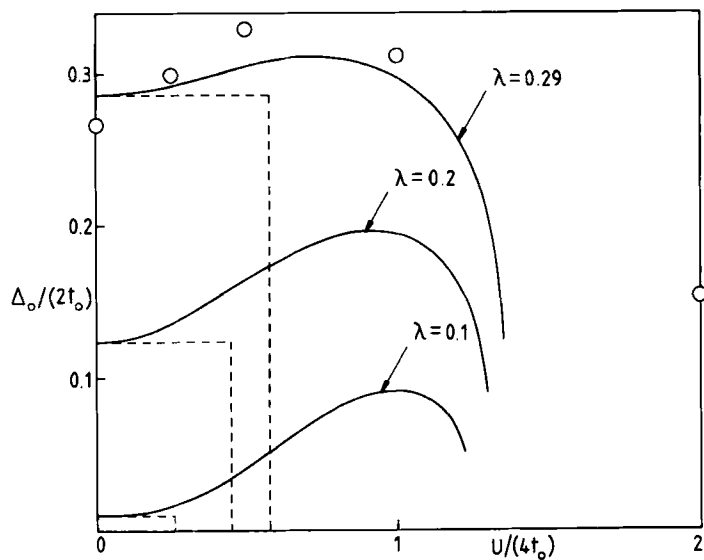
FIGURE 1 : Bond alternation parameter Δ_o as a function of the on-site Coulomb interaction U for three different values of the electron-phonon coupling λ. Full lines indicate the present variational results, broken lines correspond to the mean-field solution and the circles are the Monte Carlo data of Hirsch[4].

$$\Delta_o(U) \approx \Delta(U) \approx \Delta(0)\exp[0.13(U/4\lambda t_o)^2] \ . \tag{10}$$

This shows that the initial increase of bond alternation with U is the stronger the smaller λ. Furthermore, in this region the increase of the gap parameter Δ is simply due to increase in bond alternation Δ_o. If U becomes larger, Δ increases faster than Δ_o ; on the other hand the physical meaning of Δ and in particular its relation to the quasi-particle excitation spectrum will have to be clarified. The correlation parameter η increases linearly initially, $\eta \approx 1.4(U/4t_o)$, which justifies the expansion in powers of η for small U.

If U increases further the approximation used in Eq. (7) is no more valid and one has to minimalize Eq. (5) numerically with P_{nm} given by Eq. (6). The bond alternation parameter Δ_o obtained in this way is shown in Fig. 1 for three different values of λ and compared with results obtained by Hirsch[4] for $\lambda = 0.29$ using a Monte Carlo procedure. The initial increase with U is fully confirmed. The bond alternation reaches a maximum around $U \approx 4t_o$ and subsequently decreases. However, for $U \gtrsim 4t_o$ the present approach becomes questionable since η becomes larger than 1 and the expansion (5) is no more valid. Nevertheless the close agreement with the Monte Carlo data indicates that the location of the maxima is essentially correct.

4.   CONCLUSION

The results of our variational procedure show that a small U enhances bond alternation; this effect is the more pronounced the smaller the electron-phonon coupling λ. If λ is determined from properties of small organic molecules one obtains a value $\lambda \approx 0.1$ [8]. In this case the correlation induced increase of bond alternation

can be as large as a factor of 10, the maximum value being reached for $U \approx 4t_0$. Our variational energy with $\Delta_0 \neq 0$ turns out to be lower than the exact energy of the one-dimensional Hubbard model[9] (which corresponds to $\Delta_0 = 0$) for all values of U where our procedure is appropriate, i.e. for $U \leq 4t_0$. This indicates that the system exhibits bond alternation for all values of U. A detailed prediction for the large U behaviour is beyond the present approximation, but the ground state is expected to go over smoothly into that of the spin-Peierls phase where the bond alternation decreases as $U^{-3/2}$ [10].

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