LA-UR--86-2207

DE86 012434

CONF-8606133 -- 5

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RECEIVED BY O-11 JUL 07 1986

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SUBMITTED TO Proceedings of the International Conference on Science and
Technology of Synthetic Metals held June 1-6, 1986, in Kyoto,
Japan.

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ELECTRON-ELECTRON INTERACTION EFFECTS IN QUASI-ONE-DIMENSIONAL CONDUCTING POLYMERS AND RELATED SYSTEMS

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ABSTRACT

We review recent results on the role of electron-electron (e-e) interactions in quasi-one-dimensional conducting polymers and related systems. Within the Peierls-Hubbard model, the effects of both short-range (on-site U and nearest neighbor V_1) and long-range ($V_j, j \geq 2$) are examined, the former using quantum Monte Carlo and the latter with exact diagonalisation of finite size systems and analytic arguments. We also discuss optical absorption properties in the presence of electronic correlation, focusing on the weak and strong coupling limits.

I. INTRODUCTION

It has recently become increasingly clear that both electron-phonon (e-p) and electron-electron (e-e) interactions are important in real quasi-one-dimensional materials, such as conducting polymers and charge transfer salts. Although purely e-p interaction models, such as the original SSH Hamiltonian for trans-polyacetylene [1], capture the novel localised, nonlinear excitations that have created considerable interest in these systems, they miss such important experimentally observed features as negative spin densities on alternate carbon atoms [2,3], the strong shift of neutral soliton absorption from "mid-gap" [4], and the ordering of excited states in finite polyenes [5]. Accordingly, in the past several years there have been numerous efforts to study the role of e-e interactions – often called "correlation effects" – in conducting polymers. In this contribution, we present a brief, selective review of our own recent work on several aspects of this problem. Further details and a more complete bibliography of the relevant literature are provided in the references. In the ensuing sections we review our quantum Monte Carlo results for ground states and nonlinear excitations in the presence of short-range e-e interactions, recall the nature of the broken symmetry ground states for long-range interactions, and finally discuss some work in progress aimed at understanding the optical absorption of conducting polymers in the weak and strong e-e interaction limits.

II. THEORETICAL BACKGROUND AND APPROACH

Our goal is to obtain a detailed understanding of the interplay of e-p with both short and long range e-e interactions. Thus rather than treat approximately a semi-realistic model of a specific quasi-one-dimensional

conducting polymer, we shall attempt to treat exactly (at least in the numerical sense) a simplified but qualitatively correct class of models. These are described by the "Peierls-Hubbard" Hamiltonian, $H = H_{1-e} + H_{e-e}$, where

$$H_{1-e} = \frac{1}{2M} \sum_i p_i^2 + \frac{K}{2} \sum_i (u_i - u_{i+1})^2 + \sum_{i,\sigma} (t_0 + \alpha(u_i - u_{i+1}) + (-1)^i t_1) (c_{i+1,\sigma}^\dagger c_{i,\sigma} + c_{i,\sigma}^\dagger c_{i+1,\sigma}) \quad (1.a)$$

and

$$H_{e-e} = \frac{U}{2} \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} + V_1 \sum_i n_i n_{i+1} + \sum_{j \geq 2} V_j \sum_i n_i n_{i+j}, \quad (1.b)$$

where $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ and $n_i = \sum_\sigma n_{i,\sigma}$. Importantly, this Hamiltonian - perhaps generalised to include intra-molecular phonons coupled to the electrons - can serve as a theoretical starting point not merely for conducting polymers but also for other quasi-one-dimensional systems, both with half-filled bands (i.e., N electrons on N sites, so that $\rho \equiv N_e/N = 1$, as for example in the mixed stack charge transfer salts [6]) and with other band fillings (e.g., TTF-TCNQ at 19 Kb, near the $\rho = 2/3$ limit [7]). For definiteness, we will focus here on the applications to conducting polymers, taking trans - $(CH)_x$ and cis - $(CH)_x$ or polythiophene as the respective prototypes for the degenerate and non-degenerate ground state cases. In the context of $(CH)_x$, the dynamical variables in H represent the molecular displacements (u_i) from the hypothetical equal bond length positions and the momenta (p_i) of the backbone (CH) units and the electrons - $c_i^\dagger(c_i)$ creates (annihilates) an electron at site i - that form the π -molecular orbital. In (1) K represents the elastic potential for the lattice, M is the (CH) unit mass, t_0 describes the bare electron hopping integral and α its modulation due to e-p coupling, $U(> 0)$, and $V_1(> 0)$ model the on-site and nearest neighbor Coulomb repulsions, and the $V_j(> 0)(j \geq 2)$ describe the long-range e-e interactions. Note that t_1 represents an extrinsic "dimerising" modulation to the hopping integral, so that $t_1 = 0$ for polymers with two-fold degenerate ground states (e.g., trans - $(CH)_x$ and $t_1 \neq 0$ for polymers with non-degenerate ground states [8] (e.g., cis - $(CH)_x$ or polythiophene). Typically, calculations are carried out in the adiabatic limit, in which the quantum nature of the phonons is ignored and H is treated as an energy functional, to be minimised over phonon coordinates. Treating the single particle Hamiltonian in this manner leads [1] to the predictions that the ground state is indeed dimerised (and that there exists a corresponding $2k_F$ bond order wave (BOW)) and that, for $t_1 = 0$, the nonlinear excitations include kink solitons [1] (K^0 , K^+ , and K^-) and polarons [8-11] (P^+ and P^-), whereas for $t_1 \neq 0$, there are only polarons and bipolarons [8,10-11] (BP^{--} , BP^{++} , and BP^0 , which is nothing but a singlet exciton in which the charges are bound by strong e-p coupling).

III. SHORT-RANGE INTERACTIONS: QUANTUM MONTE CARLO STUDIES

Since our results on the effects of short range (U and V_1 only) e-e interactions have been discussed extensively elsewhere [12], here we simply recall two sets of points relevant to our present discussion. First, dimerisation does persist in the presence of correlations, and (for the relevant range of e-p coupling) is in fact enhanced (for $V_1 = 0$) from its value when only H_{1-e} is present. Adding V_1 further enhances the dimerisation. Importantly, this confirms the expectation that the Hartree-Fock approximation, which predicts [13] the absence of a BOW above $U/t_0 \sim 2$, fails qualitatively for moderately strong e-e interactions. Second, the solitons of trans - $(CH)_x$ remain stable, with the important qualitative differences that the degeneracy between K^0 and $K^\pm$ is broken and, consistent with the ENDOR data [2,3], negative spin densities appear on alternate carbons in the case of the neutral soliton. In addition, soliton doping persists, i.e., the

K^+K^+ state is favored over the doubly charged dimer. To the extent that they overlap, these results are entirely consistent with those obtained in related Monte Carlo [14] and other exact [15-16] or renormalisation group [17] many-body methods.

IV. LONG-RANGE INTERACTIONS: ANALYTIC AND NUMERICAL RESULTS

To complement the results on short-range electron-electron interactions outlined above, we survey here some recent results on long-range interactions [18]. Although limited at present to ground states of the half-filled ($\rho = 1$) systems, these results are interesting both because they are sharp and because they provide a link to the chemical literature on finite polyenes, where long-range interaction models of the Pariser-Parr-Pople type [16,19] have been extensively studied. Here we simply state our conclusions and refer readers to the literature for details [18]. If in the Hamiltonian (1) the parameters V_j satisfy $V_{j+1} + V_{j-1} \geq 2V_j$ - the "convexity" condition - then the ground state for the $\rho = 1$ system is a $2k_F$ charge density wave (CDW) - that is, electron density peaked on the lattice sites - if

$$\frac{1}{2}U + \sum V_{2j} < \sum V_{2j+1}, \quad (2.a)$$

whereas it is a $2k_F$ bond order wave (BOW) - that is, electron density peaked between the sites - if

$$\frac{1}{2}U + \sum V_{2j} > \sum V_{2j+1} \quad (2.b)$$

If the interactions are non-convex - so that $V_{j+1} + V_{j-1} < 2V_j$ for some j - then it is possible to have a non- $2k_F$ CDW ground state. These results apply in the limit of 0^+ e-p coupling; obviously, for example, a strong intersite e-p coupling (the α of Eq. (1)) will compete with the tendency to form a $2k_F$ CDW if Eq. (2.a) holds, but will enhance the tendency towards a $2k_F$ BOW if Eq. (2.b) is valid. Further, in finite systems and for non-zero dimerisation, coexistence regions appear near the boundary between the inequalities. One specific result worth emphasizing is the prediction that a BOW (hence dimerised) ground state exists for both the Ohno and the Mataga-Nishimoto parametrisations of the PPP Hamiltonian [see, eg., Ref. 20].

V. OPTICAL ABSORPTION IN THE PRESENCE OF ELECTRON-ELECTRON INTERACTIONS

In Section III we have already indicated briefly that the striking nonlinear excitations of the single particle theory are expected to remain relevant at least for some properties even in the presence of relatively strong e-e interactions. Since within the single particle theory perhaps the clearest signatures of these excitations are their intra-gap optical absorptions, observable both in doped samples and in photo-induced photoabsorption, it is essential to understand how these intra-gap features change in the presence of e-e interactions. Unfortunately, this is a hard problem, for it in effect requires knowledge of the many-particle wave functions of the excited states in addition to the ground state. Indeed, an important challenge to theory over the next few years is to improve on the semi-quantitative discussion given below of the weak and strong e-e interaction limits.

We begin by recalling briefly the results for $\alpha(\omega)$, the optical absorption as a function of photon frequency (ω), in the single particle theory. For kink solitons (see, eg., Ref. 21), associated with the single localised electronic level at mid-gap is a strong intra-gap absorption having, in the strictly one dimensional continuum model, a $(\omega - \Delta_0)^{-1/2}$ singularity at the absorption edge $\omega = \Delta_0$. By the optical sum rule, the strength in this absorption is removed from the inter-band transition, leading to a "bleaching" above $\omega = 2\Delta_0$. For polarons (see Fig. 1 and Ref. 22) the two localised electronic levels (at $\pm\omega_0$) lead to three distinct intra-gap absorptions, for which analytic expressions are available [22] in the continuum limit: (1) α_1 , a δ -function transition at $\omega = 2\omega_0$; (2) α_2 , a (strong) low energy feature exhibiting a $(\omega - (\Delta_0 - \omega_0))^{-1/2}$ singularity

Fig. 1. The optical transitions allowed to a single polaron. For a charged bipolaron, only $\alpha^{(2)}$ and $\alpha^{(3)}$ are allowed.

Fig. 2. The relative integrated intensities for the transitions involving localized levels of polarons/bipolarons plotted as functions of the locations of these levels in the gap.

at the absorption edge $\omega = \Delta_0 - \omega_0$; and α_3 , a (weak) high energy feature which vanishes as $(\omega - (\Delta_0 + \omega_0))^{1/2}$ at the absorption edge $\omega = \Delta_0 + \omega_0$. The relative integrated intensities, as functions of ω_0 , the location of the localized electronic levels, are shown in Fig. 2. For charged bipolarons [22], there are also two localized electronic levels (at $\pm\omega'_0$, with $\omega'_0 < \omega_0$ for the same bare parameters in H) but the occupancy of these levels (fully occupied for BP^{--} , empty for BP^{++}) precludes the δ -function transition at $\omega = 2\omega'_0$. Thus the two intra-gap transitions for the bipolaron are the (strong) transition α_2 at $\omega = (\Delta_0 - \omega'_0)$ and the (weak) α_3 at $\omega = \Delta_0 + \omega'_0$.

To discuss the changes due to e-e interactions, we focus on the cases of the kink and the bipolaron, as these have been of greatest recent experimental interest. Further, for simplicity we consider only the effects of U (and in some indicated cases, V_1). In the case of the kinks, for weak e-e coupling involving U only, we find [23] (using first order perturbation theory) that the optical transition energy, $(TE)^0$, associated with the presence of a neutral kink shifts upward from mid-gap toward the band edge (consistent with earlier experiments [4]) to $(TE)^0 = \Delta_0 + U/3\ell_K$, where ℓ_K is the width of the kink. Similarly, the transition energy for the charged solitons, $(TE)^\pm$, shifts down to $(TE)^\pm = \Delta_0 - U/3\ell_K$. Thus the difference, $(TE)^0 - (TE)^\pm = 2U/3\ell_K$. Importantly, recent optical modulation data on trans-(CH)₃ [24] reveal a (negative) change in absorption at 1.40 eV associated with (the bleaching of) the K^0 transition (from neutral kinks in the pristine material) and a (positive) change in absorption at 0.45 eV associated with the (appearance of the) $K^\pm$ transition. Taking $\ell_K \approx 7$, the difference of 0.95 eV implies $U \approx 10\phi V (\approx 4t_0)$. This is well into the intermediate coupling range, where perturbation theory should in fact break down. Indeed, for U of this size the single particle picture itself breaks down, and there is no longer any a priori relation between, for example, the optically excited state of a charged kink ($(K^+)^\pm$) and the state involving a neutral kink (K^0) plus a hole (-e). One must calculate total energies of both ground and excited N electron states. Nonetheless,

as indicated in Section III above, correlated states associated with solitons do exist even for large U , and one can define (and measure) the associated optical transition energies. At present, in the difficult intermediate coupling regime ($U \simeq 4t_0$), there are no definitive theoretical results on optical absorption. For strong coupling, however, one can show that (with U only) $(TE)^0 - (TE)^\pm \simeq U$. Thus as the strength of the electron-electron interaction parameter U of Eq. (1) increases, this difference in transition energies crosses over from a (U/t_k) to a U behavior; to understand the detailed nature of this crossover requires accurate many-body calculations for intermediate coupling.

For bipolarons, the corresponding calculations [25] yield, in first order weak e-e coupling (U only), $(TE)^{++} \simeq \Delta_0 - \omega_0 - U/3\ell_{BP}$ and $(TE)^{--} \simeq \Delta_0 + \omega_0 - U/3\ell_{BP}$, so that both absorptions are shifted down. The first non-vanishing changes in intensities are currently being investigated [25], but the essential feature that $I^{++} > I^{--}$ is not expected to change dramatically. This is important, particularly for comparisons to the recent experimental data on (presumed) bipolaron absorption in polythiophene, taken using both doped samples [26] and photoinduced techniques [27]. Both these experiments show two peaks [26], occurring at $(TE)^{++} \simeq 0.42\text{eV}$ and $(TE)^{--} \simeq 1.60\text{eV}$ in the doped samples [26] and at $(TE)^{++} \simeq 0.45\text{eV}$ and $(TE)^{--} \simeq 1.25\text{eV}$ in the photoinduced data [27]. Since the band edge is agreed to be in the range 2.2-2.4 eV, both the existence of two intra-gap absorptions and the fact that the sum of the transitions energies is less than the gap are in agreement with the theoretical expectations for weak e-e interactions. Unfortunately, the experimental integrated intensities of the two absorptions are nearly equal, so that our theoretical expectation fails in an important way. If one ignores this and nonetheless fits the data to the perturbative formulae, one again finds that, due to the $1/\ell_{BP}$ factors, the value of U lies in the intermediate coupling range. Interestingly, for strong coupling, with both U and V_1 present, the correlated state corresponding to the bipolaron is also expected to have two intra-gap absorptions [25], with $(TE)^{++} = V_1$ and $(TE)^{--} = U - 2V_1$; recall that in this limit the band edge is determined by the e-e interactions and is at $U - V_1$. Note again the crossover from a U/ℓ_{BP} to a U behavior. Preliminary lowest order estimates [25] suggest roughly equal intensity for the two transitions, with the lower transition expected to be slightly stronger. In view of the uncertainties, it seems premature to attempt a detailed, quantitative interpretation of the experiments, and it is clear that crucial theoretical issues – for instance, the sensitivity of the weak-coupling intensity ratio to effects beyond the scope of the simple 1-d Hamiltonian, and (again) calculations for intermediate coupling – remain open.

VI. SUMMARY AND CONCLUSIONS

In the past few years, the role of "correlation effects" in conducting polymers has gradually come into clearer focus. On the basis of both experimental results and theoretical expectations, it is apparent that these effects can cause important new qualitative and quantitative differences from the single particle picture but that they do not destroy the interesting and important nonlinear excitations predicted by the $H_{e-e} = 0$ models. While theorists debate how best to deal with the (difficult but apparently relevant) intermediate coupling regime, one area of clear experimental opportunity remains optical absorption. By focusing on coordinated photoinduced/doped sample photoabsorption experiments, time resolved in the sub-picosecond range and on well-characterised, highly oriented samples (so that polarised excitation/probe techniques can be used), the experimentalists can provide perhaps the best insight yet into the excitation structure in conducting polymers.

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