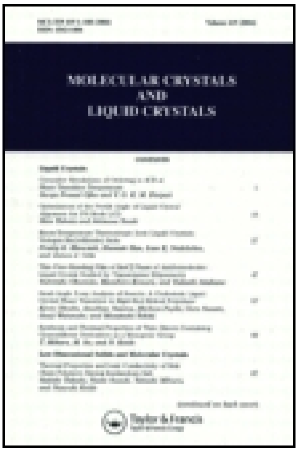

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Localized Excitations in Competing Bond-Order-Wave, Charge-Density-Wave and Spin-Density Wave Systems

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LOCALIZED EXCITATIONS IN COMPETING BOND-ORDER-WAVE, CHARGE-DENSITY-WAVE AND SPIN-DENSITY WAVE SYSTEMS

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Abstract The localized excitations in the competing bond-order-wave(BOW), charge-density-wave(CDW), and spin-density-wave(SDW) systems are investigated within the Bogoliubov-de Gennes formalism using an extended Peierls-Hubbard model. An extensive study of localized excitations over a wide range of the on-site e-ph coupling λ_2 and the Hubbard interaction U leads to the following observations: (a) As λ_2 increases at fixed U, the number of bound states inside the gap changes from two to four for the STE case and from two to three for the polaron case. (b) A non-monotonic dependence of the lattice relaxation energy on λ_2 is predicted within the lattice relaxation approach developed by two of us earlier, and is attributed to a crossover from the weak-coupling to strong-coupling behavior showing up as the emergence of new bound states inside the gap. Moreover, the non-radiative transition rate of STE is also calculated and is used to tentatively interpret the very short life-time of STE in PtCl complexes.

INTRODUCTION

For the last two decades the experimental and theoretical studies of quasi-one-dimensional systems, like conducting polymers, charge-transfer solids, charge-density-wave systems and halogen-bridged mixed-valence, transition-metal linear-chain complexes (HMMC or MX chains) have attracted great interest of physicists and chemists, since these compounds are ideal prototypes for the study of competing symmetry broken ground state such as BOW, CDW and SDW, which is evidenced by the large amount of experimental and theoretical investigations devoted to them[1]. From the theoretical point of view, the phase diagram of these compounds has been extensively studied within the one-band[2] and multi-band[3] versions of the the extended Peierls-Hubbard model[4].

The localized excitations in these compounds are accompanied by strong lattice distortions. Hence the lattice relaxation effects are essential in studying their dynamics. The lattice relaxation theory for polarons and solitons in quasi-1D systems, developed by two of us earlier[5] has been applied to these systems with competing $e-e$ and $e-ph$ interactions. In particular, a non-monotonic dependence of the relaxation rate upon the coupling strength is predicted from the theory. Such unexpected behaviour is mainly due to the change of the number of the bound states in the energy gap as a function of the coupling strength[6]. It is interesting to note that as for homogeneous states, these competing ground states may coexist (like BOW and CDW) or exclude each other (like SDW and CDW without BOW), but the local distortions of the order parameters can always coexist, only subject to the symmetry requirements of the problem. For example, a BOW kink will be accompanied by a CDW polaron, and *vice versa*. Similarly, a self-trapped exciton (STE) in the CDW dominating regime will contain local SDW distortion and *vice versa*[7]. We would like to emphasize this effect and carefully examine its implications.

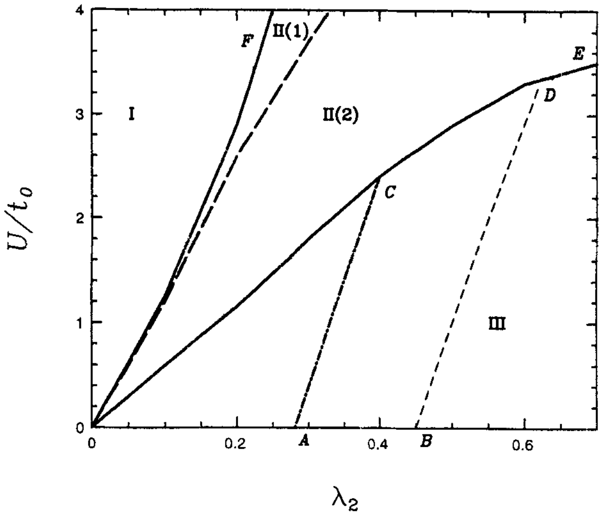
THE STRUCTURE OF STE

The model exhibiting the competition of CDW, BOW and SDW is written as [2]

$$\begin{aligned} H = & -\sum_{i,s}[t_0 - \alpha(u_{i+1}-u_i)](c^\dagger_{i+1\,s}c_{i\,s} + h.c.) - \sum_{i,s}\beta(v_{i+1}-v_i)c^\dagger_{i\,s}c_{i\,s} \\ & + U\sum_i n_{i\uparrow}n_{i\downarrow} + V\sum_{i,s,s'} n_{i\,s}n_{i+1\,s'} + \frac{K}{2}\sum_i[(u_i-v_i)^2 + (u_i-v_{i+1})^2], \end{aligned} \tag{1}$$

where the notations are the standard ones[6,7] and U, V are the on-site and nearest neighbour Coulomb repulsion, respectively. The homogeneous ground state properties of such a system have been extensively studied for both $U = V = 0$, and $U \neq 0, V \neq 0$ cases[2,7]. It is found that the intra-site and inter-site *e-ph* couplings lead to a competition between a CDW and a BOW ground state, and there are three regions where the λ_2 dominating region corresponds to the CDW state, while the λ_1 dominating region prefers the BOW order, and, finally, the small intermediate region near the phase boundary $\lambda_2 = \lambda_1/(1+2\lambda_1)$ corresponds to the coexistence of CDW and BOW[2]. In Fig.1, the numerically calculated phase diagram of this system is shown to illustrate the parameter region considered here. The region between curve OA and OB corresponds to the coexistence of CDW and BOW, and the dashed line in it denotes the phase boundary found analytically[2]. The line CD divides regions with different characteristics of localized excitations, as will be explained in the following text. On the other hand, as U and V are included, it has been shown[2,7] that the dominance of U leads to a SDW state, while the CDW state prevails in the λ_2

dominating region, and that the homogeneous CDW and SDW states cannot coexist without involving BOW. In this paper, we will focus on the properties of localized excitations in the CDW dominating region.



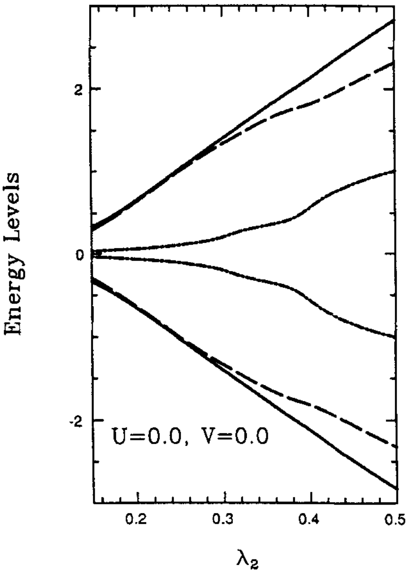


FIGURE 1. Numerically calculated phase diagram of the system for $U = V = 0.0$, as explained in the text. $\lambda_1 = 4\alpha^2/\pi K t_0, \lambda_2 = \beta^2/\pi K t_0$

FIGURE 2. Intragap levels of STE between the band edges (solid) as a function of λ_2, $\lambda_1 = 0.0$, $U = V = 0.0$.

After one electron is photoexcited, a STE is obtained from the self-consistent BdeG calculation. The gap levels of STE as functions of λ_2 are plotted in Fig. 2. As expected, the energy gap increases with the increase of the coupling constant λ_2. The two localized bound states near the midgap are split off from the top of the valence band and the bottom of the conduction band in the weak coupling range. As the coupling constant λ_2 increases to around $\lambda_2 = 0.28$, two *new* bound states emerge out from the continuum resulting in totally four localized bound states inside the gap. These two new bound states play an important role in the calculation of the lattice relaxation rate. As λ_2 increases further, no more new bound state will be split off from the continuum. The crossover from 2-bound-states region to 4-bound-states region in the phase diagram is indicated by curve CD in Fig. 1.

RELAXATION PROCESS OF STE

Lattice Ralaxation Energy

A key quantity in the lattice relaxation theory is the lattice relaxation energy E_r which in the present context can be written as[5]

$$E_r = \frac{S\hbar\omega_b}{t_0} = \frac{1}{\pi\lambda_2}\sum_n |\gamma_n^i - \gamma_n^f|^2, \tag{2}$$

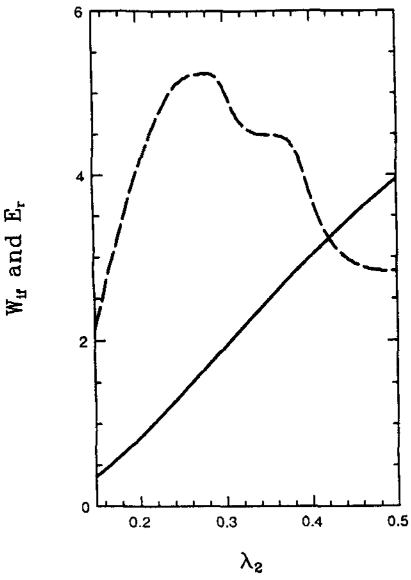
where γ_n^i and γ_n^f are dimensionless staggered lattice distortions in the initial and final states, respectively. S is the Huang-Rhys factor. In the non-radiative decay process, the initial state is the STE state, whereas the final one is the CDW ground state with constant γ_n^f. The curves of E_r and the energy difference between the initial and final states in the relaxation process of STE W_{if} as functions of λ_2 are plotted in Fig. 3. In this figure, as expected, W_{if} is a monotonically increasing function of λ_2. However, an abnormal behavior was found for the E_r curve. The lattice relaxation energy first increases in the small λ_2 region, and then decreases when λ_2 is greater than about 0.28. An amazing point is that this crossover from the weak-coupling behavior (where E_r increases with the increasing coupling strength) to the strong-coupling behavior (where E_r decreases and saturates with increased coupling) takes place *exactly when new bound states are split off from the continuum.* However, this is not so surprising because there are only two bound states for exciton in the weak-coupling continuum model, but four bound states in the strong coupling limit[2]. Therefore, the crossover should show up as appearance of new bound states inside the gap, giving rise to a downturn of the lattice relaxation energy. Since the non-radiative relaxation rate depends on E_r in an exponential way, this crossover is also the origin of the non-monotonic behavior of the transition rate.

Non-radiative Transition Rate

The non-radiative transition rate in the low temperature limit is written as

$$W = \sqrt{\frac{2\pi}{\hbar\omega_b W_{if}}}\left(\frac{S}{p}\right)^p e^{(p-S)}\left(\frac{1}{4\hbar}G_1(1-\frac{p}{S})^2 + \frac{1}{2\omega_b}G_2\frac{p}{S}\right), \tag{3}$$

where $p = W_{if}/(\hbar\omega_b)$, G_1 and G_2 are electronic matrix elements. These matrix elements depend on the overlap integral which is sensitive to the presence of new bound states[7]. The multi-electron overlap integral $< e_f|e_i >$ is related to the configurations of the initial and the final states. Since these states correspond to different lattice configurations, the overlap integral in general is not vanishing. It is also noticed that the overlap integral has a general increasing tendency with the increase of the coupling strength. This increasing feature is due to the appearance of new bound states as well. Considering all the factors analyzed above, it is not difficult to understand the non-monotonic behavior of the non-radiative transition probability curve (in the logarithmic scale) plotted in Fig. 4. The shoulders in the curve are caused by the overlap integral $< e_i|e_f >$, which takes very small values when the initial and final states are nearly orthogonal to each other for certain values of λ_2. The exact meaning of such a quasi-orthogonality deserves further study.



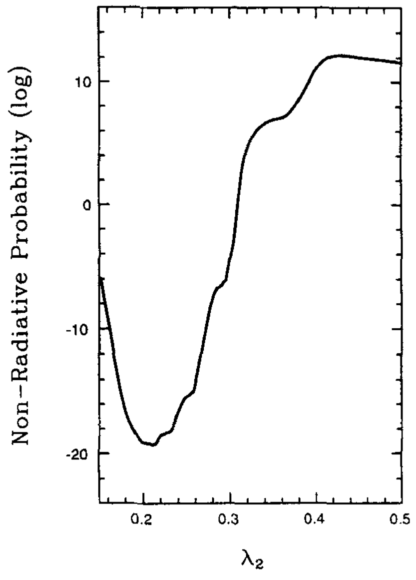


FIGURE 3. The energy difference between the initial and the final states W_{if} (solid) and the lattice relaxation energy E_r (dashed) as functions of λ_2, $N = 64$, $\lambda_1 = 0.0$, $U = V = 0.0$.

FIGURE 4. The non-radiative relaxation rate as a function of λ_2, $N = 64$, $\lambda_1 = 0.0$, $U = V = 0$.

DISCUSSIONS

First we note that the time-resolved photoluminescence (PL) measurements[8] yield very short life-time of the order of 100 ps for STE in PtCl samples. If we adopt the parameters suggested in Ref. 9, $K = 6.16eV/\AA^2$, $\beta = 2.36eV/\AA$, $t_0 = 0.7eV$, $\lambda_2 = 0.41$, $\hbar\omega_b = 0.038eV$, the non-radiative decay rate of STE is estimated to be $5.7 \times 10^{10} sec^{-1}$, *i.e.*, slightly larger than the observed value. Very interesting results on PL of mixed crystals $PtCl_{1-x}Br_x$ were reported in Ref. 10. It has been observed that the linewidth of PL almost does not change with x, while one would expect broadening in the middle range of mixing because STE on Br and Cl should be quite different. On the other hand, the intensity of PL drops by a factor of 100 when x increases from 0 to 1. It seems to us that a natural explanation would be that the PL is mainly coming from Cl but not from Br. This would happen if we assume that parameters for Br is in the transition region with high relaxation rate.

In summary, it has been shown that the number of bound states within the charge transfer gap changes from two to four for the STE case as λ_2 increases above the critical value even if the Coulomb interactions are included. Moreover, the lattice relaxation approach to quasi-one-dimensional systems has been applied to study the non-radiative transitions. It is found that a non-monotonic dependence of the relaxation rate on the intra-site *e-ph* coupling λ_2 is mainly due to the emergence of new bound states within the gap. Here we have considered a specific system of competing CDW and BOW instabilities, but the above effects may be more generic in quasi-one-dimensional systems, especially for those with competing interactions.

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