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THE EXTENDED PEIERLS-HUBBARD MODEL: OFF-DIAGONAL TERMS

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ABSTRACT

We investigate the effects of including "off-diagonal" terms – nearest-neighbor bond-bond repulsion (W) and bond-site repulsion (X) – in the extended Peierls-Hubbard model. As a specific illustration we study the ground state dimerization in the one-dimensional, half-filled-band models that have been widely applied to conjugated polymers such as *trans*-polyacetylene and related charge density wave systems.

INTRODUCTION

The continuing debate on the relative importance of electron-phonon (e-p) versus electron-electron (e-e) interactions in conducting polymers and related materials has recently acquired a new dimension with the suggestion [1] that standard Hubbard [2] or Pariser-Parr-Pople (PPP) [3] models, which involve only site-diagonal Coulomb interactions, fail to capture the true effects of e-e interactions. The specific observation [1] is that the translational invariance of the Coulomb repulsion between electrons requires that, in addition to site-diagonal terms which can be represented entirely in terms of the density operator, **there are** *off-diagonal* terms – e.g., nearest-neighbor bond-bond (called "W") and mixed bond-site (called "X") repulsions – in the Wannier function representation of the Coulomb interaction. Although these terms were indeed recognized and analyzed in the early discussions of both the PPP [3,4] and Hubbard [2] models, the justification for neglecting them did not focus on competing e-e and e-p interactions or on the potential effects of quasi-one-dimensionality. Hence the issue of the effects of these terms requires revisiting [1, 5, 6]. In particular, in the context of *trans*-$(CH)_x$ the possible effect of off-diagonal terms on dimerization is of vital interest. If one includes e-e interaction effects using only the standard site diagonal Hubbard terms U and V, one finds unambiguously using exact (numerical) many-body methods that for the expected range of e-p couplings the on-site Coulomb repulsion actually enhances dimerization up to fairly large values [7,8]. These results are still widely regarded as counter to the conventional wisdom that Coulomb interactions should suppress the build up of charge anywhere [illegible] bond repulsion W and bond-site repulsion X should suppress dimerization, since they must oppose the build-up of charge on the bonds. Thus, the absence of these terms in the standard extended Peierls-Hubbard (PH) models suggests *a priori* that these models may artificially favor the continuation of dimerization in the half-filled band into the region of intermediate to strong Coulomb interaction. More generally, the omission of such off-diagonal terms raises significant questions about the appropriateness of PH or PPP-like models for describing the whole class of novel solid state materials, including high temperature superconducting copper oxides, "heavy fermion" systems, organic synthetic metals (both conducting polymers and the incredible variety of charge transfer salts), and halogen-bridged transition metal chains. In view of this wide range of potential applications, the issue of off-diagonal terms clearly merits a thorough and definitive investigation. In this and related articles [9] we carry out such a detailed study, using both strong and weak coupling perturbation theory and exact diagonalization of finite-size systems. Limitations of space compel us to focus here solely on the exact diagonalization results; the additional studies will be reported elsewhere [9]. We find that for the expected range of parameters the inclusion of off-diagonal Coulomb terms does <u>not</u> alter qualitatively the conclusions based on models including only site-diagonal terms. In particular, counter to the simple intuition, in the relevant parameter range the dimerization initially <u>increases</u> as W increases from zero, remains approximately constant for intermediate values of W, and drops suddenly to zero only for (unphysically) large values of W. Further, the major effect of X on the specific problem of dimerization is merely to renormalize the hopping; however, since the X term breaks the charge-conjugation symmetry of the standard PH model, in other contexts, such as optical absorption, it may play a more important role.

THE MODEL

To analyze the effects of off-diagonal Coulomb terms in quasi-one-dimensional systems, we consider the modified Peierls-Hubbard Hamiltonian [1,5,6,9]

$$\begin{aligned} H = &-\sum_\ell (t_0 - \alpha\delta_\ell) B_{\ell,\ell+1} + \frac{k}{2}\sum_\ell \delta_\ell^2 \\ &+ U\sum_\ell n_{\ell\uparrow}n_{\ell\downarrow} + V\sum_\ell n_\ell n_{\ell+1} + X\sum_\ell B_{\ell,\ell+1}(n_\ell + n_{\ell+1}) + W\sum_\ell (B_{\ell,\ell+1})^2 \quad , \end{aligned} \tag{1}$$

where $n_{\ell\sigma} = c_{\ell\sigma}^\dagger c_{\ell\sigma}$, $n_\ell = n_{\ell\uparrow} + n_{\ell\downarrow}$, $B_{\ell,\ell+1} = \sum_\sigma (c_{\ell\,\sigma}{}^\dagger c_{\ell+1\,\sigma} + c_{\ell+1\,\sigma}{}^\dagger c_{\ell\,\sigma})$, t_0 is the hopping integral for the uniform lattice, α is the electron-phonon coupling, δ_ℓ is the relative displacement between the ions at sites ℓ and $\ell+1$, and k represents the cost of distorting the lattice. U describes the on-site Coulomb repulsion and V the nearest-neighbor repulsion. X is a "mixed" term involving both on-site and bond-charge effects, and W is the bond-bond charge repulsion. For $U, V, W, X = 0$, this model reduces to the SSH Hamiltonian [10], in the (standard) limit of classical ion displacements. For $W, X = 0$, this Hamiltonian is the conventional extended Peierls-Hubbard model that has widely been used [8] to model conducting polymers and in particular to investigate the competition between e-p and e-e interactions in these systems. When both W and X are included, the model contains all effects of Coulomb interactions — both on- and off-diagonal — up to and including nearest neighbor interactions [1-6].

When the off-diagonal terms are not *a priori* negligible, the central issue is the extent to which they produce results qualitatively different from those predicted in their absence. Since these terms all

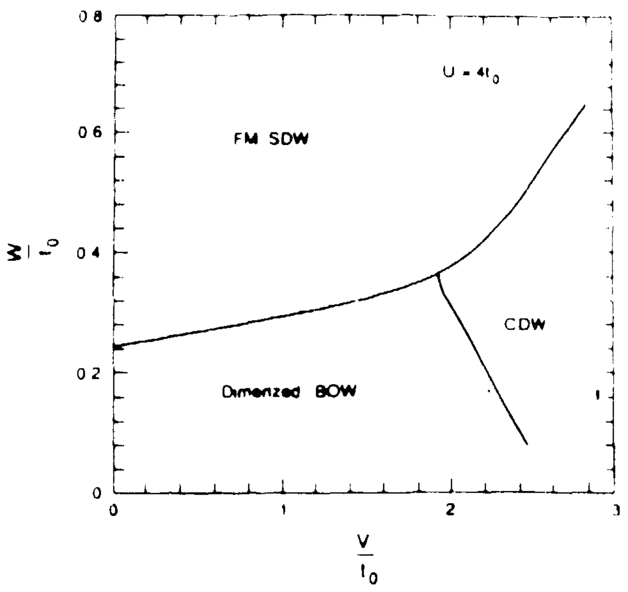


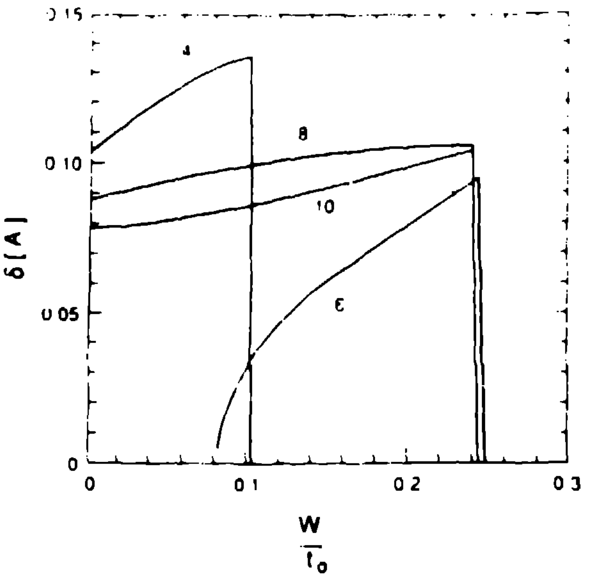
Fig. 1. The phase diagram as a function of V/t_0 and W/t_0 for intermediate coupling $U = 4t_0 = 10$eV, and $X = 0$. Phase boundaries are plotted for a 8-site ring. The ground-state changes discontinuously across solid lines, smoothly across the dotted line.

derive from the (screened) Coulomb interaction [1-6], one must anticipate that $U > V, X, W$ and hence must adopt a method that gives correct results in this parameter regime. Since in many materials one expects $U \simeq 4t_0$, to be certain of the results we use (numerically) exact many-body methods known to be reliable in the intermediate coupling regime.

EXACT DIAGONALIZATION: RESULTS AND DISCUSSION

In the region of intermediate e-e coupling anticipated to apply to many novel materials, we have calculated numerically the "exact" ground state of finite rings described by the Hamiltonian (1) using a version of the Lanczos method [11]; details will be published elsewhere [9]. To demonstrate the convergence of our results as a function of system size, we investigate 4, 6, 8, and 10 site rings. We focus on the phase diagram as a function of W and V at fixed $U = U_0$. For comparison and definiteness, we use the conventional SSH-polyacetylene parameters $\alpha = 4.1\text{eV}/\AA, k = 21\text{eV}/\AA^2$, and $t_0 = 2.5$eV. Fig. 1 shows the phase diagram for an 8-site ring; comparison with results on 4-, 6-, and 10-site rings suggests this diagram reflects the infinite-ring behavior. In Figs. 2 and 3 we show the actual value of δ_0, the optimal dimerization, versus W for 4, 6, 8, and 10 site rings when $U_0 = 4t_0 (= 10\text{eV})$, $V = 0$ and $V = 3$eV, respectively. Several points are immediately apparent from these figures.

First, the dimerized/BOW persists for a substantial range of Coulomb repulsion, both diagonal and off-diagonal. In particular, as shown in Fig. 2, even for $V = 0$, W does not destroy dimerization until $W_c \simeq 0.24t_0 = 0.6$eV. Indeed, dimerization increases monotonically with W before dropping rapidly to zero in a "first order phase transition" at $W = W_c$; elsewhere [9] we describe strong coupling arguments that provide an intuitive explanation of these results. The existence of real materials with $W > W_c$ remains an open question; it is conceivable that the recently observed organic ferromagnetic materials may be modeled using parameters in this range. However, for $(CH)_x$ and the other conjugated polymers, the experimentally observed dimerization requires, within the model Hamiltonian, $W < W_c$. Importantly, *one still finds dimerization for strong, internally consistent Coulomb interactions*; the assumption of weak e-e interactions is not required. This is fortunate, for in the case of $(CH)_x$, such an assumption appears inconsistent with both observed spin density ratios [12] and optical absorption [illegible]



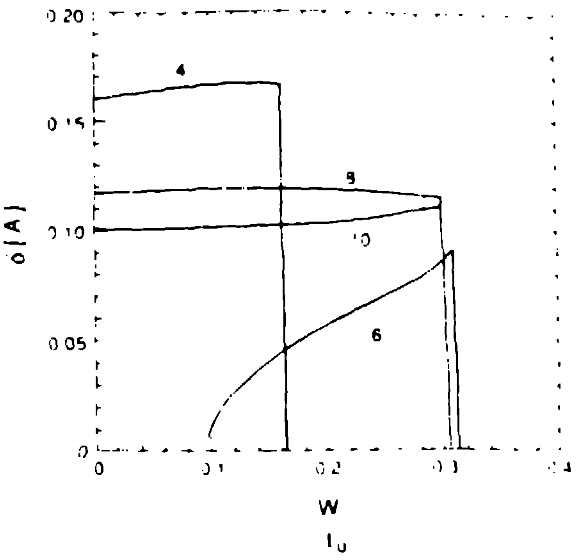


Fig. 2 (left). Dimerization as a function of W/t_0 for $U = 4t_0 = 10$eV and $V, X = 0$ for 4-, 6-, 8-, and 10-site rings. For the 4-site ring, the dotted line gives results for the lowest energy dimerized state even though for this small ring the ground state is not dimerized for intermediate values ($0.10 < W/t_0 < 0.225$) of W/t_0.

Fig. 3 (right). Dimerization as a function of W/t_0 for $U = 4t_0 = 10$eV, $V = 3$eV, and $X = 0$ for 4-, 6-, 8-, and 10-site rings. The 4-site ring is not dimerized for intermediate values ($0.16 < W/t_0 < 0.29$) of W/t_0.

larger values of W, and again W <u>increases</u> dimerization (slightly) until the BOW/FM SDW boundary is reached. This is indicated quantitatively in Fig. 3. Note the increase in W_c relative to Fig. 2; this is as expected from Fig. 1.

Second, both Figs. 2 and 3 show that the distinction between "Jahn-Teller" ($4N$) and "non-Jahn-Teller" ($4N+2$) systems persists even away from the band theory limit. However, they also suggest that systems with $N \geq 8$ are near the converged large N behavior. Incidentally, the dotted regions of the 4-site ring results in Figs. 2 and 3 reflect the dimerization observed in the BOW phase. However, the actual ground state of the 4-site system at values of W in these dotted regions is a different, small-ring phase, which does not appear in the larger rings. Thus the solid line for the 4-site system, which shows the dimerization going to zero at relatively small values of W, although strictly correct, is essentially an artifact of the small system size. The dotted line, which explicitly ignores this small-ring phase and plots the dimerization assuming the BOW state remains the ground state until the transition to a ferromagnetic SDW, shows more clearly the true finite size effects on W_c and δ_0 vs. W.

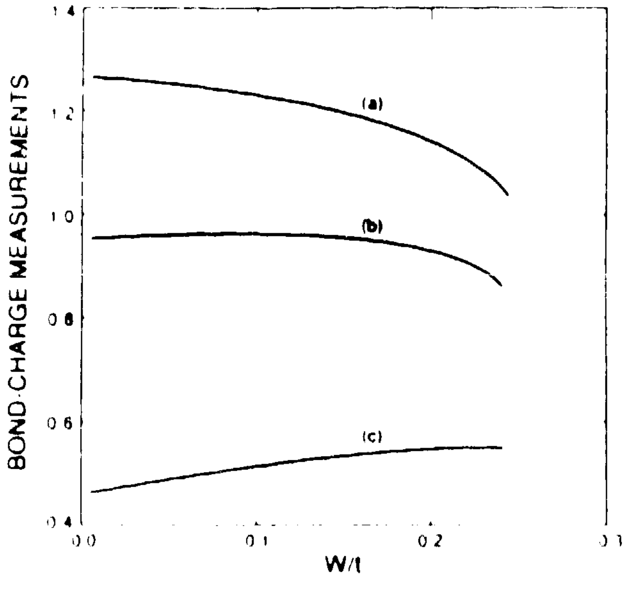
Third, the phase boundaries in Fig. 1 in general reflect a "first order transition" in the dimerization order parameter, δ_0: that is, there is a sudden qualitative change in the nature of the ground state, and δ_0 drops immediately from a finite value to zero. However, for short segment of the BOW/CDW boundary near $W = 0$ the range is roughly $0 < W < 0.1$ — the transition becomes second order. Except for this short segment, the dimerized phase has non-zero dimerization on its boundary.

Increasing W, of course, must suppress bond-bond correlations. In Fig. 4, the bond-bond correlation, average bond charge, and alternating bond charge are plotted as a function of W for intermediate coupling, $U_0 = 4t_0$ and $V = 0$, on the 8-site ring. As expected, the bond-bond correlation $\langle B^2\rangle = \frac{1}{N}\sum B^2_{i,i+1}$, which couples directly to W in the Hamiltonian, is suppressed monotonically as W is turned on. Counter to simple intuition, however, the *average* bond charge $\langle B\rangle$ $\frac{1}{N}\sum B_{i,i+1}$

does *not* fall off as dramatically as the correlation and indeed, for small W, the bond charge stays remarkably flat. Meanwhile, the *alternating* bond charge, which is related to the dimerization by $\langle B' \rangle = \frac{1}{N}\sum(-)^l B_{l,l+1} = k\delta/\alpha$, *increases* with W, as we have seen earlier. In sum, although W does suppress bond-bond correlations, the effects on average and alternating bond charge are quite different, and, in particular, we observe that W enhances the dimerization.

Inspection of the Hamiltonian (1) shows that when U is very large so that the probability of double occupancy is very small and $n_\ell + n_{\ell+1} \simeq 2$, the term proportional to X acts simply to "renormalize" the hopping from t_0 to $t = t_0 - 2X$. Surprisingly, even for intermediate coupling this remains the primary effect of X; this is indicated in Fig. 5, which shows the dimerization versus W plot for several values of t_0 and X. In Fig. 5, curve (a) is for $t_0 = 2.5, X = 0$. That labeled (b) is actually two curves, one for $t_0 = 2.0, X = 0$ and one for $t_0 = 2.5, X = 0.25$. They are essentially indistinguishable on this scale. Similarly, curve (c) is again two curves: $t_0 = 1.5, X = 0$ and $t_0 = 2.5, X = 0.5$. Although the values of both W_c and δ are again virtually indistinguishable, one can see a slight enhancement ($\sim$ 0.3%) of dimerization with X ($t_0 = 2.5$eV, $X = 0.5$eV) beyond what one would expect from simply renormalizing the band width ($t_0 = 1.5$eV, $X = 0$). However, as far as dimerization in the half-filled band is concerned, one can in effect use the $X = 0$ results with t_0 determined by the actual band width to determine both δ and W_c; if non-zero X is used, t_0 must of course be suitably increased to compensate, so that the actual band width, now given by $4t$, remains correct.

Although the off-diagonal terms produce only minor quantitative effects on dimerization, for other observables they can have important qualitative consequences. The mixed bond-site term X breaks charge conjugation/particle-hole symmetry; its inclusion in models of $(CH)_x$ may thus help explain the puzzling "intensity anomaly" in polaron/bipolaron optical absorption [13] experiments and also the ratio of neutral ($S^\circ - S^\circ$) to charged ($S^+ - S^-$) soliton pairs in the decay channels of electron-hole pairs in photo-excitation of trans-$(CH)_x$ [8]. In both these cases, the X term may well be more important than the straightforward next-nearest neighbor hopping term, t_2; within a tight-binding model, $t_2 \propto e^{-\kappa_0 a} t_0$. Further, when X terms are included in H, the hopping in effect acquires a band-filling dependence; this may be quite significant in applying Hubbard-like models to situations other than the half-filled band.



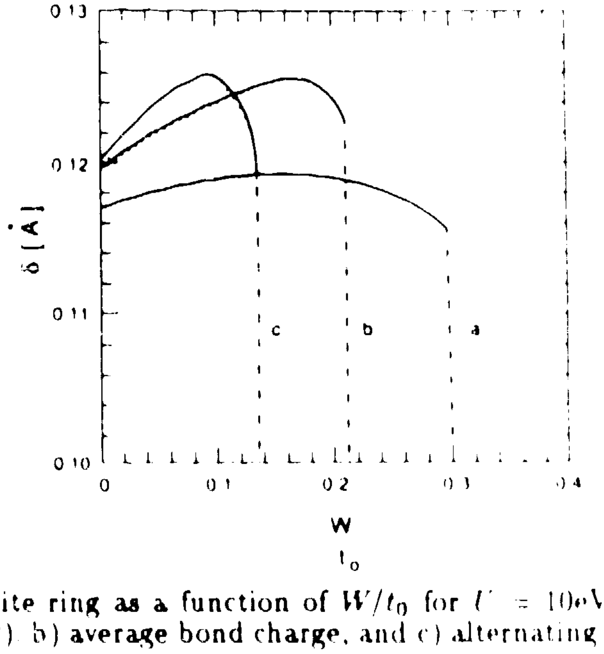


Fig. 4 (left). Bond-charge measurements on the 8-site ring as a function of W/t_0 for $U = 10$eV and $V = 0$: a) bond-charge correlation (multiplied by 1/2), b) average bond charge, and c) alternating bond charge, which is proportional to the dimerization.

Fig. 5 (right). Dimerization as a function of W/t_0 for $U = 10$eV and $V = 3$eV. The individual curves are for values of (t_0, X) equal to (a) (2.5 eV, 0); (b) (2.5 eV, 0.25 eV) and (2.0 eV, 0); and (c) (2.5eV, 0.5eV) and (1.5eV, 0). The dotted lines are the $X = 0$ curves; the solid lines are for non-zero X.

Finally, we turn to the general issue of the applicability of the standard Hubbard model. Here it is useful to place our work in the context of several recent articles that, in one way or another, have revisited the original analyses that justified the "zero differential overlap" [4,14] approximation that neglects off-diagonal terms [2]. First-order perturbation theory [1] is not a reliable basis on which to question the validity of the extended Hubbard model, since conclusions based on perturbation theory about the effects of off-diagonal terms on dimerization are not valid for realistic, self-consistent values of the Coulomb interaction parameters. Although our study focused explicitly on (an exact solution for) short-ranged Coulomb effects, involving only on-site and nearest neighbor interactions, our results are consistent with two recent variational studies [15, 16] involving (approximate) solutions for the full (screened) Coulomb interaction. Further, for the expected region of parameters, the variational results on the full Coulomb problem are consistent with early (Gutzwiller) variational calculations in the pure Hubbard model [17]. In summary, the familiar Hubbard and extended Hubbard models remain valid and useful theoretical starting points for understanding the role of electron-electron interactions in a variety of novel real materials.

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