The Density Matrix Renormalization Group Studies of Metal-Halogen Chains within a Two-Band Extended Peierls-Hubbard Model

Y. Anusooya[1], Swapan K. Pati[1] and S. Ramasesha[1,2]

[1] Solid State and Structural Chemistry Unit
Indian Institute of Science, Bangalore 560 012, India
[2] Jawaharlal Nehru Center for Advanced Scientific Research
Jakkur Campus, Bangalore 560 064, India

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The phase diagram of halogen-bridged mixed-valent metal complexes (MX) has been studied using a two-band extended Peierls-Hubbard model employing the recently developed Density Matrix Renormalization Group method. We present the energies, charge and spin density distributions, bond orders, charge-charge and spin-spin correlations, in the ground state for different parameters of the model. The effect of bond alternation and site-diagonal distortion on the ground state properties are considered in detail. We observe that the site-diagonal distortion plays a significant role in deciding the nature of the ground state of the system. We find that while the CDW and BOW phases can coexist, the CDW and SDW phases are exclusive in most of the cases. We have also studied the doped MX chains both with and without bond alternation and site-diagonal distortion in the CDW as well as SDW regimes. We find that the additional charge in the polarons and bipolarons for hole doping are confined to a few sites, in the presence of bond alternation and site-diagonal distortion. For electron doping, we find that the additional charge(s) is(are) smeared over the entire chain length and although energetics imply a disproportionation of the negatively charged bipolaron, the charge and spin density distributions do not reflect it. Positively charged bipolaron disproportionates into two polarons in the SDW region. There is also bond order evidence for compression of bond length for the positively charged polaronic and bipolaronic systems and an elongation of the bonds for systems with negatively charged polarons and bipolarons.

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I. INTRODUCTION

The halogen-bridged mixed-valent metal complexes (HMMC) are quasi-one-dimensional chains that exhibit both Peierls distortion and mixed valency. This is attributed to the presence of strong electron-electron interactions as well as strong electron-lattice interactions. Besides, the degeneracy of the ground state of the HMMC chains supports solitonic excitations as in polyacetylenes. These aspects of HMMCs have resulted in considerable theoretical and experimental focus in recent times [1–6].

The HMMCs are composed of transition metal (M) ions which are bridged by halide (X) ions. Each metal ion is surrounded by four monodentate ligand molecules such as ethylamine (L), or two bidentate ligand molecules such as ethylenediamine, cyclohexanediamine (L_2), etc. Symbolically, HMMCs can be represented as $[M^{3-\rho}L_4][M^{3+\rho}X_2L_4]Y_4$, where M can be Pt, Pd or Ni and X can be Cl, Br or I; ρ denotes the deviation of the metal valency from the average value of $+3$; and Y is a counter ion such as X^- or ClO_4^- for charge neutrality. The d_{z^2} orbital on the metal-ion is singly occupied when its oxidation state is $+3$. Along the $M - X$ backbone, the electrons are delocalized due to the overlap of the $d_{z^2}(M)$ and $p_z(X)$ orbitals. If the electron-electron interactions are weak compared to the electron-phonon interactions, the diagonal electron-

lattice interactions would dominate. This would result in a Jahn-Teller distortion of opposite phases at successive metal-ion sites. The metal-ion site at which the d_{z^2} orbital is stabilized would be doubly occupied while that at the adjacent metal site would be empty leading to a CDW state. In the opposite limit, the strong electron-electron interactions force single occupancy of the metal d_{z^2} orbitals and the chain would be undistorted as there is no electronic stabilization associated with the distortion due to single occupancy of the metal orbitals. In this limit, a SDW state would result. Platinum being a $5d$ system, the $d-$orbitals are more diffused resulting in weaker electron-electron interactions and indeed, the broken symmetry state observed in the Pt complexes is usually a CDW state. At the other end is the nickel system with compact $d-$orbitals and one usually observes SDW states in the Ni complexes. The amplitude of these CDW or SDW distortions can be tuned continuously by changing the metal ion, the halide ion, the ligand, or the counter ions.

The CDW ground state in these systems has two degenerate configurations and hence there is a possibility of soliton-like excitations, besides polaronic excitations. The solitonic states in the MX chains are more localized and are believed to be longer lived than the solitons in polyacetylene chains. In the halogen bridged mixed-valent platinum complexes (HMPC) [5], evidence for midgap absorption, associated with solitons, comes

from the high pressure studies of the optical spectra, wherein a band at half the charge-transfer excitation energy is found on application of pressure. The IR and Raman studies of a series of HMMCs with decreasing metal-metal distances have also been studied to simulate pressure and determine several microscopic parameters essential for theoretical modelling of the $PtCl$ chains [7]. The electrical conductivity and electron spin resonance (esr) studies [8] of halogen doped HMPC systems show that for low-doping concentrations, polarons are formed which lead to enhanced conductivity and the charge carriers are found to have a spin. At increased dopant levels, the esr intensity reduces although the conductivity increases. Furthermore, optical absorption studies show the appearance of peaks below the optical gap. Hence, these studies suggest that two positively charged polarons yield either two positively charged solitons or a bipolaron, both of which do not have a spin. Photoinduced IR absorption studies [9] on HMPC systems with weak interchain interactions have shown evidence for photogenerated solitonic states, besides polaronic states. For large interchain coupling, the energy of formation of solitons is high and the midgap absorption band in such systems was absent, although the polaronic absorptions could be observed in these systems.

The MX chains were modelled by using a half-filled single-band Hubbard-Peierls model including nearest-neighbour electron-electron interactions by many authors [4,10–12]. Nasu, in the mean-field limit, obtained a phase-diagram for the nature of the ground state, in the parameter space of U, the on-site electron correlation strength, V, the nearest neighbour electron-electron interaction parameter and S, the strength of site-diagonal electron-phonon coupling. The mean-field phase diagram showed regions where, CDW and SDW ground states exist as well as regions of coexistence of these two phases. It was further shown, within the mean field theory for electrons and an adiabatic approximation for the phonons that the origin of the photoinduced absorption was a distant hole-polaron or an electron-polaron pair in the excited state of the MX chain. However, this model apart from the approximation in which it was solved for, was quite inadequate due to the neglect of the p_z orbitals on the halogen sites. Ichinose [13] mapped the model to an anisotropic spin chain, in the limit of small on-site correlations and adiabatic electron-phonon coupling to describe the topological excitations of the MX chain. Onodera [14] considered the continuum limit of the Ichinose model and showed that it leads to the Takayama-Lin-Liu-Maki model, which is also the continuum limit of the discrete Su-Schreiffer-Heeger (SSH) model. He showed that the MX chains can support solitons as in polyacetylene. A model similar to the SSH model was studied by Baeriswyl and Bishop [15] who showed the existence of a charge-transfer state in the limit of strong electron-phonon interactions. The intrinsic defect states such as the polarons, bipolarons and solitons, in this limit, were observed to be strongly localized.

Gammel et al first modelled the MX chains by employing a two-band $U - V$ model (consisting of the metal d_{z^2} orbital and the halogen p_z orbital) at $\frac{3}{4}^{th}$ filling. This model was studied by them in different approximations. In the period 4 case, they observed that the BOW phase exists only in a very small region near the site energies of M and X being zero, unlike in the single-band model where the BOW is found in a wide range of parameter values. Moreover, they characterized the lowest state in that region to be of mixed CDW/BOW character. They also predicted long period charge density wave ground states in the system, from an analysis of the model in the localized limit. They studied the topological excitations of the model treating the lattice in adiabatic approximation and the electron-electron interactions in the Hartree-Fock (both restricted and unrestricted) approximation for various parameter values to characterize these excitations in different systems. For small MX chains, they went beyond the Hartree-Fock approximation and studied the properties of the chain by employing exact diagonalization methods. They also studied the model including the phonon dynamics but treating the electron-electron interactions in the mean field limit. For small Hubbard interaction strengths, perturbation theory was employed to study the model. Huang and Bishop [3] studied the two-band model both in the mean-field and random phase approximations to study the lattice- and spin-polaronic defects in Ni complexes. They found relative lattice-distortion around the defect center besides the charge or spin disproportionation. The effect of interchain interactions on the nature of the ground state and also on the energy gaps in the system were studied by including them self-consistently in finite MX chain calculations, within a two-band model [16]. The effect of interchain interactions on the stability of nonlinear lattice relaxation was considered by Mishima [17] in the mean-field approximation within the one-band extended Hubbard-Peierls model. Sun et al [18] employed a one-band model and in the mean-field approximation showed that the electron-electron interaction reduces the CDW gap in MX complexes. There is also an all-electron local density approximation calculation for MX chains which focuses on the band-gap, dimerization and SDW instabilities in these compounds [19].

All the studies so far carried out on the MX chain systems suffer from the disadvantage that they treat electron-electron interactions in the mean-field approximation, except in the case of small chains where model exact solutions are obtained. The exact studies on small chains are often inconclusive due to finite size effects. However, the recently developed Density Matrix Renormalization Group (DMRG) method has proved to be very accurate for quasi-one-dimensional systems [20]. In this

paper, we report results of our extensive investigations of the MX chain systems employing the DMRG method. We have studied the MX chains with upto 70 sites (35 MX units), employing the two-band extended Peierls-Hubbard model. We have studied the neutral as well as charged MX chains to understand the properties of ground state as well as the photogenerated gap states for many values of the model parameters. Besides energies, we have studied the charge and spin correlations in the system, charge and spin densities as well as bond orders to properly characterize the ground states in different regions of the parameter space. The paper is organized as follows. In the next section we introduce the model Hamiltonian and the DMRG method as applied to the MX chains. In the third section, we discuss results for the ground state of the neutral and doped systems.

II. MODEL HAMILTONIAN AND THE DMRG METHOD

We have studied the HMMC systems employing the $U - V - \delta$ model. The Hamiltonian of this model, $\hat{H}$, for the metal-halogen chain can be written as a sum of the noninteracting term, $\hat{H}_0$, which includes the renormalized static electron-lattice interactions and an electron-electron interaction term, $\hat{H}_1$, given by

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \tag{1}$$

$$\hat{H}_0 = \sum_{i=1}^{N} \sum_{\sigma} t_i [a^{\dagger}_{X,i\sigma} a_{M,i\sigma} + a^{\dagger}_{M,i\sigma} a_{X,i+1\sigma} + H.C.]$$
$$+ \sum_{i=1}^{N} \sum_{\sigma} [\epsilon_{M,i} a^{\dagger}_{M,i\sigma} a_{M,i\sigma} + \epsilon_{X,i} a^{\dagger}_{X,i\sigma} a_{X,i\sigma}] \tag{2}$$

$$\hat{H}_1 = \sum_{i=1}^{N} U_M \frac{\hat{n}_{M,i}(\hat{n}_{M,i} - 1)}{2} + \sum_{i=1}^{N} U_X \frac{\hat{n}_{X,i}(\hat{n}_{X,i} - 1)}{2}$$
$$+ \sum_{i=1}^{N} V_i [\hat{n}_{M,i} \hat{n}_{X,i+1} + \hat{n}_{X,i} \hat{n}_{M,i}] \tag{3}$$

where t_i is $t(1 - (-1)^{(i)}\delta)$. The summations run over all the N MX pairs and the upper limit of the summation is chosen to reflect open boundary condition corresponding to a chain. $a^{\dagger}_{X,i\sigma}$ ($a^{\dagger}_{M,i\sigma}$) creates an electron with spin σ in the halogen (metal) orbital in the ith unit cell and $a_{X,i\sigma}$ ($a_{M,i\sigma}$) is the adjoint of the corresponding creation operator. The operators $\hat{n}_{X,i}$ ($\hat{n}_{M,i}$) are the number operators for the halogen (metal) orbital in the ith unit cell. $\epsilon_{M,i}$ ($\epsilon_{X,i}$) is the site energy of the metal (halogen) orbital in the ith unit cell. U_M (U_X) is the on-site electron-electron repulsion parameter for the metal (halogen) orbital. The nearest neighbour electron-electron interaction terms V_is are calculated using Ohno [21] interpolation scheme,

$$V_i = 14.397[28.794/(U_M + U_X)^2 + r^2]^{-1/2} \tag{4}$$

where r is the distance between the nearest neighbours of the MX chain. The distance r between the pairs depends on the alternation parameter δ. All the parameters are defined in units of the uniform transfer integral t.

We have employed the Density Matrix Renormalization Group (DMRG) method to obtain the ground state properties of the above Hamiltonian for large $N (\geq 35)$ where N is the number of MX pairs. In the DMRG method for the MX chains, we start with two MX units(4 sites) and obtain the ground state of this cluster with six electrons corresponding to $\frac{3}{4}^{th}$ filling by an exact diagonalization procedure. We now imagine the chain to be built up of two halves, namely the left-half and the right-half. We construct the reduced many-body density matrix of the left-half, $\rho^{(2)}_{0,L}$, in the basis of the Fock space states of the left half of the chain from the ground state eigenfunction by integrating over the Fock space states on the right-half as,

$$(\hat{\rho}^{(2)}_{0,L})_{\mu\nu} = \sum_{\mu'} C_{\mu\mu'} C_{\nu\mu'} \tag{5}$$

where $|\mu>$ and $|\nu>$ are the Fock space states of the left-half chain and $|\mu'>$ the Fock space states of the right-half chain. $C_{\mu\mu'}$ is the coefficient associated with direct product functions $|\mu>$ and $|\mu'>$ in the ground state eigenfunction. The dimensionality of the Fock-space $|\mu>$ for a system consisting of n units is $l = 4^{2n}$. The density matrix is simultaneously block diagonal in both the particle-number sector and in the M_s^L sector where M_s^L is the z-component of the total spin of the left-half block. We take advantage of this while diagonalizing the density matrix by diagonalizing each of the blocks independently. This also allows us to label each density matrix eigenvectors by the particle-number, p_L besides M_s^L. After diagonalization, the Fock space on the left is truncated by retaining only m of the density matrix eigenstates corresponding to the m highest density matrix eigenvalues. If we had retained all the l density matrix eigenvectors to serve as basis functions of the Fock space of the left-half, we would have merely effected an unitary transformation of the basis functions. The $l \times l$ Hamiltonian matrix $\hat{H}_L(n)$ for the left part of the chain are obtained in the basis of the Fock space states. This matrix $\hat{H}_L(n)$ is renormalized using the matrix $\hat{O}_L(n)$ whose columns are the m eigenvectors of the corresponding $l \times l$ density matrix. Thus the transformation matrix $\hat{O}_L(n)$ is a $(m \times l)$ matrix. The renormalized Hamiltonian matrix $\tilde{H}_L(n)$ is given by

$$\tilde{H}_L(n) = \hat{O}_L^{\dagger}(n) \hat{H}_L(n) \hat{O}_L(n) \tag{6}$$

The renormalized left Hamiltonian matrix is now an $m \times m$ matrix representation of the left half-Hamiltonain

in the basis of the density matrix eigenvectors. The operators $a^\dagger_{M,i}$ and $a^\dagger_{X,i}$ and $\hat{n}_{M,i}$ and $\hat{n}_{X,i}$ corresponding to each site in the left part of the chain are also obtained as matrices in the basis of the Fock space $|\mu>$ and are later renormalized to obtain renormalized matrices in the basis of the eigenvectors of the density matrix of the corresponding half-chains, in a manner similar to the construction of $\tilde{H}_L(n)$. The density matrix, the transformation matrix $\hat{O}_R(n)$, the renormalized Hamiltonian matrix $\tilde{H}_R(n)$, for the right part as well as the renormalized second-quantized site operators for the right part are all obtained analogously. Unlike in the calculations involving spin chains and Hubbard chains [22], the MX chains do not have the reflection symmetry and all the quantities should be calculated separately for the right and the left halves of the chain. For this reason, we also cannot iterate the DMRG procedure to obtain self-consistent density matrices for fragments of different sizes of the targetted MX chain, a method that is usually employed to obtain more accurate properties for a chain of given length, in systems with reflection symmetry [20].

To get the Hamiltonian for the system with $(n+1)$ unit cells, a MX unit is added in the middle of the chain. The Hilbert space of the new Hamiltonian matrix corresponding to $(n+1)$ unit cells is the direct product of m states, $|\mu>$ from left block and $|\mu'>$ from right block and 4 states, $|c>$ or $|c'>$ (corresponding to $|0>$, $|\downarrow>$, $|\uparrow>$, and $|\uparrow\downarrow>$ configuration at the new site) from each of the newly added unit cell, with the restriction that the total M_s value for the full chain is equal to the desired value and that the total system is $\frac{3}{4}^{th}$ filled.

The Hamiltonian for $(n+1)$ unit cell system can be written as

$$\hat{H}(n+1) = \tilde{H}_L(n) + \tilde{H}_R(n) + \hat{n}_c\epsilon_c + \hat{n}_{c'}\epsilon_{c'}$$
$$+\frac{U_c}{2}\hat{n}_c(\hat{n}_c-1) + \frac{U_{c'}}{2}\hat{n}_{c'}(\hat{n}_{c'}-1)$$
$$+t_n[\tilde{a}^\dagger_L(n)a_c+h.c.] + t_{n+1}[a^\dagger_c a_{c'}+h.c.]$$
$$+t_{n+1}[a^\dagger_{c'}\tilde{a}_R(n)+h.c.] + V_n\tilde{n}_L(n)\hat{n}_c + V_{n+1}\hat{n}_c\hat{n}_{c'}$$
$$+V_{n+1}\hat{n}_{c'}\tilde{n}_R(n) \qquad (7)$$

where the operators $\tilde{a}^\dagger_L(n)$, $\tilde{a}^\dagger_R(n)$ and their adjoints as well as $\tilde{n}_L(n)$, $\tilde{n}_R(n)$ are the renormalized operators expressed in the truncated density matrix eigenvector basis. The operators, $\hat{a}^\dagger_c$ ($\hat{a}^\dagger_{c'}$) and their adjoints as well as $\hat{n}_c$ ($\hat{n}_{c'}$) are expressed as matrices in the Fock space basis. The matrix representation of the Hamiltonian $\hat{H}(n+1)$ in the direct products basis is obtained as appropriate direct product of the operators occuring in the Hamiltonian.

The eigenvalues and eigenvectors for this $(n+1)$ unit cell are obtained and the reduced density matrices for the left and right half of the chain, each with $(n+1)$ sites are constructed from the ground state eigenfunction. In the next iteration, the procedure is repeated by adding a XM unit in the middle of the chain. Alternately we have to add MX and XM units in the middle of the chain so that the successive sites of the full chain at any iteration is not occupied by like ions.

We have optimized the DMRG cut-off, m, by comparing the ground state energy per MX unit for different cut-offs for chain lengths ranging between 25 to 35 MX units. We have presented these energies in table 1. We find that a value of $m = 80$ is quite satisfactory. We have used the DMRG cut-off, $m = 80$, in all our calculations. The dimensionality of the Hilbert space corresponding to $M_s = 0$ (4n sites system) or 0.5 (4n+2 sites system) and $N_e = \frac{3}{2}N$ varies in the range 6400 to 7000, depending upon the model parameters, for this value of m. The resulting Hamiltonian matrix is very sparse. The total number of nonzero matrix elements are ≈ 350000. We exploit the sparseness of the Hamiltonian matrix to reduce the storage requirement as well as CPU requirement by avoiding doing arithmetic with zeroes. We have used the Davidson algorithm for symmetric Hamiltonian matrix to get the lowest few eigenvalues. Davidson algorithm, which is a hybrid of coordinate relaxation method and Lanczos method has been widely used in quantum chemical computations and is known to be both robust and rapidly convergent. The properties of the chain are computed by using the renormalized matrices for the site operators and product operators (for bond order calculations) after reaching the desired length of the chain.

We have compared the DMRG results with results from exact diaganolization for small systems. The exact diagonalization of the model has been carried out using the Diagrammatic Valence Bond (DVB) method. The DVB method exploits the total spin conservation property of the model Hamiltonians and employs a valence bond (VB) basis in which the Hamiltonian is represented as a matrix [23]. As the VB basis is nonorthogonal, the resulting Hamiltonian matrix is nonsymmetric. We have used Rettrup's algorithm which is similar to Davidson's algorithm for symmetric matrices, to obtain the lowest few eigenvalues and eigenvectors of the nonsymmetric matrix [24]. This exact diagonalization calculation is quite straightforward for chains of upto seven MX units.

Table 2 compares the exact ground state energies with the DMRG ground state energies for two different parameter sets of the Hamiltonian. Also given for comparison are the dimensionalities of the Hilbert space for $M_s = 0$ in the VB scheme (exact) with the $M_s = 0$ in the DMRG scheme (with cut-off). The DMRG scheme is found to reproduce accurately the ground state energies where such comparison is possible. We have also compared the DMRG properties such as charge density, $<\hat{n}_i>$, spin density, $<S^z_i>$ and bond order, $-\frac{1}{2} < a^\dagger_{i\alpha}a_{j\alpha} + a^\dagger_{i\beta}a_{j\beta} + h.c. >$ with exact properties (table 3 and 4). We find that the DMRG ground state properties are in very good agreement with the exact

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properties.

III. RESULTS AND DISCUSSION

We have studied the ground state of the MX chains in different regions of parameter space to study the phase transformation from CDW phase to SDW phase. The parameters U_M, U_X, and ϵ_M, ϵ_X characterize the metal ion and the halide ion. The orbital energy of the halide ion, ϵ_X, is specified relative to the orbital energy of the corresponding metal ion of the uniform MX chain. ϵ_X is always negative reflecting the larger electronegativity of the halides compared to the metal ions. In the halide series, larger negative ϵ_X represents chloride while the least negative ϵ_X represents iodide reflecting the electronegativity variations in the halogen group. The on-site repulsion parameter U_X is positive and decreases as we go down the series from Cl^- to I^-. The Hubbard parameter for the metal ion, U_M, decreases as we go from the I row transition elements to the III row transition elements. The parameters U_M, U_X and ϵ_X are varied from $U_M = 2.5t$, $U_X = t$, $\epsilon_X = -2t$ to $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_X = -t$ corresponding to the MX pairs $NiCl$ to PtI respectively. The ϵ_M values depend upon the strength of the diagonal electron-lattice coupling and so does the alternation δ in the transfer integrals. The coupling constants for the diagonal and off-diagonal couplings are assumed to be independent. Accordingly, we independently vary the transfer integrals as well as the site energy at the metal site, ϵ_M. This is one of the crucial differences between a polyene chain and the MX chain. In the former, the site-diagonal electron-phonon coupling is taken to be zero while in the MX chains it is nonzero by virtue of the crystal-field environment provided by the halide ions surrounding the metal ions. The dimerization parameter, δ, has been varied between 0.0 and 0.2. In what follows, we first discuss the results of our study of MX chains at $\frac{3}{4}^{th}$ filling and then discuss our results for these chains with one and two excess (fewer) electrons.

A. MX chains at $\frac{3}{4}^{th}$ filling

In fig.1 we present the dependence of the ground state energy per MX unit (ϵ_{MX}) of the MX chains for different values of δ for one set of parameters. The convergence to the infinite chain value is monotonic and from below. We have defined ϵ_{MX} as half the total energy difference between successive iterations which differ by two MX units. This definition corresponds to the energy of an embedded MX unit and is akin to the rings. It is well known that the energy per site of Hubbard, extended Hubbard as well as spin rings converges to the limiting value from below [25]. In table 5, we have shown the dependence of fractional stabilization of the MX chain on introducing alternation for several sets of parameters. We find that the alternation lowers ϵ_{MX} in all the cases we have studied but the extent of stabilization is rather small and insensitive to variations in U_M and ϵ_X when the diagonal electron-phonon coupling is neglected. While from finite chain studies it is not possible to reliably deduce whether for a given set of parameters, the distortion of the chain is unconditional (independent of the lattice stiffness), our results indicate the dominant role of diagonal electron-phonon interactions in determining the extent of bond alternation. In fact, in systems where bond alternation is indeed found, the magnitude of the alternation is very large.

In fig.2 we present the charge densities at the metal and halide sites in the alternating ($\delta = 0.1$) MX chains without diagonal distortions ($\epsilon_M = 0$) for two extremal values of U_M and ϵ_X. We find that the charge densities at the metal sites are very nearly uniform in both cases. For small values of ϵ_X and U_M, the charge density in the metal orbital is larger at $\approx 1.2 \pm 0.08$ while it is more uniform with values in the range $\approx 1.06 \pm 0.04$ for large U_M and large ϵ_X. The charge densities at the halide sites are uniform and closer to 2 electrons when ϵ_X and U_M are large. While the alternation in the transfer integral along the chain seems to promote mixed valency, large electron-electron repulsion at the metal site and large site energy of the halogen orbital has the effect of suppressing mixed valency. This is in conformity with experiments wherein mixed valency is found in MX chains with heavier transition elements as well as heavier halogen atoms. Increasing the alternation in transfer integral does not change the picture significantly. There is a slight increase in the amplitude of the charge density wave in the most favourable case we have studied, corresponding to $U_M = 1.5t$ and $\epsilon_X = -t$ (fig.3).

In fig.4, we show the plot of charge density at metal sites in the presence of diagonal distortion ($\epsilon_M \neq 0.0$) for alternation $\delta = 0.1$ for the two extremal cases we have studied, namely, large U_M, large ϵ_X and small U_M and small ϵ_X for one particular value of ϵ_M. We see a dramatic change in the charge density distribution in both cases. In the favourable case, the disproportionation of the metal ion in 3+ oxidation state into 2+ and 4+ oxidation states is almost complete. While even in our least favourable case, the amplitude of the CDW is quite significant. In the latter case increasing ϵ_M increases the amplitude rapidly. This result underlines the importance of diagonal distortion in producing a CDW ground state.

The variation in bond order along the MX chain is plotted for several values of the parameters in fig.5 only for the left half of the chain. The amplitude of the bond order wave (BOW) behaves similar to the amplitude of the CDW. The diagonal distortion has a strong effect on the BOW amplitude. Even in the most unfavourable case of $U_M = 2.5t$ and $\epsilon_X = -2t$, the BOW picks up

sufficient amplitude for the site diagonal distortion we have considered. The earlier prediction of Gammel *et al* [1] that a BOW cannot exist for negative halide site energy with site diagonal distortion lowering the metal-ion site energy is not borne out by our calculations.

The spin density distribution (fig.6) shows a trend opposite to what is observed with CDW and BOW instabilities. For large U_M and large ϵ_X, in the uniform MX chain, the SDW amplitude is fairly large. Introducing off-diagonal alternation reduces the amplitude, although the alternation in the spin density still exists. However, on introducing diagonal distortion, all the metal sites become completely nonmagnetic. This behaviour shows that when the CDW/BOW amplitude is large the amplitude of the SDW is small. Fig.7 brings out this trend by comparing the charge and spin densities at metal sites for different values of the site-diagonal distortion parameter ϵ_M. It is also interesting to note that for one set of parameter values, the CDW and the SDW phases coexist (fig.7 ii).

We have also characterized the ground state in various regimes of the parameters by studying the spin-spin and charge-charge correlation functions. Although these correlation functions have been computed for open chains, they can be Fourier transformed, if one assumes that the correlations in the interior of the open chain are close to what would be seen in a ring. This assumption was first made by Affleck *et al* [26] to obtain the structure factors from open chain DMRG calculations of spin systems. In our calculations, we have discarded the last three unit cells on either ends of the chain and have assumed the correlations to have a reflection symmetry about the middle bond. This would enable us to Fourier transform the correlation functions.

In fig.8, we show the spin-structure factor, $S(q)$, for various values of the model parameters. In the CDW phase which corresponds to small U_M, small ϵ_X and nonzero site-diagonal distortion and alternation, we find that $S(q)$ is very small. However, for large U_M, large ϵ_X, zero site-diagonal distortion but with nonzero δ, the structure-factor is large and peaks at $q = \pi$. This result reflects the spin ordering of the ground state. The uniform structure factor in fig.8a and fig.8d confirms the ground state to be in CDW phase. This result is also consistent with the charge and spin density and the bond order data discussed above. In fig.9 we show the structure factor corresponding to the charge-charge correlation function. Here again, for large U_M and large negative ϵ_X, the structure factor is almost uniform and does not show any pronounced peaks. However, for small U_M, small negative ϵ_X and nonzero site-diagonal distortion, the structure factor peaks at π corresponding to the existence of a CDW phase. The importance of the diagonal distortion is underscored by the fact that even for δ, small U_M and small negative ϵ_X, the peak at π in the strcuture factor though discernible, is not pronounced.

It is also interesting to note that $\rho(q)$ shows small oscillations away from the peak at π which could be due to incipient long-wave length CDW distortions which could have nonzero amplitude in the thermodynamic limit as suggested by Gammel *et al* [1].

B. MX chains marginally away from $\frac{3}{4}^{th}$ filling

The DMRG method for MX chains cannot access the energy levels that have been studied by optical spectroscopies. The reason being, there are a large number of low-lying excitations in long MX chains which intrude while targetting excited states and absence of the symmetries in open chains rules out the possibility of avoiding the intruder states. Hence, we have been unable to study the optical properties of long MX chains by this technique. However, there is considerable interest in the photogenerated gap states which arise from the dissociation of the excitons produced in an optical experiment. These states are typically, the positive and negative polarons and bipolarons and the charged and neutral solitons of the system. The DMRG method can easily access the polaronic and bipolaronic states. In what follows, we present results of the DMRG study of these species at representative points in the parameter space, namely $U_M = 1.5t, \epsilon_X = -t$ and $U_M = 2.5t, \epsilon_X = -2t$ corresponding to the CDW and SDW regimes. These parameters are taken together with $\epsilon_M = 0.0$ or t and $\delta = 0.1, U_X = 0.5t$ to explore the importance of site-diagonal distortion in the two regimes.

We first discuss the energetics of the polarons and bipolarons, for the chosen parameter set. In table 6 is given the energy for doping of MX chains of 35 units with one or two holes and one or two electrons. The magnitude of doping energy increases with increase in strength of electron correlations. The stabilization energy on doping with one(two) hole(s) is(are) almost equal in magnitude to the energy required for creating one(two) electron(s) doped chains respectively. Neither the bond alternation nor the site-diagonal distortion energy at the metal site have any noticeable influence on the doping energetics. However, the positively charged bipolaron and the negatively charged bipolaron are not placed symmetrically around the ground state in the energy scale. From the energetics, one can see that at larger correlation strengths, the positively charged bipolaron is less stable than the two positively charged polarons. This is also true for negatively charged bipolaron irrespective of Hubbard U. Thus, it appears from the energetics that both the positively and the negatively charged bipolarons should dissociate into two polarons.

The definitive proof for the disproportionation of the bipolarons comes from comparing the charge and spin density distributions of the bipolarons with those of the

polarons bearing charges of the same sign. The charge densities at the metal site for the polarons and bipolarons are shown in fig.10. The polaron charge densities for (I) $U_M = 1.5t$, $\epsilon_M = 0.0$, $U_X = 0.5t$ and $\epsilon_X = -t$ are shown in fig.10a, and for (II) $U_M = 2.5t$, $\epsilon_M = 0.0$, $U_X = 0.5t$ and $\epsilon_X = -2t$ are shown in fig.10c. The data for bipolarons for the parameter set (I) are shown in fig.10b and for the set (II) are shown in fig.10d. For the parameter set I (fig.10a and b), the additional charge is uniformly distributed over the entire chain for the (i) positively charged polaron/bipolaron, (ii) the neutral chain and (iii) for the negatively charged polaron/bipolaron. For the second set of parameters, *i.e.* at large U_M, we observe more localized charge distribution for both the positively charged polarons and positively charged bipolarons. We also observe two broad peaks (fig.10d) in the charge distribution of the positively charged bipolaron which is indicative of disproportionation of the positively charged bipolaron into two positively charged polarons. However, in the case of the negatively charged polarons and bipolarons, the Hubbard U prevents the localization of charge. An earlier mean-field study [1] found the negatively charged polaron and bipolaron to be more localized than the positively charged polaron and bipolaron. Our DMRG results correspond to an on-site halide repulsion parameter U_X, which is smaller than the metal on-site repulsion parameter, U_M and our study should have enhanced this difference between the hole-defects and the electron-defects predicted by the mean-field analysis. It appears, therefore, that the mean-field approximation gives wrong trends for charge distributions of the defects. On physical grounds, one should expect that the on-site repulsions spread out the excess negative charge more than excess positive charge.

The evidence for the disproportionation of the positively charged bipolaron into two polarons is more pronounced when alternation in the chain is introduced (fig.11). The charge density distribution of the polaron (fig.11a) shows a single hump while that for the bipolaron (fig.11b) shows two humps. The hole charge density is mostly confined to one sublattice of the metal ion, the one in which the metal-halogen bond is shorter accommodates the excess charge. The halogen charge density distribution is not affected significantly by doping. The spin density distribution shows the disproportionation more clearly as seen from the two separate envelops for the spin density in the bipolaron (fig.11d) compared to a single envelop in the polaron spin density distribution (fig.11c). This break-up of the bipolaron is observed only for hole doping.

The effect of site-diagonal distortion on the disproportionation is very dramatic. We compare the charge density distribution for the positively charged polarons and bipolarons with (fig.12a) and without (fig.12b) site diagonal distortion. In both the cases, the localization of excess charge is confined to only one sublattice. In the system with site-diagonal distortion, the sublattice with nonuniform charge density is on the metal site for which the metal-halogen bond is long, corresponding to a negative ϵ_M while in the absence of site-diagonal distortion, these metal-sites have uniform charge distribution. This is seen as a change over in the charge density humps from the upper envelop in fig.12a to the lower envelop in fig.12b. The disproportionation of the positively charged bipolaron is again found only for systems with large on-site repulsions, U_M.

The difference between MX chains at $\frac{3}{4}^{th}$ filling and MX chains with one- and two-hole dopings, can be seen clearly, if the difference in charge density between corresponding metal sites of the neutral and doped chains is plotted as a function of site number. We show in fig.13 these difference plots for systems with site-diagonal distortion for weak and strong correlation cases. The envelop of the charge density distribution of the polaron and the bipolaron show a single peak at small correlation strengths, while the same for strong correlations exhibits two distinct peaks for the bipolaron (fig.13a, iv). A similar behaviour is also found in the spin density distribution (fig.13b, iv).

The negatively charged bipolaron does not disproportionate even upon introducing the site-diagonal distortions. In fig.14, we show for small and large U_M values, the charge density (fig.14a) and spin density (fig.14b) distributions at the metal sites. Apart from exhibiting mixed valency, the charge and spin density distributions are uniform on each sublattice for the negatively charged bipolarons.

The bond order distributions in the negatively and positively charged bipolarons are almost similar to what is found in neutral chains. These are shown in fig.15 only for the left half of the chain. There is a tendency for the negatively charged bipolarons towards the elongation of the bonds (as seen from smaller bond orders in the middle of the chain), while the positively charged bipolarons have an opposite tendency *i.e.*, towards bond length contraction. This agrees with an earlier study of the lattice distortions of doped MX chains [3]. However, these marginal differences in the bond order variations are reduced on introducing site-diagonal distortions. The essential difference between the positively and negatively charged bipolaron lies in the disproportionation of the former into positively charged polarons in the strong correlation limit, in the presence of alternation and site diagonal distortion.

In summary, we have studied the phase diagram of MX chains within a two-band extended Peierls-Hubbard model employing the density matrix renormalization group method. We find that the site energy associated with site-diagonal distortion is the single most important parameter for the transition from a SDW phase to a CDW phase in the ground state of the system.

The variation of other parameters, such as, site energy of the halide site, on-site Hubbard U of the halide ion and bond alternations do not change the nature of the ground state significantly. On the otherhand, for the doped MX chains, both the bond alternation and site-diagonal distortion play a major role. For positively doped systems, introduction of bond alternation leads to the localization of charge and spin densities. In the presence of site-diagonal distortion, we observe that the positively charged bipolaron disproportionates into two positively charged polarons in strong correlation limit. The negatively charged bipolarons do not show evidence for disproportionation even for the longest chain length and for the parameters we have studied. We also find that there is a contraction of bond length in the case of positively charged polarons and bipolarons and elongation for the corresponding negatively charged species.

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Tables

Table 1. Energy per MX unit for systems with different DMRG cut-offs, m, for the parameters set $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 1.5t$, $\epsilon_X = -2t$ and $\delta = 0.1$.

N of MX units	$m = 70$	$m = 80$	$m = 90$
25	1.413177	1.413175	1.413168
27	1.413158	1.413157	1.413156
29	1.413202	1.413177	1.413170
31	1.413159	1.413157	1.413156
33	1.413181	1.413173	1.413169
35	1.413159	1.413157	1.413156

Table 2. Comparison of dimensionality and energy per MX unit with exact calculation. p is the site number and P_{exact} and P_{DMRG} are the dimensionality in the exact and DMRG calculation (with DMRG cut-off $m = 80$). $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.0$. A in the table corresponds to $U_M = 1.5t$ and B to $U_M = 2.5t$.

p	A				B			
	P_{exact}	P_{DMRG}	E_{exact}	E_{DMRG}	P_{exact}	P_{DMRG}	E_{exact}	E_{DMRG}
6	90	90	4.3834	4.3834	90	90	13.4129	13.4129
8	784	784	7.2669	7.2669	784	784	20.0065	20.0065
10	5400	3873	10.4504	10.4505	5400	3930	26.7485	26.7485
12	48400	7482	13.4510	13.4527	48400	7687	33.4120	33.4130
14	364364	6277	16.6227	16.6229	364364	6356	40.1543	40.1544

Table 3. Comparison of charge densities and spin densities for 14 sites chain with exact calculation. p is the site number. A and B correspond to the parameter values quoted in table 2.

p	charge density				spin density			
	A		B		A		B	
	Exact	DMRG	Exact	DMRG	Exact	DMRG	Exact	DMRG
1	1.9083	1.9082	1.8795	1.8794	0.0096	0.0095	0.0059	0.0059
2	1.7124	1.7123	1.7456	1.7455	0.0270	0.0269	0.0123	0.0123
3	0.9449	0.9447	0.7752	0.7752	0.0745	0.0744	0.0570	0.0569
4	1.7491	1.7491	1.8383	1.8383	-0.0045	-0.0045	-0.0025	-0.0025
5	1.1393	1.1392	1.0054	1.0054	0.0805	0.0806	0.1294	0.1295
6	1.7366	1.7365	1.8495	1.8495	0.0191	0.0191	0.0074	0.0074
7	1.1092	1.1091	1.0387	1.0387	-0.0297	-0.0299	-0.0854	-0.0856
8	1.7639	1.7639	1.8751	1.8752	0.0004	0.0004	0.0029	0.0029
9	1.1393	1.1394	1.0776	1.0777	0.1678	0.1680	0.2348	0.2351
10	1.7752	1.7753	1.8820	1.8819	0.0149	0.0150	0.0064	0.0064
11	1.1809	1.1812	1.1007	1.1010	-0.0771	-0.0773	-0.1229	-0.1232
12	1.7508	1.7507	1.8763	1.8763	0.0081	0.0080	0.0049	0.0049
13	1.1351	1.1353	1.0815	1.0814	0.1988	0.1991	0.2431	0.2433
14	1.9550	1.9550	1.9745	1.9745	0.0108	0.0108	0.0068	0.0068

Table 4. Comparison of DMRG bond orders for the 14 sites MX chain with exact calculation. p refers to the (p, p+1) bond and A and B correspond to parameter values in table 2.

p	A		B	
	Exact	DMRG	Exact	DMRG
1	0.1594	0.1596	0.1700	0.1702
2	0.5438	0.5440	0.5468	0.5468
3	0.4452	0.4452	0.3772	0.3772
4	0.3662	0.3660	0.2926	0.2926
5	0.4068	0.4068	0.3198	0.3198

Table 5. Fractional stabilization of energy defined as $(E(\delta) - E(0))/E(0)$ of MX chains with respect to uniform chain for different parameter sets. I: $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$; II: $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$; III: $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$; IV: $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$ and V: $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -2t$.

δ	I	II	III	IV	V
0.10	-0.0043	-0.0127	-0.0007	-0.0017	-0.0560
0.15	-0.0109	-0.0319	-0.0026	-0.0055	-0.0990
0.20	-0.0210	-0.0598	-0.0054	-0.0104	-0.1489

Table 6. Energy (in units of t) for doped MX chains of 35 units with one and two holes as well as one and two electrons, for various representative parameters of the Peierls-Hubbard model. I corresponds to $U_M = 1.5t$, $U_X = 0.5t$ and $\epsilon_X = -t$ and II to $U_M = 2.5t$, $U_X = 0.5t$ and $\epsilon_X = -2t$.

	I				II			
doping	$\epsilon_M = 0.0$		$\epsilon_M = t$		$\epsilon_M = 0.0$		$\epsilon_M = t$	
	$\delta = 0.0$	$\delta = 0.1$	$\delta = 0.0$	$\delta = 0.1$	$\delta = 0.0$	$\delta = 0.1$	$\delta = 0.0$	$\delta = 0.1$
2 holes	-9.6308	-9.7157	-9.3790	-9.1630	-12.2875	-12.3646	-13.5137	-13.4442
1 hole	-4.8361	-4.8944	-4.6590	-4.5038	-6.1595	-6.2060	-6.8225	-6.7591
1 electron	4.9375	4.9451	5.2900	5.3242	6.1935	6.2158	6.8850	6.9995
2 electrons	10.3529	10.3245	10.7410	10.8901	13.9677	13.9482	13.9909	14.0724

Figure Captions

1. Plot of energy per MX unit vs $1/N$ for different values of δ for $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0.0$ and $\epsilon_X = -t$. (i) $\delta = 0.0$ (square) (ii) $\delta = 0.1$ (circle) (iii) $\delta = 0.15$ (triangle) (iv) $\delta = 0.2$ (diamond).

2. Charge density of M and X vs unit cell index. Open and filled symbols are for M and X charge densities, respectively. Squares represent the charge density for $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.1$ and cirlces for $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$ and $\delta = 0.1$.

3. Charge density of M vs unit cell index for different values of δ, for $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$ and $\epsilon_X = -t$. (i) $\delta = 0.0$ (square) (ii) $\delta = 0.1$ (circle) (iii) $\delta = 0.15$ (triangle) (iv) $\delta = 0.2$ (diamond).

4. Charge density of M vs unit cell index in the presence of site-diagonal distortion. (i) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -t$ and $\delta = 0.1$ (square). (ii) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -2t$ and $\delta = 0.1$ (circle).

5. Bond order vs bond index. (i) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.1$ (square). (ii) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -t$ and $\delta = 0.1$ (circle). (iii) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$ and $\delta = 0.1$ (triangle). (iv) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -2t$ and $\delta = 0.1$ (diamond).

6. Spin density of M vs unit cell index in different parameter regions. (i) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.0$ (square). (ii) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.1$ (circle). (iii) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$ and $\delta = 0.1$ (triangle). (iv) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -2t$ and $\delta = 0.1$ (diamond). Zeroth line is shown by dots.

7. Variation of (a) charge densities and (b) spin densities with site-diagonal distortion, ϵ_M, vs unit cell index for $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_X = -2t$ and $\delta = 0.1$. (i) $\epsilon_M = 0.0$ (open square) (ii) $\epsilon_M = 1.0$ (open circle) (iii) $\epsilon_M = 2.0$ (filled square) (iv) $\epsilon_M = 3.0$ (filled circle).

8. Spin structure factor vs momentum, q (in degrees) for (a) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.0$. (b) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.2$. (c) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$ and $\delta = 0.2$. (d) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -2t$ and $\delta = 0.1$.

9. Charge structure factor vs q (in degrees) for (a) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.0$. (b) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -t$ and $\delta = 0.2$. (c) $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$, $\epsilon_X = -2t$ and $\delta = 0.2$. (d) $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -t$ and $\delta = 0.1$.

10. Charge density of metal site vs unit cell index for a uniform MX chain. (a) polaron and (b) bipolaron for $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$ and $\epsilon_X = -t$. (c) and (d) for polaron and bipolaron respectively, for $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = 0$ and $\epsilon_X = -2t$. (i) positively charged (square), (ii) neutral (circle) and (iii) negatively charged (triangle) systems, in all the figures (a)-(d).

11. Charge density and spin density of metal site for positively doped MX chain for $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = 0$ and $\epsilon_X = -2t$. Charge density for (a) polaron and (b) bipolaron. Spin density for (c) polaron and (d) bipolaron. In all the figures (a)-(d), (i) $\delta = 0.0$ (square), (ii) $\delta = 0.1$ (circle) and (iii) $\delta = 0.2$ (triangle).

12. Charge density of metal site for positively charged polaron (squares) and bipolaron (circles) for $U_X = 0.5t$ and $\delta = 0.1$. Open symbols for $U_M = 1.5t$ and $\epsilon_X = -t$ and filled symbols are for $U_M = 2.5t$ and $\epsilon_X = -2t$, (a) for $\epsilon_M = 0.0$ and (b) for $\epsilon_M = t$.

13. Difference in (a) charge density and (b) spin density of metal sites with respect to neutral system for positively charged polaron and bipolaron for the same set of parameters as in fig.12 with the single $\epsilon_M = t$.

14. Charge and spin density of metal sites with respect to neutral system for negatively charged (i) polaron and (ii) bipolaron in the presence of site-diagonal distortion. (a) and (c) for $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -t$ and $\delta = 0.1$ for charge and spin density respectively. Similarly (b) and (d) for $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_M = t$, $\epsilon_X = -2t$ and $\delta = 0.1$ for charge and spin density respectively.

15. Bond order vs bond index for bipolaron. (i) positively charged (squares), (ii) neutral (triangles) and (iii) negatively charged (circles) systems. For $U_M = 1.5t$, $U_X = 0.5t$, $\epsilon_X = -t$ and $\delta = 0.1$ and (a) for $\epsilon_M = 0$ and (b) for $\epsilon_M = t$. For $U_M = 2.5t$, $U_X = 0.5t$, $\epsilon_X = -2t$ and $\delta = 0.1$ and (c) for $\epsilon_M = 0$ and (d) for $\epsilon_M = t$.