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Effective electron Hamiltonian for a quasi one-dimensional system. The $(TMTSF)_2X$ and the $(TMTTF)_2X$ systems

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Abstract. In this paper we have introduced a variational approach to investigate the ground state of a model which includes both the Holstein electron-phonon interaction and the extended Hubbard electron-electron interaction. We have considered a variational state for the phonon subsystem which generalizes the previous used forms. This state allows to take into account the possibility of extended phonon mediated correlations. The effective electron Hamiltonian, which we have obtained, includes first and second neighbor electron-electron interaction terms. We have treated exactly, through a Lanczos method, this effective model in the one-dimensional case. We have applied our method to two Bechgaard salts and in these cases we have estimated the correlation parameters. We have shown that the introduction of electron-phonon interaction allows an estimate of the on site U and nearest-neighbor V Coulomb repulsion, which are in agreement with the experimental optical spectra of the above mentioned two compounds.

PACS. 63.20.Kr Phonon-electron and phonon-phonon interactions – 71.38.+i Polarons and electron-phonon interactions – 72.80.Le Polymers; organic compounds (including organic semiconductors)

1 introduction

An accurate treatment of electron-electron and electron-phonon interactions, beyond the usual approximations, has became crucial in order to understand the physical behavior of numerous compounds synthesized in the latest two decades. The study of quasi-one dimensional organic conductors [1] and the discovery of superconductivity in some of these materials [2] has found recently a renewed interest in connection with new materials such as cuprate superconductors and fullerenes.

This problem has generated a wide interest in the analysis of models in which the above mentioned interactions are considered through the introduction of few parameters, which try to preserve the essential features of the physical systems. The Holstein-Hubbard model (HHM) is the prototype of these Hamiltonians since the electron-electron and the electron-phonon couplings are considered by means of only local terms. In the present paper we will consider this model and an extension of it, which includes also the nearest-neighbor Coulomb interaction and two different hopping integrals.

There is a quite general agreement that an accurate solution of the HHM model, in the whole regime of parameters, will be able to give an understanding of many physical properties of the new materials. However, in spite of the simplicity of the model, it is needed a great effort in order to achieve accurate solutions. Therefore many authors have preferred to deal with effective electron-electron Hamiltonians [3–5] or quasi particle phenomenological models (see for instance the boson-fermion model [6] for the high T_c superconductors). This approaches have obtained many successes in order to explain some experimental properties [4,5,7], however a microscopic basis of these models is required. Moreover the new organic conductors show, by varying temperature, pressure and density of charge carriers, a rich phase diagram [8] which needs a detailed description.

Another strategy is to study the electron-phonon Hamiltonians in the few particle limit by using small cluster exact calculations [9,10] or variational methods [11–14]. The reliability of this last approach is connected with the form of the trial wave function which should be as general as possible. We have used [13–15] a trial state which can be applied suitably in the whole region of parameters when we deal with the one particle or two particle problems in a one-dimensional system. The aim of these investigations is to gain a complete description of the few particle electron system which, we hope, could be also fruitful in the analysis of a many particle system.

What we have learned from our previous works [13–15] on the HHM is the importance of the extension of the phonon induced correlations to the nearest-neighbor

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sites and the role of the anomalous fluctuations of the oscillator positions in the very important intermediate regime of parameters.

In the present work we have studied a many electron system in the framework of the HHM by including these two fundamental elements for the phonons subsystem which has been treated by a variational method. Then we have derived an effective electron-electron Hamiltonian in which the parameters depend on the phonon variational variables. This effective model has been solved exactly (numerically) by means of a modified Lanczos algorithm.

Actually, the way to include in the calculation scheme the effect of the anomalous fluctuations has been clearly described in the pioneering work of Zheng [16] and in the further developments due to Lo and Sollie [17]. In the present work we will follow their approach, but we will show that the introduction of extended correlations allows to obtain a more accurate trend of the ground state energy E_{GS} as function of the coupling parameter λ. Our method is especially suitable away from the adiabatic limit.

We have also reported an application of our method to study two quasi one-dimensional systems which show strong electron-electron interaction and electron-phonon couplings in the intermediate regime.

We have analyzed the effect of correlations on the electron mobility in such compounds by using an approach introduced by Mila [1] for the extended Hubbard model. We have observed how the reduction of kinetic energy is caused by on-site Coulomb repulsion and by polaronic effects, while the role of the intersite Coulomb interaction is negligible.

2 The effective electron model

We consider a system of electrons in the framework of an extended Hubbard model, which is also coupled to a collection of Einstein oscillators. The model Hamiltonian is

$$\hat{H}_{HH} = -t \sum_{\langle ij\rangle,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} + U \sum_{i} \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} + V \sum_{\langle ij\rangle} \hat{n}_i \hat{n}_j + \hbar\omega \sum_i b^{\dagger}_i b_i + \chi \sum_{i,\sigma} c^{\dagger}_{i,\sigma} c_{i,\sigma}(b^{\dagger}_i + b_i) \quad (1)$$

here $\hat{n}_{i,\sigma} = c^{\dagger}_{i,\sigma} c_{i,\sigma}$, $\hat{n}_i = \hat{n}_{i,\uparrow} + \hat{n}_{i,\downarrow}$ and the symbol $\sum_{\langle i,j\rangle}$ denotes the sum over nearest-neighbor sites. The operator $c^{\dagger}_{i,\sigma}$ ($c_{i,\sigma}$) creates (annihilates) an electron with spin projection σ in the site labeled by i, while $b^{\dagger}_i$ (b_i) creates (annihilates) a quantum of oscillation energy $\hbar\omega$ on the mode localized in the ith site. The parameters of the model are: the hopping integral t, the Hubbard on-site repulsion U, the nearest-neighbor interaction V and the coupling constant χ.

We consider the following transformation

$$\hat{U} = e^{-\hat{R}};$$
$$\hat{R} = -\left(\frac{\chi}{\hbar\omega}\right) \sum_{ij,\sigma} f(\mathbf{r}_i - \mathbf{r}_j) c^{\dagger}_{i,\sigma} c_{i,\sigma} (b^{\dagger}_j - b_j) \quad (2)$$

here $f(\mathbf{r}_i - \mathbf{r}_j) = f(\mathbf{r}_j - \mathbf{r}_i)$. The transformation (2) is expressed in terms of ordinary phonons coherent states and it is related to the perturbation of the mean displacement of the jth oscillator due to the presence of a particle in the ith site.

The transformed phonon and particle operators will be

$$e^{\hat{R}} c_{i,\sigma} e^{-\hat{R}} = c_{i,\sigma} e^{\hat{\Gamma}(i)};$$
$$\hat{\Gamma}(i) = -\left(\frac{\chi}{\hbar\omega}\right) \sum_j f(\mathbf{r}_i - \mathbf{r}_j)(b^{\dagger}_j - b_j) \quad (3)$$

$$e^{\hat{R}} b_i e^{-\hat{R}} = b_i - \frac{\chi}{\hbar\omega} \sum_{j,\sigma} f(\mathbf{r}_i - \mathbf{r}_j) c^{\dagger}_{j,\sigma} c_{j,\sigma}. \quad (4)$$

By using equations (3, 4) it is easy to obtain

$$\tilde{H} = e^{\hat{R}} \hat{H}_{HH} e^{-\hat{R}} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3 \quad (5)$$

where

$$\hat{H}_1 = -t \sum_{\langle ij\rangle,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} e^{-\hat{\Gamma}(i)} e^{\hat{\Gamma}(j)} + U \sum_i \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} + V \sum_{\langle ij\rangle} \hat{n}_i \hat{n}_j + \hbar\omega \sum_i b^{\dagger}_i b_i. \quad (6)$$

$$\hat{H}_2 = \left(\frac{\chi^2}{\hbar\omega}\right) \sum_{ij,\sigma\sigma'} \{[\sum_n f(\mathbf{r}_i - \mathbf{r}_n) f(\mathbf{r}_j - \mathbf{r}_n)] - 2 f(\mathbf{r}_i - \mathbf{r}_j)\} c^{\dagger}_{i,\sigma} c_{i,\sigma} c^{\dagger}_{j,\sigma'} c_{j,\sigma'} \quad (7)$$

$$\hat{H}_3 = \chi \sum_{i,\sigma} c^{\dagger}_{i,\sigma} c_{i,\sigma} (b^{\dagger}_i + b_i) + \hbar\omega \sum_{ij,\sigma} f(\mathbf{r}_i - \mathbf{r}_j) c^{\dagger}_{i,\sigma} c_{i,\sigma} (b^{\dagger}_j + b_j). \quad (8)$$

The results can be usefully reported by using the following adimensional parameters

$$\lambda = \frac{\chi^2}{2t\hbar\omega}; \quad \gamma = \frac{\hbar\omega}{t}.$$

In the non adiabatic ($\gamma \gg 1$) or in the strong coupling ($\lambda \gg 1$) limit, the eigenvectors of the model are the Lang-Firsov [18] small-polaron (SP) solutions. The Lang-Firsov transformation can be obtained from equation (2) if we put

$$f(\mathbf{r}_i - \mathbf{r}_j) = \delta_{ij}. \quad (9)$$

The SP approximation is rather poor for small and intermediate values of λ and γ for two main reasons.

First of all the SP state has the same phonons quantum fluctuations than the bare state, while in the intermediate regime of the parameters the electron-phonon interaction leads to a renormalization of the phonon vacuum. Indeed, in this regime, the phonons vacuum cannot be described

simply as a set of displaced oscillators, since the fluctuations around the mean position are anomalous.

Secondly in the SP states the presence of a particle in a particular site generates only local distortions, while it is well-known from the polaron theory (see Ref. [12] and reference therein) that, again for intermediate values of λ and γ, the perturbation of the phonons field due to the presence of a particle extends along the lattice.

Corrections to the SP approximation has been introduced in order to consider the effects of the anomalous fluctuations. Such procedures are known as squeezed state (SS) [16] or correlated squeezed state (CSS) [17] approaches.

Squeezed states are good approximations to the exact phonons states since, even if they are harmonic, they introduce position fluctuations which are different whit respect to the bare phonons due to a renormalization of the phonons frequencies [19].

Zheng *et al.* [16,17,20] have used the SS approximation but have retained the relation (9). This choice could be a serious limit to the theory because it leads to consider only on-site phonon mediated electron-electron interaction. In a previous work [15] we have shown that, in the intermediate regime of the parameters for a two particles system, the phonon mediated correlations extend significantly until the first-neighbor sites. Therefore in the present work we will assume the following form for the $f(\mathbf{r}_i - \mathbf{r}_j)$ coefficients

$$f(\mathbf{r}_i - \mathbf{r}_j) = \begin{cases} 1 - f_0 & \text{if } i = j \\ f_1 & \text{if } i \text{ and } j \text{ are nearest neighbors.} \end{cases}$$

In the following we will consider a one-dimensional system, however the calculation can be extended easily to higher dimensions.

In such a case the effective phonon mediated electron-electron interaction $\hat{H}_2$ will be

$$\hat{H}_2 = \epsilon_0 \sum_{i,\sigma} \hat{n}_{i,\sigma} + U_0 \sum_i \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} + V_0 \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j + W_0 \sum_{\langle\langle l,m \rangle\rangle} \hat{n}_l \hat{n}_m. \quad (10)$$

Here $\sum_{\langle\langle\ \rangle\rangle}$ indicates the sum over the second neighbors. The parameters which appear in $\hat{H}_2$ depend on the two new variational variables f_0, and f_1 above introduced. They are

$$\epsilon_0 = -\frac{\chi^2}{\hbar\omega}(1 - f_0^2 - 2f_1^2);$$
$$U_0 = -2\frac{\chi^2}{\hbar\omega}(1 - f_0^2 - 2f_1^2); \quad (11)$$

$$V_0 = -2\frac{\chi^2}{\hbar\omega} f_0 f_1; \quad W_0 = \frac{\chi^2}{\hbar\omega} f_1^2. \quad (12)$$

We can eliminate the phonons operators by using the CSS approximation [17]

$$|\psi_s\rangle = e^{-\hat{S}}|0\rangle = \exp\left\{\alpha \sum_i (b_i^\dagger b_i^\dagger - b_i b_i)\right\} \times \exp\left\{(\beta/2) \sum_{\langle i,j \rangle} (b_i^\dagger b_j^\dagger - b_i b_j)\right\}|0\rangle. \quad (13)$$

By following reference [19] we can obtain the effective electron Hamiltonian

$$\tilde{H}_{eff} = -te^{-G} \sum_{\langle i,j \rangle} c_{i,\sigma}^\dagger c_{j,\sigma} + \epsilon_{eff} \sum_{i,\sigma} \hat{n}_{i,\sigma} + U_{eff} \sum_i \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} + V_{eff} \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j + W_{eff} \sum_{\langle\langle l,m \rangle\rangle} \hat{n}_l \hat{n}_m + \hbar\omega \sum_{\mathbf{q}} \sinh\left\{2[\alpha + 2\beta\cos(qa)]\right\} \quad (14)$$

with

$$G = \frac{\lambda}{\gamma N} \sum_{\mathbf{q}} e^{-4[\alpha + 2\beta\cos(qa)]}[f_0 + 2f_1\cos(qa)]^2 \times |e^{-\imath\mathbf{q}\cdot\mathbf{R_i}} - e^{-\imath\mathbf{q}\cdot\mathbf{R_j}}|^2$$

and

$$\epsilon_{eff} = \epsilon_0; \qquad U_{eff} = U + U_0;$$
$$V_{eff} = V + V_0; \qquad W_{eff} = W_0.$$

The effective Hamiltonian (14) results from high-energy non logarithmic contribution of the coupled electron-intramolecular-phonons system. This is certainly appropriate when $\gamma \gtrsim 1$. However, when γ and U become sufficiently small, singular logarithmic (and even power law) charge-density-wave electron correlation, together with strong retardation effect, can strongly modify the phonon spectrum and the form of the effective low-energy Hamiltonian [21]. Thus, in the adiabatic regime for small U values and at half-filling, Hamiltonian (14) in not able to reproduce the Peierls instability and one has to introduce dimerization through a further variational parameter to take into account this effect. Anyway we will limit in the present case to consider the case $U > 4\lambda$ where our approach should be reliable (see Sect. 3 for more details).

Parameters in the effective electron model (14) will be fixed by minimizing the ground state energy $E_{GS}(f_0, f_1, \alpha, \beta)$ with respect to the four phonons variables: f_0, f_1, α, β. It should be noticed that the repulsive term due to the second neighbor interaction cannot be omitted if we want to avoid an unphysical behavior of the energy. In fact if we omit this term the energy will not be bounded from below for $f_1 \to \infty$. Moreover the balance between f_0 and f_1 in determining the corrections to the on-site and to the intersite interactions turns to be fundamental in order to grant the existence of only one stable minimum of $E_{GS}(f_0, f_1, \alpha, \beta)$. The possibility

in our approach to have negative V_{eff} values implies that, if we study the superconducting phase, we can have a gap which has not only a s-type symmetry but also a d-type symmetry or a mixed one.

We want to stress that our approach is significantly different from the one adopted in reference [20], where the renormalized first-neighbor interaction derives from a further linear term in the starting model which introduces an interaction between the particles and the nearest-neighbor oscillators.

3 Numerical results

In this section we will discuss numerical results based on the model (14) in the case of $V = 0$ (*i.e.* the simple Hubbard model for the electron-electron interaction). We have chosen to consider first this single case in order to illustrate the method of calculation adopted in the present paper. In this section all the parameters which have the dimension of energy will be expressed in t units.

It is well-known that the Holstein-Hubbard model has a very rich phase diagram which includes charge and spin instabilities.

In the non-adiabatic limit ($\gamma \to \infty$) the model maps on the simple Hubbard model

$$\hat{H} = -e^{-2\lambda/\gamma} \sum_{<i,j>,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} + (U - 4\lambda) \sum_{i} \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow} - 2\lambda \sum_{i} \hat{n}_{i}. \qquad (15)$$

In a one-dimensional system and at half filling, the ground state of the model (15) manifests a commensurate spin density wave (SDW) or a commensurate charge density wave (CDW) ordering in relation to the fact that the correlations are dominated by the Coulomb repulsion ($U > 4\lambda$) or by the electron phonon interaction ($U < 4\lambda$) respectively.

In the Holstein model (see Hamiltonian (1) with $U = 0$ and $V = 0$) the Peierls lattice instability and the related (π-mode) CDW appears (for all the values of the coupling strength), if we consider a 1D system at half filling in the adiabatic limit ($\gamma = 0$). In this case the lattice can be treated classically. Monte-Carlo calculations [23] have shown that at half filling, when γ is finite and $U = 0$, a dimerized state is stable if λ exceeds a critical value $\lambda_c(\gamma)$ which gets with continuity the two limits $\lambda_c(0) = 0$ and $\lambda_c(\infty) = \infty$ (one has to note that there is not yet a precise determination of the $\lambda_c(\gamma)$ curve). Again at half filling by means of Monte-Carlo method, Hirsch [24] has shown, for finite γ values, that a dimerized state is stable if $U < 4\lambda$ and λ is well above $\lambda_c(\gamma)$ (however the possible change of the $\lambda_c(\gamma)$ curve due to the inclusion of U is not well-understood). As stressed above, the effective Hamiltonian (14) is not able to reproduce the above mentioned behaviour, which has been studied by means the renormalization group (RG) approach [21].

Also in the dilute limit the phase diagram is very complex, since there are the possibilities of localization transition (self-trapping) and pairing. However the different zones of such a phase diagram can be drawn with precision, at least for a 1D system, by means of a reliable variational approach [15].

While the GS of a 1D system has been well-studied at half-filling [25] less known is the GS away from half-filling where d.c. conductivity should manifest itself and the pairing instability should become also important. However also in this last case some pioneering contribution have appeared [26].

In principle our method allows an investigation of the HHM which retains the effect of the phonon coupling on the parameters of the pure electron model (14) which in turns exhibits also a very rich phase diagram including most of the cited instabilities. We note that, at variance whit the Zheng's approach [25], the p-wave and d-wave superconductor states could be stable in our model. This last phase diagram should approximate very well the exact one in the intermediate region of the parameters.

In the present paper we omit the possibility of lattice symmetry breaking (*i.e.* Peierls instability) which could be introduced in our approach by allowing staggered displacements. At the moment we intend to study specific systems (see the following section) in which the Coulomb repulsion U is comparable or even larger than the phonon coupling (*i.e.*, $U > 4\lambda$) and γ belongs to the intermediate adiabaticity region ($\gamma \sim 1$). Therefore we can reasonably assume that in this region of parameters the lattice symmetry is not removed even for the half-filling case. For instance Zheng [25] has shown, by using mean field approach, that the charge-density wave instability and the related dimerization is suppressed for $U \gtrsim 4\lambda$ in the case of $\gamma = 0.1$ and $\gamma = 1$. Analogous results have been obtained trough the RG approach [21].

It is our intent to avoid further approximations so that we have treated the effective model (14) by means of exact numerical calculations. We stress that this is not an easy task. Even if the GS of the model (14) for a finite cluster can be calculated exactly (at least to the machine precision) by means of a modified Lanczos algorithm, numerous evaluations of the GS energy have to be performed because this quantity has to be minimized with respect to the four parameters f_0, f_1, α and β, at fixed values of λ, γ and U. We have calculated the absolute minimum with a good precision (relative error less that 10^{-5}) by means of a standard quasi-Newtonian code and the number of Lanczos's algorithm calls has been ~ 100. However we have succeeded in dealing with clusters which have a size large enough (12 sites) in order to perform with confidence a finite scaling to infinite system properties.

In the framework of the model Hamiltonian (14), the total energy per site E/N for an infinite system can be well-extrapolated [1] from small cluster calculations since it scales as $1/N^2$ (see Fig. 1). The only prescription to adopt is to work with suitable boundary conditions in order to deal with systems which have a fixed type of shell (preferably open). With respect to the case of fixed

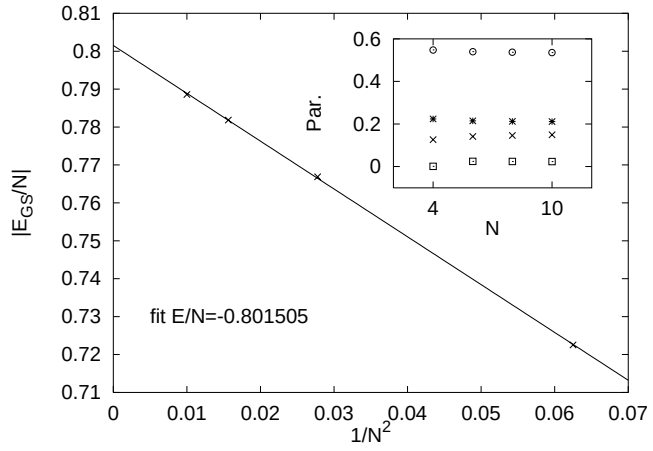

Fig. 1. The absolute value of the energy per site $|E_{GS}/N|$ is reported as a function of $1/N^2$ for the following values of the parameters: $\gamma = 0.4$, $\lambda = 0.4$, $U = 2.0$ in t units. The correspondent values of the variational parameters f_0 (circles), f_1 (stars), α (crosses) and β (squares) are shown in the inset as a function of N.

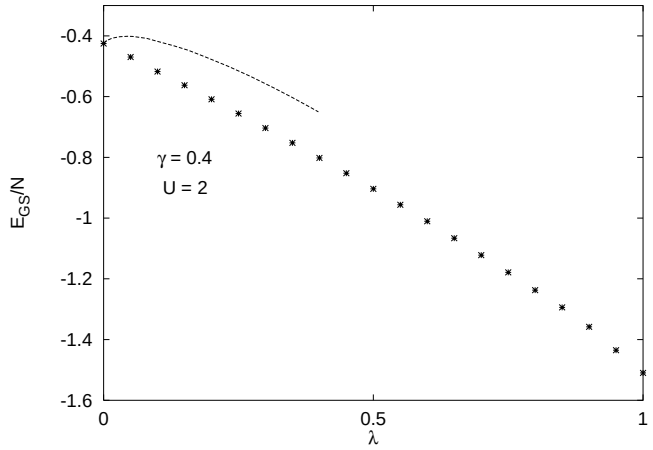

Fig. 2. Comparison between our estimate of the GS energy per site E_{GS}/N (stars) and the one reported by Lo and Sollie in reference [16] (dashes) as a function of λ for $U = 2.0$ and $\gamma = 0.4$ in t units.

parameters we have a further problem since the parameters in the effective model (14) could depend, of course, on the size of the cluster. Fortunately such a dependence is so weak (see the inset in Fig. 1) that the best strategy to adopt is to fix the parameters in (14) from the estimates we get from the largest cluster which we have considered. All the results of this section are relative to an half filled system, while the results of the next section will treat 1/4 filled case.

In Figure 2 we have compared the GS energy per site E_{GS}/N calculated by means of our approach with the same quantity E_{Lo}/N reported in reference [16] for $U = 2$ and $\gamma = 0.4$ as a function of λ. It is worthwhile to note that our variational estimate lies well below E_{Lo}/N. Furthermore unlike to E_{Lo}/N, E_{GS}/N is always lower than $E_{GS}(0)/N$, as we should correctly expect, since the exact GS energy of an interacting electron-phonon system is

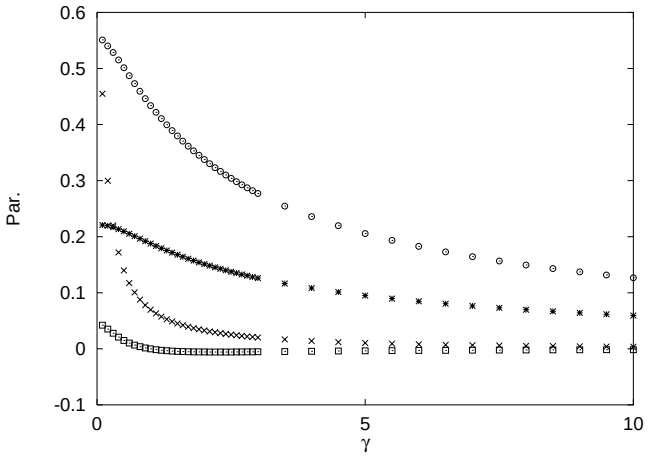

Fig. 3. Dependence on γ of the the variational parameters f_0 (circles), f_1 (stars), α (crosses) and β (squares). Here we consider $U = 1.8$ and $\lambda = 0.5$ in t units.

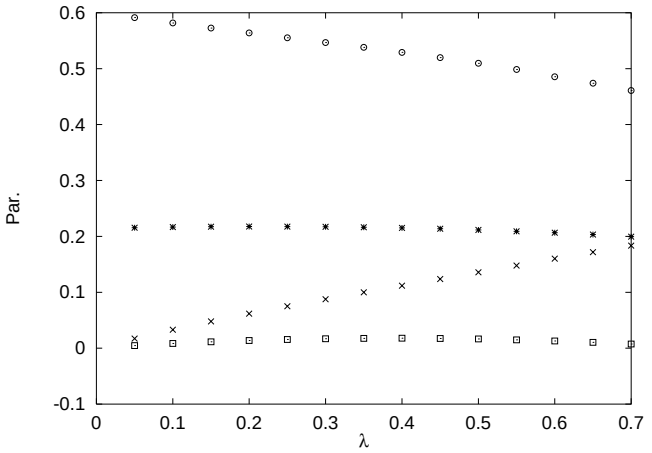

Fig. 4. Dependence on λ of the variational parameters f_0 (circles), f_1 (stars), α (crosses) and β (squares). Here we consider $U = 2.0$ and $\gamma = 0.5$ in t units.

smaller than the sum of the energies of the two independent subsystems [10].

In Figure 3 we report the dependence of the variational parameters on the non adiabaticity parameter γ for the fixed values: $U = 1.8$ and $\lambda = 0.5$. In this figure we have considered very large γ values to show that all the parameters go to zero when $\gamma \to \infty$ so that our approach tends correctly to the results of Lang-Firsov SP theory which are exact in this limit. However for small and intermediate values of γ, which are the physical relevant values, f_1 is not negligible with respect to the other parameters, while β is one order of magnitude smaller than the others. We note also that the possibility to have a gap with a d-wave symmetry is linked to f_1 and not to β.

The decreasing of the correlation extension as γ increases is reasonable if we consider that the relatively high phonon frequencies weakens the retardation effect [10].

An analogous analysis (see Fig. 4) is performed by varying now the electron-phonon coupling parameter λ (for the fixed values: $U = 2.0$ and $\gamma = 0.4$). The dependence of the *intersite parameters* f_1 and β from λ is weaker

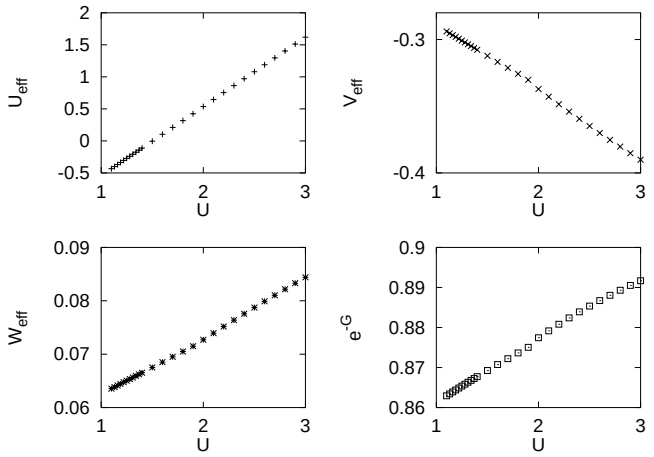

Fig. 5. The parameters of the effective electron Hamiltonian U_{eff}, V_{eff}, W_{eff} and $\exp\{-G\}$ are shown by varying the on-site Coulomb repulsion U for $\gamma = 1.0$ and $\lambda = 0.5$ in t units.

with respect to that present in the case of the *on-site* parameters. On-site squeezing becomes very important for the intermediate λ values as we can expect since the role of anomalous quantum fluctuations becomes relevant in such a regime of coupling. We do not report results of our analysis for greater values of λ since we cannot be sure that our approach is reliable in this regime of coupling since λ is too large with respect to U and a dimerized state could be stable (we note again that an approximate relation for the balance between the two kinds of interaction is $\lambda = U/4$). For very large λ values one needs the inclusion of the lattice symmetry breaking. Work in this direction is in progress.

It is possible to analyze the effect of the Coulomb repulsion increase by looking at the magnitude of the effective parameters U_{eff}, V_{eff}, W_{eff} and $\exp\{-G\}$ as a function of U. It is worthwhile to note that large values of the on-site Coulomb repulsion favour both the intersite phonon mediated correlations and the electron mobility (see Fig. 5). These conclusions are in general agreement with our previous work [15] on the study of a bipolaron in the HHM.

4 Correlation parameters in the Bechgaard salts

As an example of application of our method to real physical systems we will analyze the problem to estimate the correlation parameters in two organic conductors.

They belong to the classes of Bechgaard salts $(TMTSF)_2X$ and $(TMTTF)_2X$ (X = ClO_4^-, PF_6^- *etc.*) which are representative of strong correlated electron systems with essentially one-dimensional character. Concerning the electron properties, they manifest a complex scenario which includes spin instability, high conduction, superconductivity, unusual temperature dependence of resistivity and spin susceptibility. The crystallografic studies on these compounds show a dimerized structure along the stacks of the organic molecules. However the dimerization is not due to a Peierls instability but simply to a modulated static potential induced by the presence of the anion chains [27].

On the basis of such a consideration the kinetic part of a tight-binding model for these materials is

$$\hat{T} = -\, t_1 \sum_{i\ even,\sigma} c^{\dagger}_{i,\sigma} c_{i+1,\sigma} + h.c. \\ -\, t_2 \sum_{i\ odd,\sigma} c^{\dagger}_{i,\sigma} c_{i+1,\sigma} + h.c. \qquad (16)$$

where $t_2 < t_1$ is the hopping parameter for the longer (weaker) bonds. From stochiometeric calculations these systems results to be quarter-filled in terms of holes, therefore in the following we will refer to hole systems.

The role of both the electronic interaction and the dimerization in the Bechgaard salts has been invoked in order to explain the structure of infrared electronic spectra. Therefore it is needed a reliable estimate of correlation parameters in order to obtain a careful description of their unusual electronic properties.

An interesting method to evaluate correlation parameters has been introduced in reference [1]. It is based on the experimental evidence of the reduction of the kinetic energy due to correlations which can be evaluated from optical measurements.

In fact $E_{kin} = \langle GS|\hat{T}|GS\rangle$ (where $|GS\rangle$ is the ground state of the full Hamiltonian for the stacks and $\hat{T}$ is the kinetic energy operator (16)) can be evaluated from the sum of the frequency dependent conductivity [28–30]

$$\int \sigma(\omega) d\omega = \frac{\pi e^2}{2} E_{kin}. \qquad (17)$$

It is worthwhile to stress that E_{kin} and therefore the sum rule (17) depends on the interactions through $|GS\rangle$ (see Ref. [28] for the case of the electron-electron interaction and Ref. [29] for the electron-phonon one). On the other hand the reference kinetic energy E^0_{kin}, the ground state of $\hat{T}$, can be approximatively estimated through the known plasma frequency. Therefore the ratio E_{kin}/E^0_{kin} is an experimentally accessible quantity.

The message of work [1] is that *on the basis of a pure electron model*, in the above mentioned context, it is better to utilize [1] an extended Hubbard model, which includes not only the on-site Coulomb repulsion U, but also a term for the Coulomb repulsion V between nearest-neighbor sites. We will follow this suggestion.

Actually the conductivity spectra seem to be well-described in terms only of the on-site repulsion U [31] so that one can argue that the V values must be small. For this reason we consider also the effects of electron-phonon interaction on the reduction of the kinetic energy. Actually the experimental oscillator strength in Bechgaard salts is measured by integrating the optical absorbtion up to frequencies higher than the phonons frequencies [32] therefore it represents a measure of the total (electronic and phononic) oscillator strength.

However the functional dependence of E_{kin} on the U and V parameters is strongly affected by the choice of the ground state. We believe that the introduction of the electron-phonon interaction gives a better estimate of the curve where the ratio E_{kin}/E^0_{kin} is constant in the $U-V$ plane, and therefore a better estimate of these two parameters. In particular, as we shall see below in our approach we get a small value of V.

In order to analyze the effects of both electron-electron and electron-phonon correlations on the reduction of kinetic energy, we consider the following model, which provides also a reasonable description of the stack dimerization

$$\begin{aligned}\hat{H} = &- t_1 \sum_{i\ even,\sigma} \left\{ c^\dagger_{i,\sigma} c_{i+1,\sigma} + H.c. \right\} \\ &- t_2 \sum_{i\ odd,\sigma} \left\{ c^\dagger_{i,\sigma} c_{i+1,\sigma} + H.c. \right\} + U \sum_i \hat{n}_{i,\uparrow}\hat{n}_{i,\downarrow} \\ &+ V \sum_i \hat{n}_i \hat{n}_{i+1} + \hbar\omega \sum_i b^\dagger_i b_i \\ &+ \chi \sum_{i,\sigma} c^\dagger_{i,\sigma} c_{i,\sigma} (b^\dagger_i + b_i). \end{aligned} \tag{18}$$

We have applied the method which we have introduced in the previous section to study the model (18). In this case we obtain an effective Hamiltonian analogous to that given in equation (14), but with two renormalized hopping parameters $t_1 \exp(-G)$ and $t_2 \exp(-G)$

We have then extracted the correspondent *pure holes effective Hamiltonian* so that the study can follow the line delineated in reference [1] apart of course the minimization procedure of the GS energy with respect to the four parameters which we have introduced. We have also used clusters with two different numbers of sites ($N = 8$ and $N = 12$) to perform finite scaling.

In the calculation we have introduced the total adimensional coupling constant $\lambda = \sum \lambda_n$ (here n runs on the localized intramolecular modes) and the weighted phonon frequency [33] $\omega^{-2} = \sum_n (\lambda_n/\lambda)\omega_n^{-2}$. We have determined λ and ω by using the experimental values of λ_n and ω_n given in reference [27]. We note that these values of λ and ω, reported in Table 1 for the two classes of Bechgaard salts, fall in the zone of intermediate adiabaticity and coupling. For the values of the parameters reported in Table 1 we obtain $\exp(-G) = 0.8764$ in the case of TMTTF and $\exp(-G) = 0.9348$ in the case of TMTSF.

In Figure 6 we have reported our results for the two quoted compounds in the $U-V$ plane which give the experimental values of the reduction ratio of kinetic energy. In the inset we have reported the same curves as derived in reference [1]. Our results show the relevance to include the electron-phonon interaction and that a physically reasonable value of U/t_1 can be obtained in the $V \to 0$ limit. Moreover if we repeat the same semiquantitative analysis presented in reference [1], based on the further constraints $U(TMTTF)/U(TMTSF) \sim 1.0-1.5$ and $V(TMTTF) \sim V(TMTSF)$, we find V/t_1 less than unity for both the two compounds (see Tab. 1).

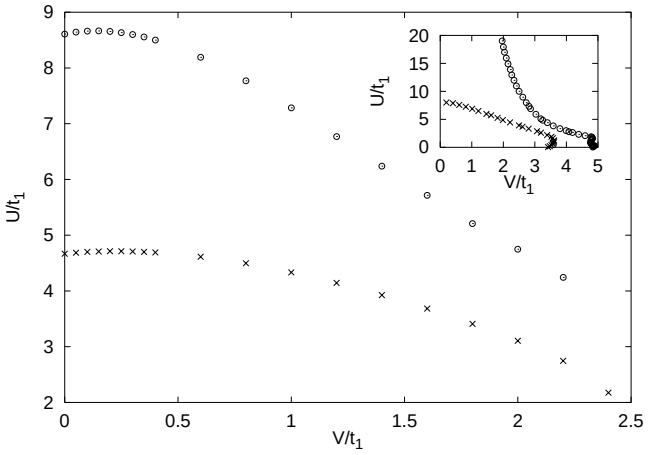

Fig. 6. Here are depicted the points of the plane U/t_1-V/t_1 for which we obtain the experimental value of the kinetic energy reduction ratio E_{kin}/E^0_{kin} for $(TMTTF)_2PF_6$ (circles) and $(TMTSF)_2ClO_4$ (crosses). In the inset there is the Figure 5 of reference [1], which reports the same quantities calculated in a pure electron model.

5 Summary and discussion

This work has been devoted to the introduction of a method which combines a variational approach with an exact finite clusters calculation. This method has been applied to the study of strong correlated many electron systems in the framework of a model which includes both the Holstein electron-phonon interaction and the extended Hubbard electron-electron interaction. The method generalizes previous developed approaches based on squeezed states by considering retardation effects. These effects, for the regime of the parameters of interest, extend the phonon mediated interactions to the first and the second neighbors. The effective electron model which we obtain has been treated exactly so that only the phonon vacuum has been approximated by using trial wave functions.

In the case of the HHM model we argue that this method should be very accurate in the regime of intermediate adiabaticity and coupling. This issue has been confirmed by the comparison between our variational results of the energy and the one obtained without considering retardation effects. Moreover our estimate of the GS energy has a correct behavior in the small coupling regime.

We have analyzed the dependence of the variational variables on the parameters of the model and we have observed how they reasonably approach the small-polaron estimates for large values of the non-adiabaticity. In the case of large U ($U/t > 4\lambda$) our calculation shows the importance of intersite effective attraction.

The second part of this work has been devoted to the study of a modified version of the HHM which is suitable to study the 1D stacks of two Bechgaard salts by considering dimerization and intersite Coulomb repulsion. We note again that the parameters of the electron-phonon coupling for these materials fall in the intermediate adiabatic regime. We recall that in this regime only intramolecular phonons are considered since acoustic phonons in the

Table 1. Parameters in t_1 units for the two Bechgaard salts $(TMTTF)_2PF_6$ and $(TMTSF)_2ClO_4$. Here we report both our estimate of the correlation parameters U_{our}, V_{our} and that of reference [1] U_{Mila}, V_{Mila}. The values of λ and γ have been determined by using the phonons frequencies given in reference [25].

compound	t_2	λ	γ	E_{kin}/E^0_{kin}	U_{Mila}	V_{Mila}	U_{our}	V_{our}
TMTTF	0.7	0.41	0.34	0.73	7.0	2.8	8.0	< 0.6
TMTSF	0.9	0.25	0.37	0.85	5.0	2.0	4.6	< 0.4

Bechgaard salts have a Debye energy less than 100 K and are related to the strongly adiabatic case. The correlation parameters for the two compounds have been estimated by following a method introduced by Mila in reference [1]. The main conclusion of our analysis is that the introduction of the electron-phonon interaction allows to assert that the intersite repulsion is small with respect to the on-site one. This result is in accordance with the recent calculations of the optical conductivity of $(TMTSF)_2PF_6$, in the infrared range. In this case the experimental data are well-described in terms only of a simple Hubbard model [31].

Furthermore the introduction of the electron-phonon interaction allows to obtain the reduction of the kinetic energy, even for small V values, without to invoke excessively large U values.

We note that we have included only nearest-neighbour Coulomb interaction V and the second neighbours interaction could be of some relevance. However including long-range repulsion is somehow arbitrary because one does not know exactly how screening will act in such systems.

The values of the on-site parameter U which we have extracted from our analysis are in general agreement with the properties of the two materials at zero pressure. In fact $(TMTSF)_2ClO_4$ has a metallic behavior at room temperature and the intermediate value of the Coulomb repulsion which we have estimated ($U = 4.6t_1$) is compatible with this behavior. Moreover Fevand and Mila [31] have widely studied, in the framework of a dimerized Hubbard model, the optical conductivity in $(TMTSF)_2PF_6$ by analyzing the effects of the intermediate on-site repulsion $U = 5t_1$ on the charge gap. The larger value $U = 8t_1$ which we have found for $(TMTTF)_2PF_6$ could justify the semimetallic behavior at room temperature and the SDW transition at the lower temperature. We recall also that a spin-Peierls transition at $T_{SP} \sim 19$ K have been observed [8] for this compound.

The physical properties of Bechgaard salts are very sensitive to the pressure. In particular the SDW is no more stable in the compounds of the TMTTF family under high pressures and a metallic state is stable for pressures greater than 25 kbar [34]. We could consider the pressure effects in our calculation by following the scheme previously introduced by one of us and co-workers [5] in the framework of extended Hubbard model.

The members of TMTSF family are organic superconductors with low $T_c \sim 1$ K. For $(TMTSF)_2ClO_4$ the superconductor state is stable at atmospheric pressure while $(TMTSF)_2PF_6$ is a superconductor [2] under pressures greater than 9.5 kbar. Our calculation shows that the intersite phonon mediated attraction (see Eq. (12)) results to be $V_0 \simeq -0.2t_1$ while the estimated upper bound for the intersite repulsion in these compounds is $V \simeq 0.4t_1$ (see Tab. 1). Therefore, according to our calculations, there is the possibility of a net attraction between particles in the nearest neighbor sites $V_{eff} = (V_0 + V) < 0$. Moreover the pressure could affect significantly the balance between these two terms allowing a transition from a net repulsion to a net attraction. There is also an indirect experimental evidence of non-isotropic superconductivity in the TMTSF family [35], even if, to our knowledge, there are not direct measures of the dependence of the gap on the momentum for these compounds. These considerations could support the hypothesis of a phonon mediated mechanism for the superconductivity in the TMTSF family which is critically driven by the value of V_{eff} at atmospheric pressure and by its variation with pressure.

We must caution to obtain stringent conclusion from the reported discussion. Rigorous results [36] of the low energy 1D continuum theory indicate that for an attractive V_{eff} which is smaller in amplitude than the repulsive local U, superconducting correlations are absent. Actually we have considered the discrete high energy case, but we cannot exclude that superconductivity in these compounds is due to some effects which we have not considered in the present case.

Finally we note that availability of very accurate measurements of reflectivity on single crystals suggest to extend the present work to the dependence on frequency of the conductivity.

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