Exact ground-state behavior of a four-atom generalized Hubbard model

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(Received 4 May 1981)

The exact ground state of a four-atom system described by the generalized form of the Hubbard Hamiltonian is obtained. Next, the solution is used to extract relevant physical information on the dynamics of the cluster states and also to check on the applicability and validity of approximations commonly invoked in the treatment of Hubbard-type models.

I. INTRODUCTION

The study of quasi-one-dimensional systems of the tetrathiafulvane-tetracyanoquinodimethane (TTF-TCNQ) type has received a great deal of attention, both by experimentalists[1–4] and theorists,[5–8] during the last decade mainly because of their remarkable electric conductivity. The model due to Hubbard,[9,10] originally intended to describe narrow-band metallic magnetism, has proved to be useful in the quest to understand the physical properties of these quasilinear organic substances. However, long-range Coulomb interactions seem to play an important role in relation to the magnetic susceptibility[11–13] and anomalies of the phonon spectrum[14] of these quasi-1D systems, which led to the introduction of a generalized version[11–13] of Hubbard's model (GHM), which incorporates Coulomb repulsion between neighbors.

While an exact solution for the ground state (GS) of the original Hubbard model[9] is available[15,16] for the 1D case, the only procedure known at present to obtain exact results for the GHM is to restrict oneself to investigating small clusters of atoms.

Work along this line has been carried out by Falicov and Harris,[17] and by Visscher and Falicov.[18] The first studied a two-electron homopolar molecule and tested it for spin- and charge-density waves; the latter considered the Pariser-Parr model[19] Hamiltonian, which is slightly more general than the GHM, found exact solutions for benzene and used them to determine correlation functions, oscillator strengths, and transition probabilities.

In this contribution we obtain an exact solution for the GS of a GHM four-atom system; this solution is then used to evaluate relevant physical parameters of the system, which provide interesting information on the dynamics of the cluster states. Finally, our exact results are employed to check on the accuracy of approximations commonly invoked[20,21] in dealing with Hubbard-type models.

II. MODEL AND GROUP-THEORY TREATMENT

The system we consider consists of four atoms located on the vertices of a square and is described by the Hamiltonian

$$H=\sum_{j=1}^{4}\sum_{\sigma}\left[-t(c_{j\sigma}^{\dagger}c_{j+1,\sigma}+c_{j+1,\sigma}^{\dagger}c_{j\sigma})+\frac{I}{2}\hat{n}_{j\sigma}\hat{n}_{j,-\sigma}+V\sum_{\sigma'}\hat{n}_{j\sigma}\hat{n}_{j+1,\sigma'}\right], \tag{1}$$

where $c_{j\sigma}^{\dagger}$ ($c_{j\sigma}$) is the creation (destruction) operator of a Wannier state associated with atom j and with spin σ, $\hat{n}_{j\sigma}=c_{j\sigma}^{\dagger}c_{j\sigma}$, t is the hopping matrix element between states on nearest-neighbor atoms, and I and V are the strengths of the intra- and interatomic Coulomb repulsions, respectively.

In this contribution we focus our interest on the important special case of only one electron per atom (i.e., we restrict our attention to a four-electron system). Having thus excluded orbital degeneracy, we are left with two allowed single-electron states per atom and consequently with

$$\binom{8}{4}=70$$

linearly independent many-electron states for the whole system. But, since the Hamiltonian H of Eq. (1) is invariant under the operations of its symmetry group $G(H)$, the 70D (dimensional) associated Hilbert space can be decomposed into a direct sum of subspaces of irreducible representations of $G(H)$, with the consequent drastic simplification in the treatment. For the case under consideration $G(H)=C_{4v}\otimes S_4$ (in the notation of Ref. 22); the group

TABLE I. Dimensionality of the Hamiltonian block matrices $H^{(\Gamma)}$ of Eq. (2). $\Gamma=(P,S)$ labels the irreducible representations of $C_{4v}\otimes S_4$, $P=A_1,A_2,B_1,B_2,E$, and $S=0,1,2$. The degeneracy of each irreducible representation is the number enclosed in parentheses.

C_{4v} / S_4	$A_1(1)$	$A_2(1)$	$B_1(1)$	$B_2(1)$	$E(2)$
$S=0(1)$	5	1	3	3	4
$S=1(3)$	1	3	2	1	4
$S=2(5)$	0	0	1	0	0

C_{4v} is formed by the eight operations which leave a square invariant, while S_4 is the permutation group of electron coordinates. The irreducible representations of S_4 are labeled by the three different values the total spin S can take, i.e., $S=0$, 1, and 2.

We use the notation[22]

$$\langle\Lambda,i,\lambda|H|\Gamma,j,\gamma\rangle=\delta_{\Gamma\Lambda}\delta_{ij}H^{(\Gamma)}_{\lambda\gamma} \quad , \tag{2}$$

where $|\Gamma,j,\gamma\rangle$ is the Hilbert-space-basis vector which transforms according to the jth row of the irreducible representation labeled by Γ. Finally, γ is an enumeration index whose range is the dimensionality of the Hamiltonian block matrices $H^{(\Gamma)}$.

Because of the low dimensionality of the latter (see Table I) it is possible to obtain most of the relevant physical information analytically; in this way we found that the GS energy of the system corresponds[23] to

$$\{B_1,S=0\}, \quad \text{for } I>2V \tag{3a}$$

$$\{A_1,S=0\}, \quad \text{for } I<2V \quad . \tag{3b}$$

These results are valid for all values of t and both states have the same energy eigenvalue for $I=2V$.

III. DYNAMICS OF THE SYSTEM

In order to understand the behavior of the system in its GS not only kinematically, but also dynamically, we evaluate the following physical parameters:

$$\alpha\equiv\langle\hat{n}_{j+}\hat{n}_{j-}\rangle \quad , \tag{4a}$$

$$\gamma\equiv\langle\hat{q}_j\hat{q}_{j+1}\rangle \quad , \tag{4b}$$

$$\mu\equiv\langle\hat{m}_j\hat{m}_{j+1}\rangle \quad , \tag{4c}$$

$$\tau\equiv\langle c^{\dagger}_{j\sigma}c_{j+1,\sigma}\rangle \quad , \tag{4d}$$

where $\hat{m}_j=\hat{n}_{j+}-\hat{n}_{j-}$ is the local z-direction magnetization operator at site j and $\hat{q}_j=\hat{n}_{j+}+\hat{n}_{j-}$ is the corresponding charge operator. The parameter α gives the double occupancy probability or intra-atomic correlation at site j, while γ and μ describe the charge and magnetic moment correlations between neighboring sites. Finally, τ parametrizes the degree of hybridization between localized Wannier states; thus its magnitude reflects the delocalization of the electron states and is related to the reduction in total kinetic energy associated with electron hybridization.

An important feature of the above-defined parameters is that they are independent of site and spin indices, due to the form of the irreducible representations given in Eqs. (3a) and (3b).

It is useful at this point to exhibit explicitly some features of the GS state vectors of the system; introducing the notation

$$(c^{\dagger}_{1\sigma},c^{\dagger}_{2\sigma},c^{\dagger}_{3\sigma},c^{\dagger}_{4\sigma})\equiv(A^{\dagger}_{\sigma},B^{\dagger}_{\sigma},C^{\dagger}_{\sigma},D^{\dagger}_{\sigma}) \quad ,$$

$\sigma=(+,-)$, and $|0\rangle$ for the vacuum state, we have

$$|\psi^{\Gamma}_{GS}\rangle=\hat{P}_{\Gamma}(k_1A^{\dagger}_{\uparrow}B^{\dagger}_{\uparrow}C^{\dagger}_{\downarrow}D^{\dagger}_{\downarrow}+k_2A^{\dagger}_{\uparrow}A^{\dagger}_{\downarrow}B^{\dagger}_{\uparrow}C^{\dagger}_{\downarrow}+k_3A^{\dagger}_{\uparrow}A^{\dagger}_{\downarrow}B^{\dagger}_{\uparrow}B^{\dagger}_{\downarrow}+k_4A^{\dagger}_{\uparrow}A^{\dagger}_{\downarrow}C^{\dagger}_{\uparrow}C^{\dagger}_{\downarrow})|0\rangle \quad , \tag{5}$$

where the k_i's are real coefficients and $\hat{P}_{\Gamma}$ is the projection operator on the irreducible representation labeled by Γ. In the $t=0$ limit all k_i's vanish except k_4 for $\Gamma=\{A_1,S=0\}$ (i.e., when $I<2V$), and k_1 for $\Gamma=\{B_1,S=0\}$ (i.e., $I>2V$); thus, in this limit

$$|\psi^{A_1,S=0}_{GS}\rangle=\frac{1}{\sqrt{2}}(A^{\dagger}_{\uparrow}A^{\dagger}_{\downarrow}C^{\dagger}_{\uparrow}C^{\dagger}_{\downarrow}+B^{\dagger}_{\uparrow}B^{\dagger}_{\downarrow}D^{\dagger}_{\uparrow}D^{\dagger}_{\downarrow})|0\rangle \quad , \tag{6a}$$

$$|\psi^{B_1,S=0}_{GS}\rangle=\frac{1}{\sqrt{3}}[A^{\dagger}_{\uparrow}B^{\dagger}_{\downarrow}C^{\dagger}_{\uparrow}D^{\dagger}_{\downarrow}+A^{\dagger}_{\downarrow}B^{\dagger}_{\uparrow}C^{\dagger}_{\downarrow}D^{\dagger}_{\uparrow}-\tfrac{1}{2}(A^{\dagger}_{\uparrow}B^{\dagger}_{\downarrow}C^{\dagger}_{\downarrow}D^{\dagger}_{\uparrow}+A^{\dagger}_{\downarrow}B^{\dagger}_{\uparrow}C^{\dagger}_{\uparrow}D^{\dagger}_{\downarrow}+A^{\dagger}_{\downarrow}B^{\dagger}_{\downarrow}C^{\dagger}_{\uparrow}D^{\dagger}_{\uparrow}+A^{\dagger}_{\downarrow}B^{\dagger}_{\uparrow}C^{\dagger}_{\downarrow}D^{\dagger}_{\downarrow})]|0\rangle \quad . \tag{6b}$$

Consequently, in the localized $t=0$ limit two cases can be distinguished: (i) For $I>2V$ the GS energy is $4V$ and the wave function is of Heitler-London type, with no double-electronic occupancy at any atomic site (i.e., $\alpha=0$, $\gamma=1$), and (ii) for $I<2V$ the GS energy is $2I$ and the electronic configuration consists of two doubly-occupied non-neighboring sites, thus originating a charge-density wave (CDW) characterized by $\alpha=0.5$, $\gamma=0$. In the first $I>2V$ case, as $|t|$ becomes nonzero, i.e., $0<|t|\ll I$, the 2^4 or 16 Heitler-London states become nondegenerate through weak hybridization, which brings about some delocalization and a reduction of the total kinetic energy of the system.

The magnitude of the delocalization is strongly influenced by the spatial spin configuration of the system and consequently by the values of μ, since the Pauli principle allows hopping only between neighbors in opposite spin states. In effect, electron transfer is blocked in the $\{B_1,S=2\}$ states, for which $\mu=+1$, while it is an important feature of the $A^{\dagger}_{\uparrow}B^{\dagger}_{\downarrow}C^{\dagger}_{\uparrow}D^{\dagger}_{\downarrow}|0\rangle$ configuration, contained in Eq. (6b) and usually referred to as a spin-density wave (SDW) and which has $\mu=-1$. In consequence, large magnetic correlation ($\mu\lesssim 1$) implies strong localization while the tendency to form a SDW is associated with some degree of delocalization of the Wannier states.

It is also interesting to point out that in the limit $|t|\ll 2V<I$ the Heisenberg Hamiltonian is related to that of Eq. (1) by means of a unitary transformation; in fact[24]

$$H\rightarrow\frac{4t^2}{I-V}\sum_j \vec{S}_j\cdot\vec{S}_{j+1}\ , \tag{7}$$

where $\vec{S}_j$ is the total spin operator associated with site j and which was defined after Eq. (4). We also notice that the denominator $(I-V)$ is precisely the energy required to excite the system from a Heitler-London GS to a configuration with one electron-hole pair on neighboring sites; since a CDW consists in periodically repeating such an electron-hole structure, this type of excitation plays the role of a seed for a CDW.

We now turn our attention to the more general case of arbitrary t values, for which the results are displayed in Figs. 1–5. Again we distinguish two regimes: $I>2V$ and $I<2V$, keeping in mind that Eqs. (3a) and (3b) are valid for all t. (i) In the $I>2V$ case the GS belongs to the irreducible representation $\Gamma=\{B_1,S=0\}$. As $|t|/I$ grows from zero to infinity the parameters α, μ, γ, and τ vary monotonically between $[0,\frac{3}{16}]$, $[-\frac{2}{3},-\frac{3}{8}]$, $[1,\frac{7}{8}]$, and $[0,\frac{1}{4}]$, respectively, as can be observed in Fig. 1. Qualitatively, these results are analogous with those obtained[20,21] in the unrestricted Hartree-Fock approximation (UHF) for an infinite system ($N\rightarrow\infty$). However, in order to make the comparison more significant, we have included in Fig. 1 the UHF results for $N=4$. There are two surprising features of Fig. 1: (a) The values of α obtained exactly and within UHF tend to different limiting values in the absence of particle correlations (i.e., as $|t|/I\rightarrow\infty$); in fact, UHF yields $\alpha=\langle\hat{n}_{j+}\rangle\langle\hat{n}_{j-}\rangle=\frac{1}{4}$, while the exact limit is $\alpha=\frac{3}{16}$. This discrepancy originates in the fact that the noninteracting ($I=V=0$) four-electron system is sixfold degenerate; this degeneracy is removed by arbitrarily small values of I or V and a well-defined nondegenerate GS emerges; nevertheless, UHF fails to yield such a GS correctly. However, for $N\gg 1$ the physical consequences of an eventual degeneracy become irrelevant. (b) As $|t|/I\rightarrow 0$ we obtain $\mu=-\frac{2}{3}$ and -1 for the exact and UHF solutions, respectively; this discrepancy is due to the loss of spin isotropy of the UHF solution.

A more relevant magnitude to characterize first-neighbor spin correlations is $\langle\vec{S}_i\cdot\vec{S}_{i+1}\rangle$, which tends to

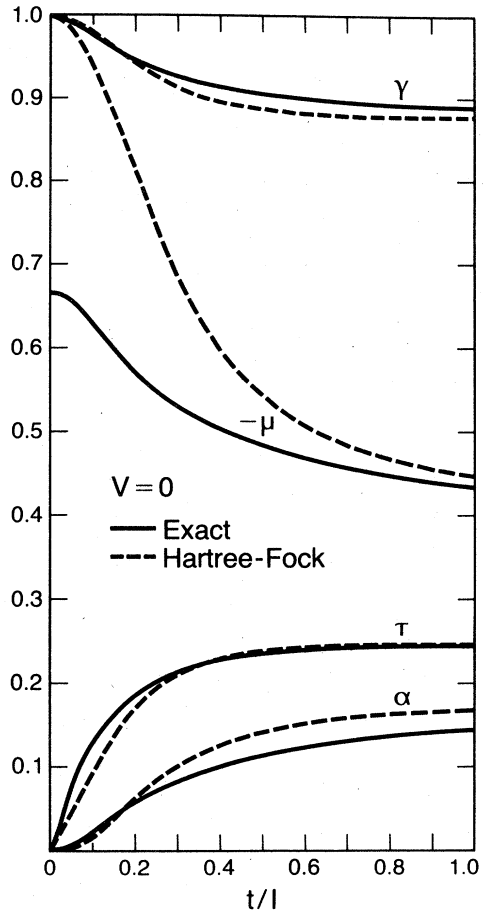

FIG. 1. Exact and Hartree-Fock values of the parameters α, γ, μ, and τ as function of t/I, illustrate their behavior in the $V<2I$ regime.

$-\frac{1}{2}$ and $-\frac{1}{4}$ for the exact and UHF solutions, respectively. (ii) The second case, namely, $I < 2V$ has a GS belonging to the $\{A_1, S=0\}$ irreducible representation; as $|t|/I$ grows from zero to infinity α, μ, γ, and τ vary monotonically in the intervals $[\frac{1}{2}, \frac{5}{16}]$, $[0, -\frac{1}{8}]$, $[0, \frac{5}{8}]$, and $[0, \frac{1}{4}]$, respectively, as displayed in Fig. 2. For $|t|/I \ll 1$ the exact and UHF results are in perfect agreement, while for $|t|/I \to \infty$ UHF yields $\frac{1}{4}$, $-\frac{1}{8}$, $\frac{7}{8}$, and $\frac{1}{4}$ for α, μ, γ, and τ, respectively. Again we understand that the small discrepancy in the asymptotic values of α and γ are due to degeneracy effects.

In spite of these small differences between UHF and the exact solution, both emphasize the fact that the system undergoes an important qualitative change for $I = 2V$, which is akin to a phase transition. In effect, for $I > 2V$ the $\{B_1, S=0\}$ irreducible representation implies some sort of short-range order characterized by the values $\alpha < \alpha_{\text{unc}} = \frac{1}{4}$, $\gamma > \gamma_{\text{unc}} = \frac{7}{8}$, $\mu < \mu_{\text{unc}} = -\frac{1}{8}$, where the subscript unc stands for uncorrelated; this short-range order is closely related to a SDW, but it occurs without symmetry breaking (i.e., the values of the parameters are site-index independent) in contrast with UHF. For $I < 2V$ on the contrary $\alpha > \alpha_{\text{unc}}$, $\gamma < \gamma_{\text{unc}}$, and $\mu > \mu_{\text{unc}}$, thus giving rise to a CDW of similar site-independent character as the SDW mentioned above. The results shown in Fig. 3 further underline the fact that UHF is well suited to tackle this problem, because of the close approximation it yields to the exact values of the GS energy.

The behavior of the delocalization parameter τ provides additional information of interest; in Fig. 4 a plot of τ vs V/I, for a fixed value of t/I is given. We observe that large values of either the intra- or interatomic repulsion parameters V and I tend to favor localization; however, τ has a sharp maximum for $I = 2V$ indicating that I and V have compensating actions just at the transition point.

On the basis of the above results we notice that if t is small and $I > 2V$, the dynamics of the system is fundamentally governed by the intra-atomic correlation parameter α, which implies that the approximation suggested by Gutzwiller[25] should work successfully. This approximation consists in assuming the

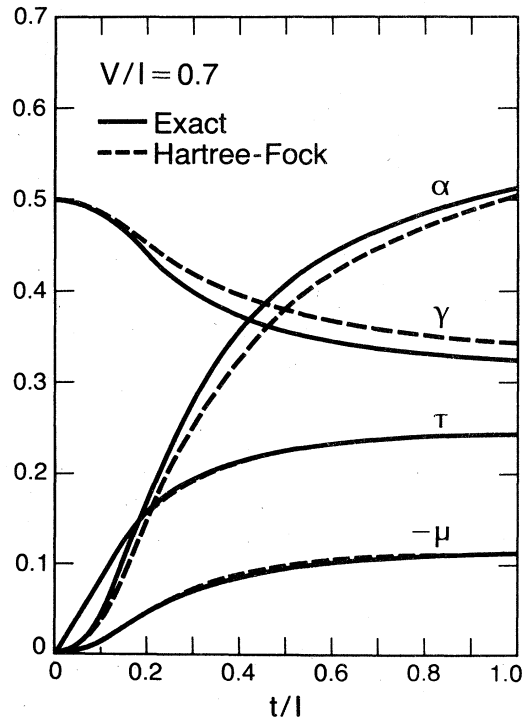

FIG. 2. Exact and Hartree-Fock values of the parameters α, γ, μ, and τ vs t/I, for the $V > 2I$ case.

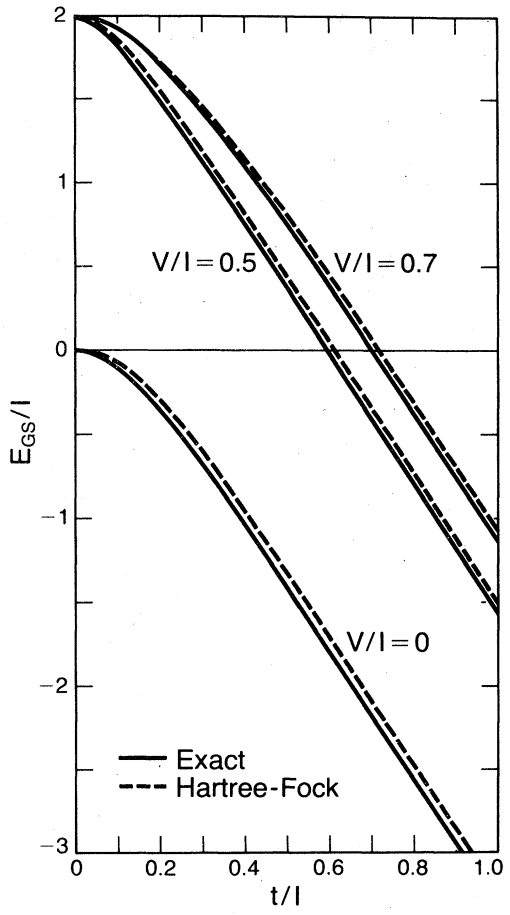

FIG. 3. Exact and Hartree-Fock results of the ground-state energy vs t, for values of V smaller ($V=0$), equal ($V=0.5$), and larger ($V=0.7$) than the critical value, with all energies measured in units of I.

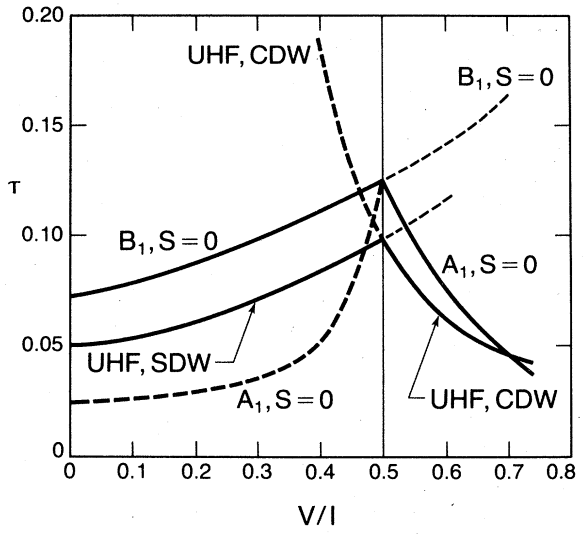

FIG. 4. Plot of the degree of hybridization τ vs V/I evaluated both exactly, using the $\{B_1,\ S=0\}$ and $\{A_1,\ S=0\}$ eigenstates, and in the unrestricted Hartree-Fock (UHF) approximation.

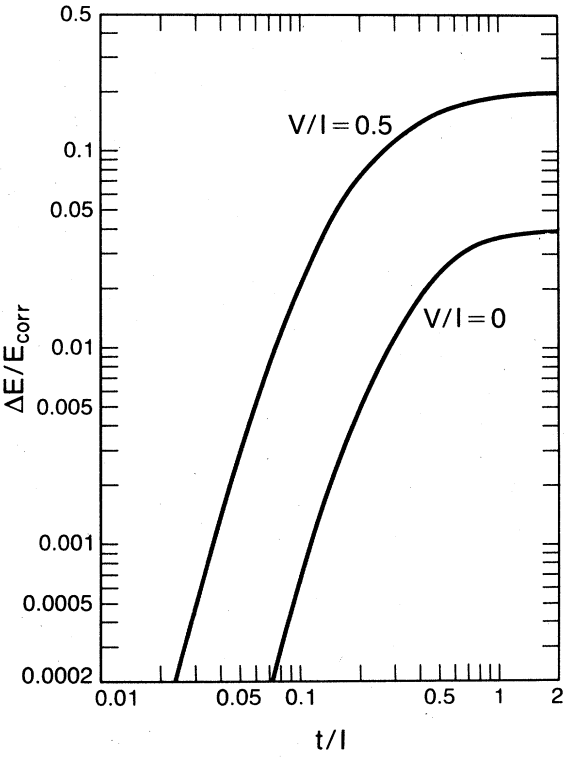

FIG. 5. Values of $\Delta E/E_{\rm corr}$, where $\Delta E \equiv E$ (Gutzwiller) $-E$ (exact), and $E_{\rm corr}$ is the *correlation* energy, as a function of t/I.

wave function

$$|\psi_\lambda^G\rangle = \prod_{l=1}^{N}[1-(1-\lambda)\hat{n}_{l\uparrow}\hat{n}_{l\downarrow}]|\psi\rangle \ , \tag{8}$$

where λ is a parameter between 0 and 1, to be determined variationally, and $|\psi\rangle$ is the state constructed as a product of the four Bloch states with lowest-lying energy eigenvalues.

The numerical results obtained using Gutzwiller's scheme, as displayed in Fig. 5, show that his method is reliable when intra-atomic correlation is the dominant factor. Further improvements could be attained, without much additional effort, by implementing the refined version of the procedure proposed by Stollhoff and Fulde.[26]

IV. DISCUSSION AND CONCLUSION

The study of a four-atom system, described by a generalized Hubbard Hamiltonian, which we have carried out above (1) yields useful information in relation to some physical properties of an infinite system of the same nature; and (2) it allows us to check on the validity of approximations usually employed in the treatment of macroscopic systems.

Regarding the properties of infinite systems ($N \to \infty$), it is apparent that the $N=4$ case contains in a qualitatively correct way most of the relevant ground-state properties. Quantitative disagreement, which is small indeed, can partially be traced to effects directly related to the correlation between degenerate states in the four atom system, which become totally irrelevant in the $N \to \infty$ limit.

As far as checking on approximate methods is concerned, we have been able to determine quantitatively the accuracy with which the ground-state energies and other relevant physical parameters are calculated, in the unrestricted Hartree-Fock (UHF) and in the Gutzwiller approximations, finding that they yield very good results in their realm of applicability.

Moreover, we have established that our four-atom system shows a spin-density wave ($I > 2V$), or charge density wave ($I < 2V$), ground state with a sharp transition between the two regimes at $I = 2V$ in agreement with previous UHF results.[20]

Finally, we mention that finite-temperature properties of this system may be worth investigating.

ACKNOWLEDGMENTS

We are grateful to Professor Leo M. Falicov for critical reading of the manuscript and enlightening comments. We also thank Professor Sergio Rodríguez and Dr. Béla Joós for clarifying discussions. One of us (M.K.) wishes to thank the warm hospitality of the Faculty of Sciences of the Universidad de Chile. This work was supported in part by National Science Foundation Grant No. DMR78-03408.

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