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Two-electron self-consistent-field study of $2k_F$ broken-symmetry states in correlated monatomic and diatomic Peierls-Hubbard chains

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The two-electron self-consistent-field (SCF2) approach in which the wave function is constructed from spin-unrestricted geminals (UG's) optimized variationally is developed. It combines restricted-geminal (RG)-SCF2 and unrestricted Hartree-Fock methods, thus accounting for both short-range (intrapair) and long-range electron correlations. On this basis ground-state properties of the extended half-filled Peierls-Hubbard chains are calculated in a wide range of site-energy modulation α and on-site electron-electron repulsion U. Treating a generalized-Peierls transition in slight-to-strong correlation regimes within the same framework, the electronic-Peierls and spin-Peierls transition areas can be conventionally differentiated by bifurcation points in which UG-SCF2 solutions separate from RG solutions. The corresponding phase diagram in the U-α plane is obtained. For the monatomic ($\alpha = 0$) chain, the predicted dimerization amplitude is in a good agreement with the earlier Peierls and spin-Peierls calculations. For the diatomic strongly correlated chain, dimerization sharply rises with α at the bifurcation point α_0 and then rapidly drops near $\alpha = U/2$; a property that can be related to phase transitions in some donor-acceptor molecular crystals.

I. INTRODUCTION

The wide variety of remarkable physical properties and phenomena in the class of materials with low-dimensional structure comprised of conjugated polymers, metal-halide chains, and donor-acceptor molecular crystals stimulates intensive theoretical investigations of them. It has long been recognized that a satisfactory description of many-body interactions in low-dimensional systems must include both electron-phonon (*e*-ph) and electron-electron (*e*-*e*) contributions. They lead to a variety of $2k_F$ instabilities involving Peierls (bond-order-wave, BOW), charge-density-wave (CDW), and spin-density-wave (SDW) instabilities resulting in broken-symmetry states. The Hubbard model with occasional long-range terms is believed to be a reliable basis for treating the effects of *e*-*e* interactions. However, their investigation is much complicated due to the inadequacy of the simple mean-field approximations for predicting the electronic and lattice properties of these systems. Even the unrestricted Hartree-Fock (UHF) method, which correctly represents electron correlations in the atomic limit, proves to be insufficient. In particular, $2k_F$ instabilities of different types in one-dimensional (1D) systems turn out to be competing, thus shrinking or collapsing the area of existence of the combined instabilities,[1,2] such as SDW-BOW predicted in the strong-correlation regime by the spin-Peierls approach.

A number of different techniques developed for the exact or approximate calculations of correlated many-electron systems,[3] mainly the resonating valence band (RVB) approach, Gutzwiller ansatz, Monte Carlo approach, spin-Hamiltonian method, perturbation, and variational techniques have been applied to the Hubbard systems, yielding a considerable body of evidence for their properties. Nevertheless, the exact or high-accuracy calculations of extended correlated systems remain much too complicated even with up-to-date computation facilities. Meanwhile, for investigations of the sophisticated models of explicitly interacting chains or considerations of clusters with the size sufficient to represent two-dimensional lattice structures, as well as for dynamics studies of correlated systems, simpler approaches, suitable for systems with several dozens of sites, are very desirable.

As it is concluded in Refs. 4 and 5 on the ground of the exact numerical valence-bond (VB) and Monte Carlo calculations of small rings, the ordinary Peierls (noninteracting electrons) and the spin Pieierls (Heisenberg antiferromagnetic model), the concepts derived from perturbation theory, can be considered as limiting cases of "generalized Peierls transition" encompassing these limits. Moreover, the analysis of the ground state in terms of VB resonating structures[4] shows that on-site *e*-*e* interactions represented by the Hubbard parameter U give rise to a barrier to resonance, thus becoming the driving force of dimerization. This finding suggests a possibility for an adequate approximate description of the dimerized ground state with the use of a simple wave function constructed self-consistently from correlated electron pairs and corresponding to a single Kekulé structure.

In this way, to go beyond Hartree-Fock approximation, the two-electron self-consistent-field (SCF2) method has been implemented.[6,7] The SCF2 wave function defined variationally as the best antisymmetrized product of strongly orthogonal two-electron functions (geminals) is exact in the opposite limits of noninteracting and strongly correlated electrons. The SCF2 method is size consistent, yielding exact results for noninteracting dimers. Besides, the optimization with respect to lattice variables can be easily included in a general SCF procedure. Applying the SCF2 approach presented in Refs. 6 and 7, the Peierls-Hubbard models for the extended chains have been considered, both for the monatomic[6,7] and diatomic[8] cases, thus resulting in correct predictions for the ground-state properties and soliton excitations within a wide parameter range.

One obvious drawback of the SCF2 method is that the wave function constructed from the spin-restricted (singlet) geminals (RG) overestimates the intrapair electron correlations whereas the interpair antiferromagnetic ones are neglected. To overcome this difficulty we developed a new SCF2 technique in which spin-unrestricted, nonsinglet, geminals (UG) are admitted, as suggested in Ref. 9. The UG-SCF2 method combines two approaches to account for electron correlations, reducing to RG-SCF2 and UHF methods as partial cases.

In this paper we present UG-SCF2 calculations for monatomic and diatomic Peierls-Hubbard chains. Although the UG-SCF2 technique is applicable to many-electron models of arbitrary structure and parametrization, the simple monatomic case considered here, due to availability of the well-established results of other calculations, presents a good basis to test the new approach in different correlation regimes. We put more emphasis on the large-U area in which the antiferromagnetic correlations are of prime importance. For less studied diatomic systems, a new feature, to our knowledge, is obtained. Namely, the UG-SCF2 calculations performed in the strong-correlation regime, which is characteristic of quasi-one-dimensional donor-acceptor crystals, show distinct interface between Peierls and spin-Peierls areas that could be related to a phase transition of some quasi-ionic crystals from regular to dimerized form.

The paper is organized as follows. In Sec. II the model Hamiltonian is specified and the UG-SCF2 method is outlined with reference to the Hubbard model under consideration. Numerical results are reported in Sec. III and discussed in Sec. IV. The concluding Sec. V outlines the further possible developments and applications of SCF2 technique. The derivation of the UG-SCF2 energy expression for the general model is sketched in the Appendix.

II. MODEL AND METHOD

The considered model of a diatomic polymer $(AB)_x$ is defined by the Peierls-Hubbard Hamiltonian which describes the chain involving N sites of two kinds, A for odd and B for even sites, with N electrons that interact adiabatically with the lattice,

$$H = \sum_{m\sigma} e_m n_{m\sigma} - \sum_{m\sigma} t_m (a^\dagger_{m\sigma} a_{m+1,\sigma} + a^\dagger_{m+1,\sigma} a_{m\sigma}) + \frac{U}{2} \sum_{m\sigma} n_{m\sigma} n_{m,-\sigma}. \quad (1)$$

Site energies e_m are specified as being modulated with amplitude $\alpha, e_m = (-1)^m \alpha$. Transfer integrals t_m between nearest-neighbor sites m and $m+1$ determine the interaction of electrons with the lattice through the linear dependence on the corresponding bond deformations (bond-length changes) q_m, $t_m = t_0 - t_1 q_m$, where t_1 is a coupling parameter. The on-site e-e repulsion potential is determined by the Hubbard parameter U.

The geminal approximation used here for the correlated ground state of (1) is based on the accurate representation of any singlet two-electron state in the so called natural form $G^\dagger |0\rangle$ where $|0\rangle$ is a vacuum state and $G^\dagger$ is a two-electron (geminal) operator defined as a linear combination of products $P^\dagger_i = A^\dagger_{i\uparrow} A^\dagger_{i\downarrow}$; the operators $A^\dagger_{i\sigma}$ are made of basis (site) operators $a^\dagger_{m\sigma}$ creating an electron with corresponding spin σ ($\sigma = \uparrow, \downarrow$) on sites m by the identical orthogonal transformations. Correspondingly, the $2M$-electron ground state can be approximated by the antisymmetrized product of functions of M correlated electronic pairs described by singlet geminals

$$|\Psi\rangle = \prod_k^M G^\dagger_k |0\rangle, \quad G^\dagger_k = \sum_i \xi_{ki} P^\dagger_i, \quad \sum_i \xi^2_{ki} = 1. \quad (2)$$

Anticommutation of the operators entering different geminals essentially simplifies calculations, thus the restriction of "strong orthogonality" is commonly used assuming each $G^\dagger_k$ is constructed only from the operators $A^\dagger_{i\sigma}$ which belong to one of nonintersecting subsets of the complete set $A^\dagger_{i\sigma}$ (it is formally provided by the condition that nonzero ξ_{ki} would not be the case for different i simultaneously). The wave function so defined is known in quantum chemistry as the antisymmetrized product of strongly orthogonal geminals (APSG) (see, for example, Ref. 10) and usually applied in molecular calculations relating orthogonal subspaces to construct geminals with subsets of basis functions.

The APSG wave function can be compared with the BCS one in "single-geminal" form, known in the theory of superconductivity. The latter involves pair products $B^\dagger_{k\uparrow} B^\dagger_{-k\downarrow}$ of operators related to the plane waves with quasimomentum k. By the transformation to real plane waves $B^\dagger_{\pm k\sigma} = A^\dagger_{k\sigma} \pm i A^\dagger_{-k\sigma}$, $k \geq 0$, the function reduces to the form (2) with $\xi_{kj} = \xi_j$, so that $G^\dagger_k$ are identical and involving all the pair operators $P^\dagger_k$, thus the strong orthogonality condition does not hold. Comparing the expansions of both wave functions on configurations $P^\dagger_{k_1} P^\dagger_{k_2} \cdots P^\dagger_{k_M}$, one can find that the APSG does not involve the configurations with $P^\dagger_{k_j}$ which belong to different subsets. Instead, all the configurations are presented in the single-geminal function, however, their weights bound to the products $\xi_{k_1} \xi_{k_2} \cdots \xi_{k_M}$ happen to be unfavorable in some cases.[11]

Like the common SCF (Hartree-Fock) wave function defined as the best, by energy, antisymmetrized product of one-electron functions, the APSG function can be treated as a basis for a two-electron SCF method in which the coefficients ξ_{ki} and geminals are optimized variationally without any *a priori* restrictions besides the strong orthogonality conditions.

Proceeding to the spin-unrestricted SCF2 approach we consider the operators $A^\dagger_{i\sigma}$, used to construct the geminal operators $G^\dagger_k$ in (1), as made up of corresponding site operators $a^\dagger_{m\sigma}$ by orthogonal transformations

$$A^\dagger_{i\sigma} = \sum_m C_{mi\sigma} a^\dagger_{m\sigma}, \qquad \sum_m C_{mi\sigma} C_{mj\sigma} = \delta_{ij} \ . \tag{3}$$

The matrix elements $C_{mi\sigma}$, together with the coefficients ξ_{ki}, are treated as variational parameters but now, contrary to the restricted SCF2 approach in which $C_{mi\uparrow} = C_{mi\downarrow}$, they may be different for different spins. Including the cross terms $A^\dagger_{i\uparrow}A^\dagger_{j\downarrow} + A^\dagger_{j\uparrow}A^\dagger_{i\downarrow}$ to $G^\dagger_k$, as proposed in Ref. 9, is inefficient in the case of fully optimized geminals. They can be eliminated by canonical transformations of pairs of operators $A^\dagger_{i\uparrow}, A^\dagger_{j\uparrow}$ and $A^\dagger_{i\downarrow}, A^\dagger_{j\downarrow}$ so the class of variational functions cannot be expanded in this way.

We apply the approximation (2) to the ground state of a chain with even $N = 2M$. For the half-filled case, each of the geminal operators involves two pair operators $P^\dagger_i$ with $i = k$ and $i = k'$ where $k' = k + M$ (here and below index k running over the range 1–M can be associated with the occupied states in the common Hartree-Fock theory, the corresponding virtual states are numbered by k', and indices i and j refer to the range 1–N).

The energy expression required to apply the variational method is derived in the Appendix. In the case of the Hubbard e-e potential for which the corresponding Coulomb and exchange integrals are equal, the general expression (A4) simplifies and can be put in the form

$$E_e = E_0 + E_1 + E_2, \tag{4}$$

$$E_0 = \sum_i \nu_i [h(ii\uparrow) + h(ii\downarrow)] + \sum_{ij} \nu_i \nu_j (ii\uparrow|\, jj\downarrow), \tag{5}$$

$$E_1 = 2\sum_k \xi_k \xi_{k'} (kk'\uparrow|\, kk'\downarrow), \tag{6}$$

$$E_2 = \sum_k \nu_k \nu_{k'} (kk - k'k', \uparrow|\, kk - k'k', \downarrow), \tag{7}$$

where $\nu_i = \xi_i^2$ with $i = k$ or $i = k'$ are occupation numbers of one-electron states $A^\dagger_i|0\rangle$ and matrix elements are specified as follows:

$$h(ii\sigma) = \sum_m (C^2_{mi\sigma} - 2t_m C_{mi\sigma} C_{m+1,i\sigma}), \tag{8}$$

$$(ij\sigma \mid i'j'\sigma') = U \sum_m C_{mi\sigma} C_{mj\sigma} C_{mi'\sigma'} C_{mj'\sigma'} . \tag{9}$$

When all $\nu_k = 1$ (and, correspondingly, $\nu_{k'} = 0$) then $|\,\Psi\rangle$ turns into a one-determinant wave function, in this case $E_1 = E_2 = 0$, so E_0 can be treated as an UHF energy generalized for the arbitrary occupation numbers. Energy rise due to nonzero $\xi_{k'}$ is compensated by the correlation terms E_1 and E_2. The energy gain connected with E_1 is favored by the rise of the negative products $\xi_k \xi_{k'}$ and the exchange integrals $(kk'\uparrow|\, kk'\downarrow)$. As a consequence, the variational optimization of geminals leads to the Wannier-type states k and k' localized near corresponding bonds, by contrast to the complete energetic equivalence of plane-wave and Wannier states in the one-determinant case. The term E_2 involves the energies of the Coulomb interaction of difference electron distributions kk and $k'k'$ for each of the spins, weighted with $\nu_k \nu_{k'}$. For a monatomic chain, this term is of importance only in the unrestricted case. For the restricted geminals, E_2 vanishes as the optimized states k and k' differ only by sign at even sites due to the charge-conjugation symmetry of the Hamiltonian (1).[7]

It should be noticed that unrestricted-geminal energy is invariant with respect to the interchange $C_{mi\sigma} \leftrightarrow C_{mi,-\sigma}$, thus any solution of the restricted-geminal variational equations at the same time satisfies the UG variational equations as it is in the case of the one-determinant Hartree-Fock theory. Evidently, for self-consistent ground-state energies the inequality $E_{\rm UG} \leq E_{\rm RG}$ holds, so that in the case of different $E_{\rm UG}$ and $E_{\rm RG}$ the former corresponds to minimum of the UG energy surface while the latter, being the minimum point on the RG surface, usually is unstable with respect to the spin extension and realizes a saddle point on the UG surface.

In the adiabatic treatment of the Peierls-Hubbard problem the total energy E_T of the chain includes the elastic energy contribution $E_{\rm latt}$,

$$E_T = E_e + E_{\rm latt}, \qquad E_{\rm latt} = \frac{K}{2} \sum_m q_m^2, \tag{10}$$

where K is the elastic constant of bonds. The equilibrium structure of the system is determined by minimization of E_T with respect to all wave function $(C_{mk\sigma}, \xi_k)$ and geometry (q_m) variables with the chain length being fixed. The orthonormal sets of coefficients $C_{mk\sigma}$ are determined with the use of the multiconfigurational-SCF optimization technique based on the pseudosecular method.[12]

III. NUMERICAL RESULTS

Applying the approach outlined above, the ground-state properties of the Peierls-Hubbard chains are calculated with the ring boundary conditions to minimize end effects. We consider normalized bond-length changes $d_m = q_m \sqrt{K/t_0}$, a dimensionless electron-lattice coupling is $g = t_1 \sqrt{K/t_0}$; measuring energy in t_0 units we set $t_0 = 1$. As a result of minimization of E_T, the ground state is obtained with the alternating charges Q_m, spin densities ρ_m, and bond lengths d_m,

$$\begin{aligned} Q_m &= 1 + (-1)^m Q, \quad \rho_m = (-1)^m \rho, \\ d_m &= d_0 + (-1)^m d, \end{aligned} \tag{11}$$

which can be characterized as CDW ($Q \neq 0$), SDW ($\rho \neq 0$), and BOW ($d \neq 0$) states or states with combining instabilities.

Most of the calculations were performed for the $N = 30$ rings with $g = 0.5$ (this can be compared with $g = 0.37$, the estimation obtained for polyacetylene within the framework of the RG-SCF2 approach[7] and $g = 0.39$ as found in the exact diagonalization study[13]). Separate results were obtained for $g = 0.75$. In addition, in the $U < 2$ region where the size effects are noticeable the $N = 50$ ring is also considered.

To elucidate the effect of removing spin restriction, let us first discuss the results of the calculations for monatomic rings without e-ph interaction. An analysis of the ground-state energies is presented in Fig. 1(a). The overall RG and UG electronic energies are close while the contributions defined by Eqs. (5)–(7) are essentially different. Particularly, the E_0 energies both monotonically rise with U, but the RG energy happens to be twice as large as the UG one. The negative correlation contribution to RG energy is connected only with E_1, which decreases with U almost linearly. In the UG case, E_1 falls much slower and after $U \approx 5$ becomes even rising so that the main energy gain at large U is determined by the E_2 contribution which, as it was mentioned, is equal to zero for the RG case.

The results for the ground-state energies calculated for the monatomic rings with e-ph interactions are given in Fig. 1(b). For convenience, the variational energies per site are referred to the corresponding exact Lieb-Wu values ε_0 calculated for the infinite undeformed Hubbard chain.[14]

The plots in Fig. 1(b) show that the UG-SCF2 solutions bifurcate from the singlet-geminal solutions when electron repulsion exceeds some threshold U_0, the bifurcation point shifting to greater U as electron-lattice interaction increases. The splitting of geminals is accompanied by a sharp rise of spin densities [Fig. 2(a)] and a drop of dimerization amplitude [Fig. 2(b)] just above U_0.

Consideration of the energy data given in Fig. 1(b) allows one to estimate the accuracy of different variational approaches. Small negative values near $U = 0$ are caused by the present choice of the $N \to \infty$ energies as the reference ones [at $U = 0$ the exact $N = 30$ and $N = 50$ energies are lower by 0.0023 and 0.0008, respectively, at $U = 5$ the corresponding differences reduce to 0.0006 and 0.0002 (Ref. 15)]. In the $U < 4$ region both SCF2 modifications are much superior to the UHF method but for large U the UHF and RG-SCF2 energies fall close together whereas the UG energy is about one-half as high. Thus, by allowing geminals to be spin split, a considerable improvement of variational results for strongly correlated chains is attained.

As can be seen in Fig. 1(b), e-ph interaction monotonically lowers the energy. At $g = 0.75$ the decrease is so considerable that the UG energy of the distorted chain for $U < 7$ appears to be lower than the exact energy for the undimerized state. This result directly proves that even in the case of strong correlation the equidistant Hubbard chain is unstable with respect to Peierls distortion, at least at e-ph interaction of sufficient strength. The similar evidence was obtained earlier for $U < 4$.[16]

In the small-U region, $U < 4$, where removing spin restrictions yields no effect, the UG-SCF2 results coincide

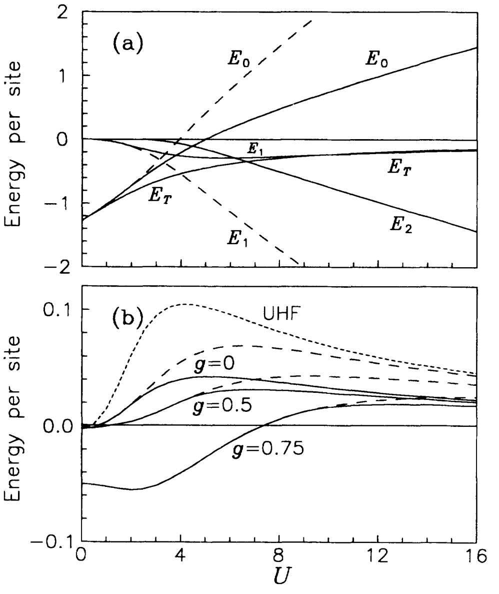

FIG. 1. Energetic characteristics of monatomic Peierls-Hubbard ring as functions of U, calculated by UG-SCF2 (solid lines) and RG-SCF2 (long-dashed lines) methods. (a) Energy contributions at $g = 0$ defined by Eqs. (5)–(7); in this scale, the close plots of UG and RG ground-state energies E are represented by a single curve. (b) Ground-state energies calculated with different g and measured with respect to the exact energies for infinite ring. Short-dashed line: the UHF energy at $g = 0$.

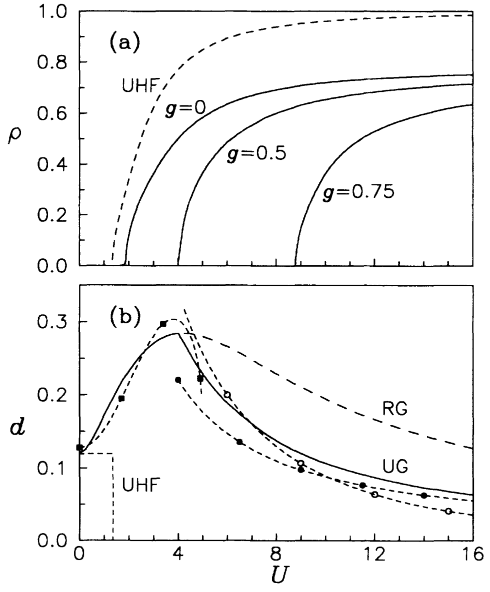

FIG. 2. Electronic and lattice characteristics of monatomic Peierls-Hubbard ring as functions of U, calculated at $g = 0.5$ by UG-SCF2 (solid lines) and RG-SCF2 (long-dashed lines) methods. (a) Amplitude of spin-density alternation ρ for different g. UHF result is depicted at $g = 0$. (b) Dimerization amplitude d. Short-dashed lines: Gutzwiller-ansatz results (dark squares) and spin-Hamiltonian calculations of the infinite-size chain with the use of mean-field (bright circles) and variational (dark circles) approximations.

with the RG ones discussed in Ref. 7. Thus we only note here that the predicted U dependence of dimerization amplitude d is in agreement with that obtained by the linked-cluster Gutzwiller-ansatz method,[16] as it is shown in Fig. 2(b).

In the large-U region, the RG and UG $d(U)$ dependencies are notably different. As can be seen in Fig. 2(b), the SDW wave arising at $U > U_0$ strongly suppresses dimerization. Besides, contrary to the RG $d(U)$ dependence, the UG $d(U)$ plot in the log-log scale can be fairly well represented by a straight line, specifically,

$$\ln d = -1.1019 \ln U + 0.3026. \tag{12}$$

At large U the half-filled Hubbard model (1) is known to be mapped on the spin-1/2 antiferromagnetic Heisenberg Hamiltonian,

$$H_s = \sum_m J_m \vec{S}_m \cdot \vec{S}_{m+1}. \tag{13}$$

For a dimerized state with the bond alternation d, the exchange parameters $J_m = 4t_m^2/U$ are

$$J_m = J[1 + \delta(-1)^m], \quad J = 4/U, \quad \delta = 2gd, \tag{14}$$

thus allowing us to compare the present results with the spin-Peierls calculations.

Most of the known studies on the spin-Peierls transition consider the behavior of the electronic energy only at small δ. One of the results available for comparison with ours within a broader δ range is obtained in Ref. 17 within the framework of Hartree-Fock approximation for Hamiltonian (1). Using the corresponding analytic expression for the ground-state energy in the form given in Ref. 18 we calculated the $d(U)$ dependence by minimizing the total energy as a function of d. With the same aim, we also used the results of the variational study of the Heisenberg chain[19] making sure that, for δ within the range 0–0.1976, the numerical data for the electronic energy per site ϵ_e are fairly well represented by the linear fit $\epsilon_e/J = -0.2207\delta - 0.4348$. The $d(U)$ dependencies thus obtained are depicted in Fig. 2(b). The plots show that the UG $d(U)$ dependency proves to be in much better agreement with both the spin-Peierls calculations than that obtained by the RG-SCF2 method predicting considerably overestimated d.

The diatomic chain is described by the Hamiltonian (1) with site-energy modulation $\alpha > 0$. As in $\alpha = 0$ case, at small U the RG-SCF2 solution is also stable with respect to spin splitting. So, to elucidate its effect at nonzero α, we consider as an example the results of the calculations with large U; the case is important for applications to charge-transfer molecular crystals. For these systems with quasi-one-dimensional structure, $U/t_0 \sim 10-70$ due to relatively small hopping integrals,[20] so we fix, for convenience, $U = 16$ and calculate the model (1) with varied α.

When considering the results obtained with the restricted geminals, depicted in Fig. 3, one can distinguish two regions of α divided by the point $\alpha \simeq U/2$. In the $\alpha < U/2$ region the chain retains to a great extent its characteristics modified by CDW driven by site-energy modulation. With α increasing, the charge transfer Q and dimerization amplitude d monotonically rise, and the growth becomes faster as the point $\alpha = U/2$ is approached.

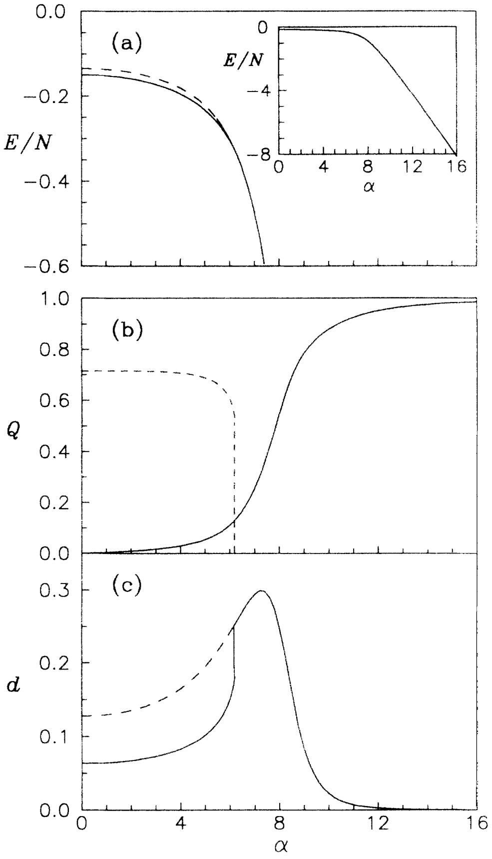

FIG. 3. Ground-state properties of diatomic Peierls-Hubbard ring as functions of site-energy modulation α calculated at $g = 0.5$ and $U = 16$ by UG-SCF2 (solid lines) and RG-SCF2 (long-dashed lines) methods. (a) Total energies per site; the inset shows the same dependencies (scaled down) in the whole α range. (b) Amplitude of charge alternation Q for both UG and RG cases; short-dashed line: UG amplitude of spin-density alternation. (c) Dimerization amplitude d.

When passing through $\alpha \sim U/2$, the energy -2α of a pair which occupy a site with lower energy $e_m = -\alpha$, exceeds, by absolute value, the on-site e-e repulsion energy U. As a result, the total energy is determined rather by site-energy modulation than by correlation and linearly decreases with α [Fig. 3(a)]. The wave function assumes one-electron character, describing pairs which occupy mainly even sites as it is represented by the charge distribution [Fig. 3(b)]. In this case the odd sites turn out to be almost empty, so bond orders and, consequently, dimerization [Fig. 3(c)] sharply drop with α above $U/2$.

Removing spin restrictions imposed on geminals leads to the bifurcation of the UG solution from the RG one only for α smaller than a critical value $\alpha_0 = 6.165$. It can be clearly seen from the behavior of the spin den-

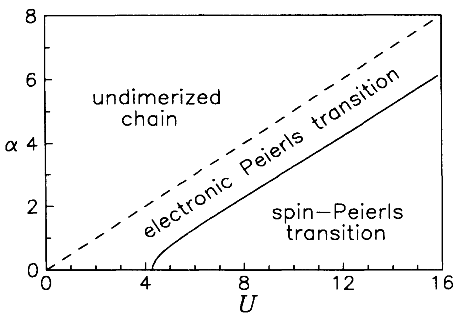

FIG. 4. U-α phase diagram for diatomic Peierls-Hubbard ring at $g = 0.5$. The location of RG-UG bifurcation points is shown by solid line. Dimerization sharply falls near $\alpha = U/2$ (dashed line).

sity which sharply drops when the critical point α_0 is approached. By contrast to this, the effect for the charge densities is negligible, and the magnitude of the charge alternation Q remains unchanged within the accuracy of calculations. The most pronounced effect concerns the α dependency of the dimerization amplitude which undergoes essential changes. As for the monatomic ring, at small and intermediate α the UG alternation remains about half as large as the RG one. The sharp rise of d at the bifurcation point α_0 suggests that an additional transition is the case, which is characterized, by contrast to the transition near $\alpha = U/2$, only by the dimerization jump without noticeable changes of charges.

The determination of the exact locations of the UG-RG bifurcation points is troublesome because of the shallow energy surface and, consequently, slow iteration convergency where the nonsinglet geminals turn into the singlet ones. Thus to diminish computations when scanning the α-U plane we searched for the points in which the RG-UG energy differences per site approach the fixed small value of 10^{-6}. The location of the RG-UG bifurcation points thus obtained at different U is shown in the U-α phase diagram (Fig. 4). As can be seen, the plot $\alpha_0(U)$ is near the straight line which is almost parallel to the line $\alpha = U/2$.

IV. DISCUSSION

The calculations performed demonstrate that the UG-SCF2 method yields the correct picture of interplay of the intrinsic BOW and SDW instabilities in the 1D Peierls-Hubbard correlated system, including also the CDW driven by site-energy modulation (a spontaneous CDW formation is possible only in models with nonzero intersite e-e potentials[21]). The method allows us to get correct predictions for electronic and lattice properties described within the same framework in the whole range from small to large U. Although electronic- and spin-Peierls transitions formally have the same general origin, the latter can be conventionally attributed to the parameter range bounded by the bifurcation points in which the UG solution becomes distinct from the RG one. The corresponding areas are designated in the U-α phase diagram (Fig. 4).

In comparison with the previous RG-SCF2 approach, the new UG-SCF2 one leads to considerable gain in variational energy in intermediate- and strong-correlation regimes due to consideration of antiferromagnetic correlations. It should be noticed here that the energy gain is yielded at the cost of higher-multiplicity pollution of the wave function. The exact ground state of the systems under consideration is singlet, so, rigorously speaking, the spin properties should be determined by the spin correlation functions. In principle, the higher-multiplicity contributions can be removed by the known spin-projection methods. However, even within the present scheme one may consider spin densities (if arising from nonsinglet contributions) to be a useful characteristic of interactions determined by spins, like it is commonly accepted in one-determinant UHF treatments.[1,2]

For the monatomic Peierls-Hubbard chain, the results of the present calculations are in line with the qualitative explanation of the effects of e-e correlation on dimerization behavior in terms of the approximate geminal approach.[22] Thus the shape of the $d(U)$ dependence is determined by two factors: (1) geminal localization which strengthens the bonds of geminal locations with loosening of the other ones, and (2) the growing weights of antibonding states k' in geminals, which acts just in the opposite direction. Geminal localization, which increases with U due to E_1 energy gain, produces dominating effect at small and intermediate U, thus forming the ascending part of the $d(U)$ dependence. With further U increase, the geminal localization approaches saturation so that the rising k'-state weights become the main factor which determines the descending tail of the $d(U)$ curve.

The dimerization reduction at large U in the UG calculations against the RG ones can be related to the localization characteristics of the optimized k and k' states used to make up the geminals. When spin restrictions imposed on the geminals are removed, the bond-type localization of these states changes to the atom-type one, that results in the reduction of the bond orders. A similar effect in the one-determinant UHF approach leads to the complete disappearance of the dimerization at large U.

Most of the previous studies on the Peierls instability emphasize the problem of existence of dimerization by examining the energy behavior at small distortions. In contrast to this, the SCF2 method is aimed to direct calculations of dimerized lattice structure affected by correlated electrons. Since the optimized geminals are localized the resulting wave function formally corresponds to a single VB structure. This imposes evident limitations near the $d = 0$ point where the contribution of another Kekulé structure is important. Nevertheless, away from this point the drawback is essentially compensated by full optimization, thus the method correctly predicts the main trends in the behavior of dimerization though, quantitatively, its magnitude sometimes turns out to be overestimated some.

For the diatomic chain, the results obtained here can be related to the problem of phase transitions in donor-acceptor molecular crystals. The alternating donor and acceptor molecules in these systems are commonly represented by the model (1) with large U, in which low- and high-energy sites are associated with donor and acceptor molecules, respectively; the interchain Coulomb interaction in the mean-field approximation is effectively taken into account by renormalization of α. Since neutral donors involve two electrons on the highest occupied orbital and the neutral acceptor has the empty lowest virtual one, the small charges Q on even sites in the model (1) correspond to the quasi-ionic state of the crystal, whereas large Q relate to the quasineutral state.

The problem of the neutral-ionic phase transition exhibited, for example, by the tetramethylparaphenylenediamine-chloranil (TMPD-CA) crystal, has been intensively investigated by the VB method (see, Ref. 23, and references therein) predicting, in accordance with the experimental evidence, a dimerized quasi-ionic phase and a regular quasineutral one. The RG-SCF2 method yields the same result. The sharp fall of dimerization when passing through the transition point dividing quasi-ionic ($\alpha < U/2$) and quasineutral ($\alpha > U/2$) regions [Fig. 3(c)] can be related to this transition. More detailed consideration is presented elsewhere.[8]

The present UG-SCF2 results can be connected with another type of phase transitions observed in tetrathiafulvalene-bromanil (TTF-BA) crystal. As it was found in,[24] this complex, remaining quasi-ionic at all temperatures, shows a sharp drop of magnetic susceptibility below 50 K accompanied by the stack dimerization. As concluded in Ref. 24, "The critical remaining question concerns the driving force behind this dimerization. Is it a spin-Peierls transition, as has been speculated?"[25] The data obtained here can provide us with further information on this problem.

The transition observed in Ref. 24 seems to be related to the bifurcation point which appears at $\alpha_0 = 0$ [Fig. 3(c)]. Really, this point is located in the quasi-ionic region without marked charge changes near the transition. Besides, dimerization rapidly falls as α decreases, passing the critical value. Magnetic properties are not calculated here. But, qualitatively, spin instability of geminals below α_0 just means the appearance of low-energy states of higher multiplicity, triplets in the first turn, which being occupied with temperature lead to paramagnetism of the system.

V. CONCLUSION

The results of this study show that the geminal technique both in the RG-SCF2 and UG-SCF2 modifications, one of the simplest approaches to go beyond Hatree-Fock approximation, appears to be a useful tool for direct unified calculations of electron and lattice properties of various extended systems in slight-to-strong correlation regimes.

Possible further developments and applications of the SCF2 approach can be outlined as follows. First, though the technique is specified in the present study for the Hubbard half-filled 1D case, its generalization for the structures with holes as well as for the 1/3- or 1/4-filled states both for short- and long-range e-e potentials is straightforward. Again, as being less critical to N limitations, the approach can be readily applied to 2D models.

Secondly, the SCF geminals can be used as a convenient basis for calculating the correlated excited states. Due to the localized character of geminals, a restricted configuration-interaction treatment leads to an exciton-like description which turns out to be more relevant for the low-energy excitations with pronounced two-electron contributions (for the monatomic chain they are of A_g symmetry, the same as that of the ground state[26]). Besides, for optimized geminals the generalized Brillouin theorem holds,[27] thus much simplifying consideration of the one-electron excitations.

Finally, the present approach is equally applicable to regularly dimerized structures or lattices distorted by kinks. Thus it is expected to be helpful for consideration of the soliton excitations not only for the monatomic Peierls-Hubbard systems,[7] but also for the diatomic ones. The latter, due to the rich picture of interplaying BOW, SDW, and CDW $2k_F$ symmetry breakings, seem to be interesting objects for investigation of the solitons of different types, e.g., such as those introduced in Ref. 28 to explain some properties of donor-acceptor crystals.

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APPENDIX A: UNRESTRICTED-GEMINAL ENERGY EXPRESSION

We sketch the derivation of the unrestricted-geminal energy expression needed to apply the variational method. The system of an even number $2M$ of electrons is assumed to be described by the Hamiltonian of the general form

$$\begin{aligned} H &= H_1 + H_2 \\ &= \sum_{ij\sigma} h(ij\sigma) A^{\dagger}_{i\sigma} A_{j\sigma} \\ &\quad + \tfrac{1}{2} \sum_{iji'j'\sigma\sigma'} (ij\sigma \mid i'j'\sigma') A^{\dagger}_{i\sigma} A^{\dagger}_{i'\sigma'} A_{j'\sigma'} A_{j\sigma} . \end{aligned} \tag{A1}$$

Since the operators $A^{\dagger}_{j\sigma}$ are made up of site operators $a^{\dagger}_{m\sigma}$ by the orthogonal transformations (3) which may be different for different spins, the transformed one- and two-electron integrals, $h(ij\sigma)$ and $(ij\sigma \mid i'j'\sigma')$, depend on spin.

When obtaining the average energy $E = \bar{H}$ in the state (2) the Wick theorem or the Feynman diagram technique can be applied. First, one can use the commutation of different geminal operators $G_k G_l^{\dagger} = G_l^{\dagger} G_k$ provided by the equality $\xi_{ki}\xi_{li} = 0$ at $k \neq l$ (the strong-orthogonality conditions). As a consequence, when considering the vacuum averages $\langle G_M \cdots G_1 \mid \cdots \mid G_1^{\dagger} \cdots G_M^{\dagger} \rangle$ the unlinked parts of the diagrams are separated contributing factors

1, as $\langle G_k G_k^\dagger \rangle = 1$ due to the normalization of G_k. Thus the average of H_1 reduces to

$$\bar{H}_1 = \sum_k \langle G_k \mid H_1 \mid G_k^\dagger \rangle = \sum_{ki} \xi_{ki}^2 \langle P_i \mid H_1 \mid P_i^\dagger \rangle . \quad \text{(A2)}$$

In the last sum, obtained after expanding G_k and $G_k^\dagger$ through pair operators P_k and $P_k^\dagger$ according to (2), only diagonal averages are retained as $\langle P_i \mid H_1 \mid P_j^\dagger \rangle = 0$ at $i \neq j$ due to the one-particle character of H_1.

The average of the two-electron operator H_2 reduces in a similar manner. Considering two ways of separation of the unlinked parts one gets

$$\begin{aligned} \bar{H}_2 &= \sum_k \langle G_k \mid H_2 \mid G_k^\dagger \rangle + \sum_{k<l} \langle G_l G_k \mid H_2 \mid G_k^\dagger G_l^\dagger \rangle \\ &= \sum_{kij} \xi_{ki} \xi_{kj} \langle P_i \mid H_2 \mid P_i^\dagger \rangle \\ &\quad + \sum_{\substack{klij \\ (k<l)}} \xi_{ki}^2 \xi_{lj}^2 \langle P_j P_i \mid H_2 \mid P_i^\dagger P_j^\dagger \rangle . \end{aligned} \quad \text{(A3)}$$

The averages of H_1 and H_2 with the pair operators in (A2) and (A3) are calculated in a straightforward way. The final energy expression is

$$\begin{aligned} E_{\mathrm{UG}} = & \sum_{ki\sigma} \xi_{ki}^2 h(ii\sigma) + \sum_{kij\sigma} \xi_{ki} \xi_{kj} (ij\sigma \mid ij, -\sigma) \\ & + \sum_{\substack{klij\sigma \\ (k<l)}} \xi_{ki}^2 \xi_{lj}^2 [(ii\sigma \mid jj\sigma) + (ii\sigma \mid jj, -\sigma) \\ & -(ij\sigma \mid ij\sigma)] . \end{aligned} \quad \text{(A4)}$$

In the one-determinant case ($\xi_{ki} = \delta_{ki} \nu_k$, $\nu_k = 1, 0$) Eq. (A4) reduces to the known UHF energy expression. Again, at $C_{mi\uparrow} = C_{mi\downarrow}$, Eq. (A4) turns into the RG energy[29] involving the two-electron integrals only of Coulomb and exchange types. In the general case the second sum in (A4) contains also generalized exchange integrals.

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[1] H. Fukutome and M. Sasai, Prog. Theor. Phys. **67**, 41 (1982).

[2] H. Fukutome and M. Sasai, Prog. Theor. Phys. **69**, 373 (1983).

[3] *Interacting Electrons in Reduced Dimensions*, edited by D. Baeriswyl and D. K. Campbell (Plenum Press, New York, 1989).

[4] S. Mazumdar and S. N. Dixit, Phys. Rev. Lett. **51**, 292 (1983).

[5] J. E. Hirsch, Phys. Rev. Lett. **51**, 296 (1983).

[6] V. A. Kuprievich, Teor. Eksp. Khim. **22**, 263 (1986) [Theor. Exp. Chem. (USSR) **22**, 245 (1986)].

[7] V. A. Kuprievich, Phys. Rev. B **36**, 3882 (1989).

[8] V. A. Kuprievich, Int. J. Quantum Chem. (to be published).

[9] A. L. Chugreev and I. A. Misurkin, Teor. Eksp. Khim. **23**, 665 (1987) [Theor. Exp. Chem. (USSR) **23**, 613 (1987)].

[10] R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic Press, London, 1969).

[11] A. V. Luzanov and V. V. Ivanov, Teor. Eksp. Khim. **26**, 385 (1990) [Theor. Exp. Chem. (USSR) **26**, 363 (1990)].

[12] V. A. Kuprievich, in *Self-Consistent Field. Theory and Applications*, edited by R. Carbo and M. Klobukowski (Elsevier, Amsterdam, 1990), pp. 136–156.

[13] V. Vaas, H. Büttner, and J. Voit, Phys. Rev. B **41**, 9366 (1990).

[14] E. H. Lieb and E. Y. Wu, Phys. Rev. Lett. **20**, 1445 (1968).

[15] K. Nashimoto, Int. J. Quantum Chem. **28**, 581 (1985).

[16] D. Baeriswyl and K. Maki, Phys. Rev. B **31**, 6633 (1985).

[17] L. N. Bulaevskii, Zh. Eksp. Teor. Fiz. **44**, 1008 (1963) [Sov. Phys. JETP **17**, 684 (1963)].

[18] G. Beni, J. Chem. Phys. **58**, 3200 (1973).

[19] D. J. Klein and M. A. Garcia-Bach, Phys. Rev. B **19**, 877 (1979).

[20] A. Painelli and A. Girlando, Phys. Rev. B **37**, 5748 (1988).

[21] S. Mazumdar and D. K. Campbell, Phys. Rev. Lett. **55**, 2067 (1985).

[22] I. I. Ukrainskii, Zh. Eksp. Teor. Fiz. **76**, 760 (1979) [Sov. Phys. JETP **49**, 381 (1979)].

[23] A. Painelli and A. Girlando, Phys. Rev. B **45**, 8913 (1992).

[24] A. Girlando, C. Pecile, and J. B. Torrance, Solid State Commun. **54**, 753 (1985).

[25] J. B. Torrance, J. J. Mayerle, and J. I. Crowley, Bull. Am. Phys. Soc. **23**, 425 (1978).

[26] Z. G. Soos, S. Ramasesha, and D. S. Galvão, Phys. Rev. Lett. **71**, 1609 (1993).

[27] B. Levy and G. Bertier, Int. J. Quantum Chem. **2**, 307 (1968).

[28] N. Nagaosa, Solid State Commun. **57**, 179 (1986).

[29] W. Kutzelnigg, J. Chem. Phys. **40**, 3640 (1964).