Peierls instability in spinless one-dimensional conductors

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The effect of nearest-neighbor Coulomb interactions on the Peierls instability of a spinless one-dimensional system is studied. Finite-size systems with half-filled bands are studied using a modified Lanczos method. Correlation functions and a qualitative phase diagram are presented. The results show that small and moderate Coulomb repulsion favors the Peierls state while large repulsion inhibits the distortion and produces charge redistribution. The coexistence of Peierls distortion and charge redistribution is found to be stable in a small region of parameter space.

I. INTRODUCTION

The effect of electron-electron interactions in the broken-symmetry states of one-dimensional systems has been the subject of a number of recent works.[1,2] It has been shown that Coulomb correlations may have an important effect on the Peierls instability of half-filled bands in both monatomic[1] and diatomic[2] systems. In the case of a monatomic system, the on-site Coulomb U increases the dimerization for U smaller than the bandwidth, and reduces the lattice distortion in the limit of strong interactions. In strongly correlated diatomic systems the site-energy difference favors the Peierls state in contrast to what occurs in the uncorrelated case.

The effect of the correlations depends strongly on the band filling.[3] It is known[4] that in the case of $\frac{1}{4}$-filled band, strong Coulomb interactions can produce a Peierls instability with wavelength $\lambda = 2a$ ($Q = 4k_F$) as opposed to the $\lambda = 4a$ ($Q = 2k_F$) instability expected in uncorrelated systems. The $\frac{1}{4}$-filled band in the strong–intra-atomic–repulsion limit ($U \to \infty$) is equivalent to a spinless $\frac{1}{2}$-filled band which stabilizes a dimerized state. This $4k_F$ instability observed[5] in a number of tetracyanoquinodimethane (TCNQ) salts can be considered as evidence of strong correlations in these systems. In this case it may be important to consider intersite Coulomb interactions. The $4k_F$ instability can be produced not only by bond dimerization but also by changes in the intramolecular energy as is pointed out in Ref. 6. It is the purpose of this paper to investigate the stability of the broken-symmetry states in a spinless one-dimensional system with nearest-neighbor interaction G for the half-filled band case. In this model there are two different broken-symmetry states: The Peierls state or dimerized bond-order wave (BOW) which is stabilized by the electron-phonon interaction and a charge-ordered state (COS) which for a rigid lattice is stable for $G > 2t$ (here t is the hopping integral). With the use of a simple real-space renormalization procedure[7] it has been shown that small values of G increase dimerization while strong Coulomb repulsion reduces the lattice distortion.

Recently Bendt[8] studied the same model by diagonaliz-ing finite systems. In Ref. 8, however, because of the method used in the calculation nothing can be concluded about the effect of dimerization on charge ordering.

We calculate the exact ground state of finite rings and present results for the equilibrium value of the dimerization as a function of the various parameters. Results for different correlation functions and structure factors are also included. These results allow us to give a complete description of the nature of the ground state. We conclude that the two kinds of broken-symmetry state compete with each other. Small or moderate values of the Coulomb repulsion G increase dimerization; however, the BOW inhibits charge ordering for $G \gtrsim 2t$. Strong electron-electron interaction stabilizes the undimerized COS.

These results are in agreement with previous calculations.[7,8] The study of the correlation function and the phase diagram obtained in this work allows us to present a better characterization of the ground state of the system. The rest of the paper is organized as follows. In Sec. II the model and the numerical method are described. Results are presented in Secs. III and IV includes a summary and discussion.

II. MODEL

Our starting point is a half-filled band described in the tight-binding approximation with nearest-neighbor repulsion by

$$H_e = \sum_i t_{i,i+1}(C_i^\dagger C_{i+1} + \text{H.c.})$$
$$+ \sum_i G_{i,i+1}(n_i - \tfrac{1}{2})(n_{i+1} - \tfrac{1}{2}) , \qquad (1)$$

where $C_i^\dagger$ creates an electron at site i and $n_i \equiv C_i^\dagger C_i$. t_{ij} is the hopping integral connecting sites i and j and G_{ij} the Coulomb repulsion between electrons at sites i and j.

The Hamiltonian Eq. (1) represents an extended Hubbard model in the limit of infinite intra-atomic Coulomb repulsion. Using a Wigner-Jordan transformation we can map H_e onto an anisotropic Heisenberg model.[9] In fact, Eq. (1) is equivalent to a spin-Peierls Hamiltonian[10] if we

take $G_{i,i+1}=2t_{i,i+1}$.

For $G_{ij}=G$ and $t_{ij}=t$, the system shows an instability at $G=2t$. If $G<2t$ the charge is uniformly distributed in the chain, while for the case $G>2t$ the ground state is a COS in which the expectation value of the charge at two neighboring sites alternates between $\frac{1}{2}(1+\delta n)$ and $\frac{1}{2}(1-\delta n)$.

We consider here the possibility of a lattice distortion of wavelength $\lambda=2a$. Including the lattice degrees of freedom in the Born-Oppenheimer approximation $M=\infty$ the total Hamiltonian is given by

$$H_T=H_e+2KNx^2 , \qquad (2)$$

where N is the number of sites, K the elastic constant, and x the bond distortion. In the dimerized state we take

$$t_{i,i+1}=t[1+(-1)^i 2\alpha x]$$

as in the SSH model for polyacetylene.[11] Here $t\alpha$ is the electron-phonon coupling constant. The Coulomb repulsion $G_{i,i+1}$ is also a function of the distance between sites i and $i+1$. However to simplify the model and reduce the number of parameters, we take in what follows $G_{i,i+1}=G$ independent of x. Then for $G=0$, Eq. (2) reduce to the SSH model which is exactly soluble. Clearly, in this limit the ground state is always dimerized.

We consider finite systems with N sites and $N/2$ particles. For $G=0$, the ground state of rings with $N=4n$ is a dimerized state for any value of α^2/K. In finite rings with $N=4n+2$, the distortion is stable only for α^2/K larger than a critical value. This behavior is a consequence of the degeneracy of the ground state. To improve the systematics of finite systems we consider rings with N sites and periodic or antiperiodic boundary conditions for $N=4n+2$ or $N=4n$, respectively. With these boundary conditions all chains are dimerized only for α^2/K larger than a critical value which itself is a function of N. The relation between $1/K$ and x is easily established. The value of x that minimizes the total ground-state energy of the system satisfies the equation

$$\frac{K}{\alpha^2}=\frac{1}{4N}\sum_k \frac{16t^2\sin^2(k+\phi)}{(\varepsilon_k^2+\Delta_k^2)^{1/2}} , \qquad (3)$$

where the sum runs over the $N/2-k$ values that give the $N/2$ lower single-particle energy states. In Eq. (3) $\varepsilon_k=-2t\cos(k+\phi)$ and $\Delta_k=(4\alpha tx)\sin(k+\phi)$. $\phi=0$ for periodic boundary conditions and π/N for antiperiodic. The k values are given by $\pi n/N$ with $n=-N/2,\ldots,N/2$. In the $N\rightarrow\infty$ limit Eq. (3) reduces to

$$\frac{K}{\alpha^2}=\frac{4t}{\pi}\frac{K(\pi/2,a)-E(\pi/2,a)}{a^2} , \qquad (4)$$

where $a=(1-z^2)^{1/2}$, $z=2x\alpha$, and K, E are complete elliptic integrals of the first and second kind. In Fig. 1 the distortion as a function of α^2/K is shown for different values of N. It has been proposed that the behavior of finite systems with α^2/K near the critical value mimic the behavior of infinite systems with infinitesimally small electron-phonon interaction. For nonzero G the Hamiltonian H_e cannot be diagonalized exactly in the $N\rightarrow\infty$
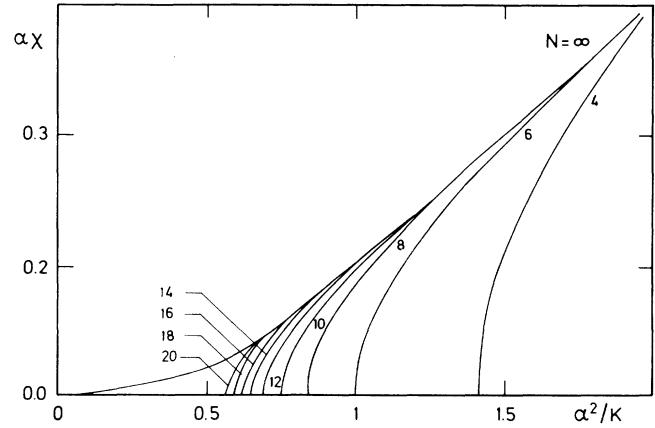

FIG. 1. Minimum lattice distortion as a function of α^2/K for different lattice size.

limit. However, different numerical approaches can be used to obtain information about the ground-state properties of finite systems[12-15] and using finite-size-scaling procedures we can infer some properties of the $N\rightarrow\infty$ limit. In this work, we diagonalized rings with different values of N in the interval (4,20). The exact diagonalization of H_e is performed by using a recently developed modified Lanczos method. This procedure which we will use has been developed in detail in Ref. 12. Here we provide a brief description of the method before making use of it. To begin with, we consider ϕ_0 as an approximation to the exact ground state ψ_0 of energy E_0 such that $\langle\phi_0|\psi_0\rangle\neq0$. Then,

$$H\phi_0=\varepsilon_0\phi_0+b\tilde{\phi}_0 , \qquad (5)$$

where $\varepsilon_0=\langle\Phi_0|H|\phi_0\rangle$ and $b=(\langle\phi_0|H^2|\phi_0\rangle-\langle\phi_0|H|\phi_0\rangle^2)^{1/2}$ the two states ϕ_0 and $\tilde{\phi}_0$ are orthogonal and define a (2×2) subspace.

Diagonalization of H in this subspace gives a better approximation of ψ_0 and E_0. The new trial state and energy are given by

$$\phi_1=\frac{\phi_0+\alpha\tilde{\phi}_0}{(1+\alpha^2)^{1/2}} \qquad (6)$$

and

$$\varepsilon_1=\varepsilon_0+\alpha b , \qquad (7)$$

where

$$\alpha=f-(f^2+1)^{1/2} \qquad (8)$$

and

$$f=\frac{\langle\phi_0|(H-\varepsilon_0)^3|\phi_0\rangle}{2\langle\phi_0|(H-\varepsilon_0)^2|\phi_0\rangle^{3/2}} . \qquad (9)$$

The method may be iterated by considering ϕ_1 as a new trial state and repeating the steps (5)–(9). For small systems, the iterative procedure covers the whole Hilbert space and rapidly converges to the exact ground state and

energy. For large systems, the method can be used to calculate approximated energies and wave functions. In the next section we present exact results for finite systems with $N \leq 20$.

III. RESULTS

The ground-state energy and eigenfunction has been evaluated for rings with different number of sites using the 2×2 procedure of the modified Lanczos method.[15] We take as initial ansatz the strong-coupling state, $|0101 \cdots \rangle$; the N numbers in the ket give the occupation of the N sites of the chain. This is a good choice for an intermediate-size lattice. However for larger systems, it gives a slow convergence rate. This limitation can be relaxed using other trial states.[15] In order to reduce the dimension of the ground-state Hilbert subspace we exploit the translation symmetry of the ring. This allows us to work with subspace dimension of the order $2\binom{N}{N/2}/N$ instead of $\binom{N}{N/2}$.

Results for the stability energy per site on dimerization ΔE as a function of αx are shown in Fig. 2 for $N = 8$ and 10. The stability energy ΔE is defined as

$$\Delta E = \frac{1}{N}[E(G,\alpha x) - E(G,0)] , \qquad (10)$$

where $E(G,\alpha x)$ is the ground-state energy of the system.

In both cases ($N = 8$ and 10), the parameter α^2/K has been chosen smaller than the critical value for $G = 0$. The curves for $G = 0$ then have an absolute minimum for $\alpha x = 0$. As G is increased a minimum occur for αx different from zero and for large values of the interaction the undistorted state is again stable. These results show
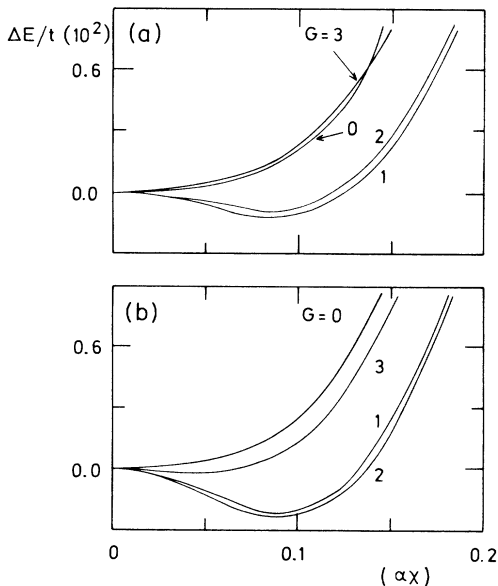
that the Coulomb repulsion favors dimerization for small or moderate values of G. The same effect has been observed using the renormalization-group approach.[7] The behavior is best illustrated in Fig. 3, where the equilibrium value of αx versus G is shown for different chains. In all the cases presented here the elastic constant α^2/K has been chosen such that for $G = 0$ the distortion $(\alpha x /t)$ is 0.2. Except for very short chains ($N = 4$), the distortion increases as G is increased, it reaches a maximum for $G \sim 2t$ and then decreases. The ground state for large values of G is undistorted. The results are not very sensitive to the size of the chain for $N \geq 12$. Similar results corresponding to Figs. 1 and 2 have been obtained independently in Refs. 7 and 8. Our results are in qualitative agreement with these works.

As mentioned above, the undistorted state with $G > 2t$ shows a COS. In what follows we discuss what happens when $G > 2t$ in the distorted chains. Information on the charge distribution on the chain can be obtained by studying the charge-charge correlation function $D(l)$, defined as

$$D(l) = \frac{1}{N} \sum_i \langle (n_i - \langle n_i \rangle)(n_{i+l} - \langle n_{i+l} \rangle) \rangle , \qquad (11)$$

where $\langle \cdots \rangle$ indicates the ground-state expectation value. For the undistorted case, it is known[16] that $D(l)$ behaves like $(-1)^l/l^\eta$ for large l. This behavior is illustrated in Fig. 4 for a ring of 20 sites. Figure 4(a) illustrates the results for $G = t$. For these values of the parameters $D(l)$ decreases with l indicating the lack of charge ordering ($G < 2t$). Note the $D(l)$ decreases more rapidly in the distorted case. The behavior is again $(-1)^l/l^\eta$; however, a good estimation of η requires longer chains or more elaborated finite-size-scaling analysis. More interesting are the results for $G > 2t$, Fig. 4(b). In this case the amplitude of the correlation function $D(l)$ saturates exponentially to a constant value, for the undistorted chain, as a consequence of charge ordering [full line in Fig. 4(b)]. Results for the distorted chain with αx obtained with the criterion used in Fig. 2 show that for

FIG. 2. Ground-state energy per unit site as a function of the distortion parameter. (a) $N = 8$, (b) $N = 10$.
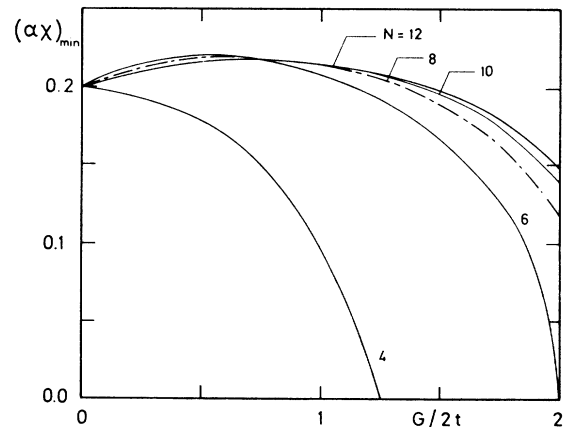

FIG. 3. Minimum lattice distortion as a function of the Coulomb repulsion parameter for different lattice size.
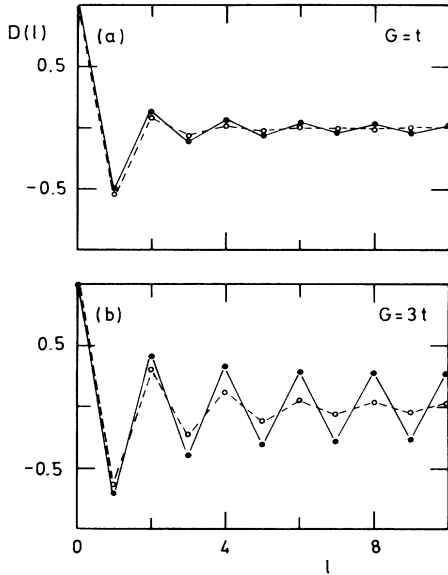
FIG. 4. Charge-charge correlation function as a function of the distance l for (a) $\delta = 0.2156$, (b) $\delta = 0.1956$. Full line, undistorted case. Dashed line, distorted case $(\delta = \alpha x)$. $N = 20$.

this parameters the dimerization inhibits charge ordering [dashed line in Fig. 4(b)] and our results suggest in $(-1)^l / l^\eta$ asymptotic law. It is also interesting to determine the charge structure factor corresponding to the correlation function $D(l)$. In Fig. 5 we show the structure factor

$$S(q) = \frac{1}{N} \sum_{i,l} e^{iql} (\langle n_i n_{i+l} \rangle - \langle n_i \rangle \langle n_{i+l} \rangle) . \qquad (12)$$
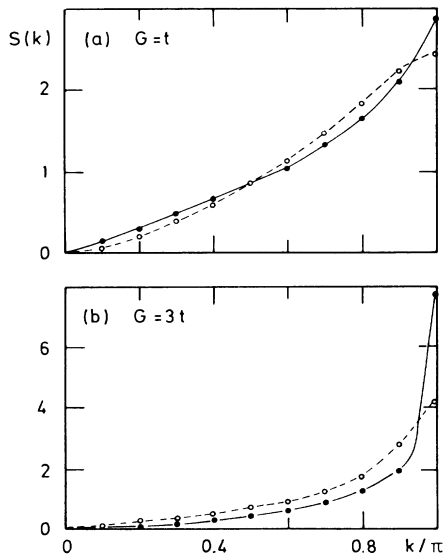
The $(-1)^l / l^\eta$ decay of $D(l)$ implies the structure factor will have a logarithmic divergence at $q = \pi/a$ for $\eta = 1$. This corresponds to the $G = 2t$ case, where the system undergoes a metal-insulator transition. For finite rings this divergence is cut off by the finite size of the system. For $G < 2t$ there is only "incipient" long-range order such that $S(q)$ peaks at $q = \pi/a$ but has a finite width. For $G > 2t$ the ground state has long-range order which for $\binom{G \to \infty}{N \to \infty}$ approaches the $| 1010 \cdots \rangle$ configuration. If we calculate $S(q)$ for this particular configuration we find $S(q) \sim \delta(\pi/a - |q|)$. In Fig. 5 we show $S(q)$ for $G = t$ and $G = 3t$. The obtained results for the undimerized chains are in good agreement with previous Monte Carlo results[16,17] and show the expected behavior. For the distorted case, the $G = t$ results present a decrease in $S(\pi/a)$ and the overall tendency is like the $G = 0$, $x = 0$ result. For $G = 3t$, the dimerization inhibits the charge ordering instability reducing $S(\pi/a)$. In this case the structure factor $S(q)$ resembles the $0 < G < 2t$ undistorted results.

Another interesting correlation function is the transfer-charge density function which measure the difference in the electronic density of the short and long bonds in the chain.

$$W(l) = \frac{1}{N} \sum_i \langle (C_{i+1}^\dagger C_i + \text{H.c.})(C_{i+l+1}^\dagger C_{i+l} + \text{H.c.}) \rangle .$$

$$(13)$$

In Fig. 6 we show $W(l)$ for $G = t$ and $3t$. Because we use antiperiodic boundary conditions for chain with length $4n$, for $N = 20$ $W(N/2) = 0$. For the undimerized systems, the charge is uniformly distributed in the chain, then a monotonic decrease towards $W(N/2)$ is expected. For a nonzero dimerization, the charge transferred between two neighboring sites depends on whether the bond is short or long. Then, oscillatory behavior is expected.
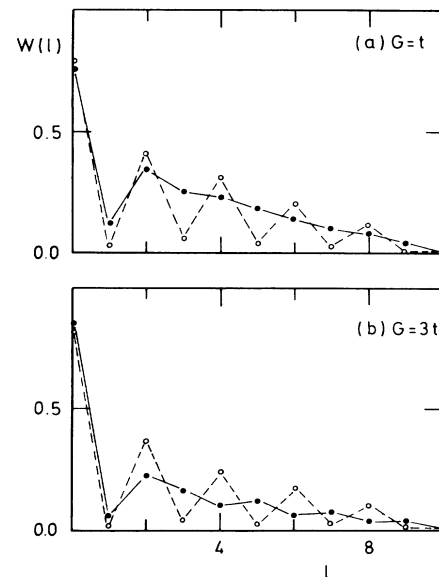

FIG. 5. Charge structure factor as a function of k. (a) $\delta = 0.2156$, (b) $\delta = 0.1956$. $N = 20$.

FIG. 6. Transfer-charge density correlation function as a function of the distance l. (a) $\delta = 0.2156$, (b) $\delta = 0.1956$. $N = 20$.

The oscillations in these functions show the existence of a bond-ordering wave. These results have been also obtained for $G = 0$, by Fradkin and Hirsch,[1] for a nonadiabatic SSH model. Finally, for completeness we give in Fig. 7, the single-particle Green's function which defines a length that measures the distance over which the electrons are localized in the ground state

$$G(l) = \frac{1}{2N} \sum_i \langle C^\dagger_{i+l} C_i + \text{H.c.} \rangle \ . \tag{14}$$

In the free-electron limit $(G = 0)$, and in the undistorted case, we obtain

$$G(l) = \frac{1}{2N} \sum_k e^{ikla} \langle n_k \rangle$$

$$= \frac{1}{N} \sum_{k(<k_F)} e^{ikla} \ . \tag{15}$$

It is easy to prove that for this case $G(l)$ decay algebraically with oscillations suggesting that the ground state is extended over all the system. In the $N \to \infty$ limit we found

$$G(l) = \frac{\sin(k_F la)}{\pi l} \ . \tag{16}$$

Equation (16) shows that for the noninteracting case $G(l)$ is zero for l even. This result is also obtained for finite ring, as is illustrated in Ref. 15.

As we note in Eq. 15, for $G = 0$, the Fourier transform of $G(l)$ is the zero-temperature Fermi function. When G is increased a tail appears at $k = k_F$ and a nonzero but small value is obtained for $G(2l)$. For $N \to \infty$ we expect $\langle n_k \rangle$ to be discontinuous at $k = k_F$ in the metallic phases and continuous in the insulating one. This change in be-
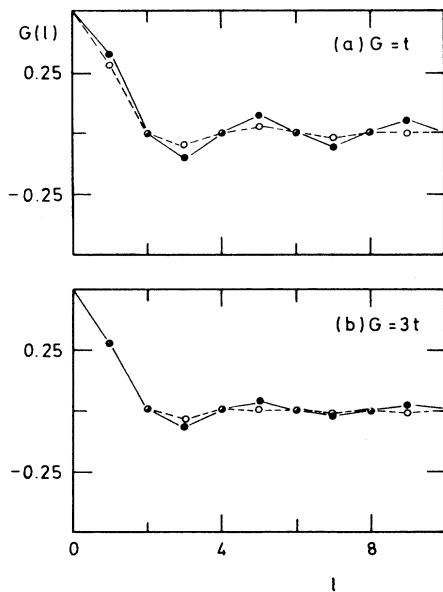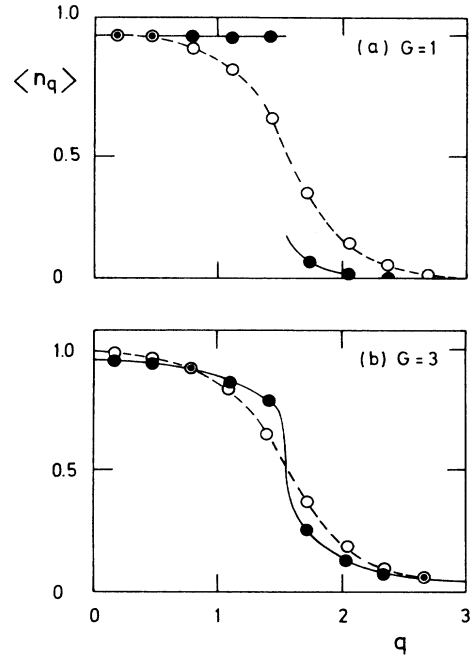

FIG. 8. The occupation number n_q for a ring of 20 sites. (a) $\delta = 0.2156$, (b) $\delta = 0.1956$.

havior is reflected in the results obtained for finite chains as is shown in Fig. 8.

Finally a phase diagram in the parameter space $(\alpha^2/K, G/2t)$ is shown in Fig. 9. As mentioned above, we expect a region near the BOW-COS boundary where both charge ordering and dimerization coexist. However, our results for finite rings suggest that this mixed phase is stable only in a small region near the boundary.

The phase diagram shown in Fig. 9 has been obtained using short rings. The extrapolation to large N is very tedious, however we expect the same qualitative behavior for large systems.
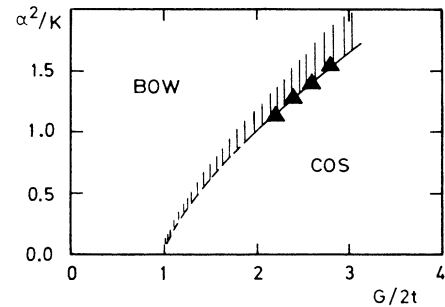

FIG. 7. Single-particle Green's function as a function of the distance l. (a) $\delta = 0.2156$, (b) 0.1956. $N = 20$.

FIG. 9. Qualitative phase diagram for the competition between charge-ordering state (COS) and bond-ordering wave (BOW).

IV. CONCLUSIONS

We have studied the effect of nearest-neighbor Coulomb interaction on the stability of Peierls states in one-dimensional spinless conductors. For the half-filled band the results can be summarized as follows.

(a) Numerical diagonalization for finite rings allows us to obtain the well-known results for the charge ordering in rigid lattices and for the Peierls instability in the $G = 0$ systems. In the rigid lattice the transition from a metallic state $(G < 2t)$ to an insulating COS $(G > 2t)$ is very well reproduced. The Peierls instability in the $G = 0$ case is sensitive to the length of the chain and on the boundary conditions; however, extrapolations to large systems reproduce again the exact results obtained for infinite systems (see Fig. 1).

(b) Small Coulomb repulsions G favor the Peierls instability. The BOW order parameter increases for increasing G, reaches a maximum for $G \simeq 2t$, and then decreases and rapidly goes to zero for G larger than a critical value G_c.

(c) The charge transfer which occurs in the rigid lattice for $G > 2t$ is totally or partially suppressed by dimerization. Coexistence of COS and BOW is found only for values of G in a small region near the distorted-undistorted boundary.

(d) The phase diagram obtained for short chains (Fig. 9) shows that in dimerized chains the critical value G_c for the occurrence of charge ordering is larger than $2t$ and as the elastic constant increases G_c tends to $2t$. The region $\alpha^2/K \sim 1$ (dashed line in Fig. 9) is not well described. Our results indicate that when G is increased the system from a distorted (BOW) to an undistorted (COS) state through a mixed phase in a continuous transition.

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