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Hubbard versus Peierls and the Su-Schrieffer-Heeger model of polyacetylene

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We have considered the competing effects of the electron-electron Hubbard repulsion and the electron-phonon interaction on the properties of a one-dimensional electron gas both within perturbation theory and by exact numerical solution of finite-length rings. We find that the perturbation-theory results provide a qualitatively correct description of the system over a considerable range of parameters. Among the more interesting conclusions we draw is that, so long as the repulsion U is less than a critical value which depends on the strength of the electron-phonon interaction, the predictions of the Su-Schrieffer-Heeger model of polyacetylene are not profoundly affected by the electron-electron repulsion. A small splitting between the charged and neutral soliton-creation energies and minor shape changes are the principle effects.

I. INTRODUCTION

It has been proposed recently by Su, Schrieffer, and Heeger (SSH) that many of the properties of the quasi-one-dimensional conductor polyacetylene $(CH)_x$ can be understood in terms of a simple model of coupled electrons and phonons, the SSH model.[1] This model is very appealing in that it is able to provide a qualitatively accurate description of many of the magnetic resonance and transport experiments that have been performed on $(CH)_x$. In light of the model's extreme simplicity, its tremendous success may seem puzzling. For instance, (1) it treats the lattice degrees of freedom classically, (2) it ignores the effects of electron-electron interactions, and (3) it is a purely one-dimensional model with no interchain coupling. Su[2] has examined the consequence of treating the lattice quantum mechanically. It is the limited goal of the present paper to study the possible effects of electron-electron interactions on the predictions of the SSH model. From a broader perspective, this paper is the beginning of a more general systematic study of the competition between electron-electron and electron-phonon interactions on the properties of a one-dimensional electron gas.[3]

Since many properties of a one-dimensional metal are only sensitive to a few parameters describing the interactions at the Fermi surface, we can sensibly hope that a simple model system will exhibit the same interesting qualitative features as more realistic models. Thus we will treat the simplest nontrivial model in which the SSH Hamiltonian is augmented by an on-site (Hubbard) repulsion U between electrons.

Similar considerations underlie the recent work of Nakano and Fukuyama[4] on the spin-Peierls system. However, their work is based on an approximate transformation to a spin Hamiltonian in which half the degrees of freedom of the system are transformed away. This approximation is only valid when the electron-electron repulsion is large compared to the one-electron bandwidth. This is almost certainly not the case in $(CH)_x$. However, the insights obtained from the work of Nakano and Fukuyama compliment the weak-coupling (perturbation theory) results discussed in the second and fourth sections of the present paper.

This paper is organized as follows: In Sec. II the model is solved approximately by first obtaining a solution in the unrestricted Hartree-Fock (HF) approximation and then doing perturbation theory about the Hartree-Fock solutions. The results are summarized in Figs. 2, 7, and 8. Perhaps the most interesting effect to emerge from these calculations is an increase in the dimerization as U increases from zero. This result is reminiscent of a similar result obtained by Chui *et al.*[5] for a continuum model of the incommensurate electron gas.

In Sec. III the results of numerical calculations on finite-ring systems are discussed and compared with the perturbative results. Comparison is also made with the exact results of Lieb and Wu[6] for the pure Hubbard model and with exact results obtained in Appendix B for a completely dimerized system. It is concluded that the present perturbative results provide a reliable description of both the ground-state properties and the low-energy excitations of the system.

Section IV contains a discussion of the effect of weak electron-electron interactions on the properties of the soliton or kink excitations that SSH have previously examined in the absence of interactions. This one section is not self-contained but draws heavily on the results of SSH. Finally, Sec. V contains a discussion of the implications of the present calculations for our understanding of polyacetylene. It is concluded on the basis of a comparison between theory and experiment that $(CH)_x$ is probably a "small-U" system, and that, therefore, the results of SSH are qualitatively correct, even in the presence of interactions. The most important modifications in the properties of the solitons due to the presence of electron-electron interactions are a surprisingly small energy splitting between a charged and neutral soliton and minor changes in the soliton width depending on its charge state. It is also shown that the Hubbard interaction decreases the soliton-creation energy. This may have the effect of increasing the importance of quantum fluctuations of the lattice. The mathematical manipulations necessary to understand the Hartree-Fock equations are summarized in Appendix A.

II. ANALYTIC RESULTS

As in the SSH model, we consider a tight-binding Hamiltonian with one state of each spin per site (corresponding to the carbon π orbital). The electrons are coupled linearly to the ionic displacements through the hopping-matrix elements between orbitals on adjacent sites. In addition, there is the following on-site "Hubbard" repulsion between electrons on the same site:

$$\begin{aligned} H = &\sum_{ns} [t_0 + \alpha(u_n - u_{n+1})](c^\dagger_{ns} c_{n+1s} + \text{H.c.}) \\ &+ U \sum_{n} (c^\dagger_{n\uparrow} c_{n\uparrow} - \tfrac{1}{2})(c^\dagger_{n\downarrow} c_{n\downarrow} - \tfrac{1}{2}) \\ &+ \tfrac{1}{2} k \sum (u_n - u_{n+1})^2 , \end{aligned} \tag{1}$$

where $c^\dagger_{ns}$ is the creation operator of an electron of spin s on site n, and u_n is the displacement of the nth ion. In this section we will consider only the properties of the half-filled band, that is, the case in which there is one electron per site. As in SSH the phonon dynamics are ignored through the neglect of the ion kinetic energy in (1).

We wish to examine the competition between the electron-phonon interactions (finite α effects) and the electron-electron interactions (finite U effects) in determining the nature of the ground state of H. Let $|\psi(\vec{u})\rangle$ be the electronic ground state of the system for a given ionic configuration $\vec{u}$. The ground-state ionic configuration is then obtained by minimizing the energy with respect to $\vec{u}$,

$$\frac{\delta\langle\psi(u)\,|\,H\,|\,\psi(u)\rangle}{\delta u_n} = 0 \; . \tag{2}$$

It is generally assumed that the uniformly dimerized configuration is the ground state. In order to determine the extent of dimerization, we find the electronic ground state $|\psi(u_0)\rangle$ in the presence of the configuration $u_n = (-1)^n u_0$. To obtain $|\psi(u_0)\rangle$ we first solve for the HF ground state and then treat the remaining interactions by perturbation theory. The energy is then minimized with respect to u_0 as in Eq. (2).

We will do calculations for rings containing N sites (with N electrons) as we will be interested in both finite and infinite rings (limit as $N \to \infty$). In this section we will consider only the case of even N. Rings with odd N behave qualitatively differently from even-numbered rings, even in the large-N limit, as they are topologically constrained to have a soliton in the ground state. We will consider odd-numbered rings in Sec. IV. For small N, there is also a qualitative difference between $n = 4n$ and $N = 4n + 2$. To understand the origin of this difference, consider the ground state of the noninteracting system $\alpha = U = 0$. For $N = 4n$, there are two zero-energy states (of each spin) with wave numbers $k = \pm\pi/2a$, where a is the lattice constant (see Fig. 1). For the half-filled band, the zero-energy states are half filled. If we now introduce almost any sort of small perturbation of magnitude V, these two states will be split to first order in V, so the change in the total energy of the system will be of the form

$$\frac{\Delta E}{N} = -\frac{VK_1}{N} - \frac{V^2}{t_0} K_2(N) \;\; \text{for } N = 4n \; , \tag{3a}$$

where K_1 and K_2 are constants. The first term in Eq. (3a) comes from the zero-energy states, and the second term comes from all the rest. For $N = 4n + 2$, there is a gap of width $2t_0 \sin(\pi/N)$ between the highest-lying filled state and the lowest-lying empty states. Thus the first, pathological term in Eq. (3a) is not present and

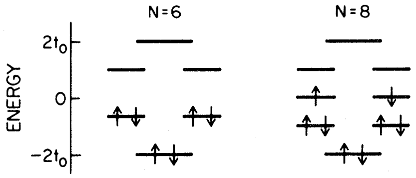

FIG. 1. Level structure for an eight-membered ring (representative of the $N=4n$ class) and a six-membered ring (representative of the $N=4n+2$ class).

$$\frac{\Delta E}{N}=-\frac{V^2}{t_0}K_2(N) \text{ for } N=4n+2 \,. \tag{3b}$$

As can be seen, the difference vanishes as $N\rightarrow\infty$. However, for fixed, finite $N=4n$, the first term in Eq. (3a) is the dominant term for sufficiently small $V\,(V \lesssim t_0/N)$. Thus for finite rings with $N=4n$, there exists a range of interaction strengths for which perturbation theory is unreliable. For this reason we will be more interested in the results for $N=4n+2$ where this pathology does not exist.

A. Hartree-Fock results

To begin with, we solve the problem in the unrestricted HF approximation. As we will see in the next two sections, the description of the low-energy excitation spectrum so obtained is good over a wide range of parameters, while ground-state properties are poorly described. For instance, the HF results incorrectly imply the existence of long-range spin correlations in the ground state of the pure Hubbard model ($u_n=0$). Presumably, these correlations mimic the true short-range correlations which affect the excitations. However, at long distances, the spin-spin correlation should properly[7] decay like $1/R$. Thus the HF results are primarily useful for obtaining the excitation spectrum (which generally cannot be obtained by perturbation theory alone), but must be augmented by perturbation theory to obtain reliable ground-state energies.

With this in mind, we construct the HF ground state as a product of one-electron states, chosen so as to minimize the expectation value of H. It is convenient to construct these states by the following procedure. First, we define the most general one-electron Hamiltonian,

$$H^{\rm HF}=\sum_{\substack{n'n\\ s's}} h_{n's',ns}c^\dagger_{n's'}c_{ns} \,.$$

Its ground state $|\psi^{\rm HF}(h)\rangle$ depends parametrically on $h_{n's',ns}$. Variation of

$$E^{\rm HF}\equiv\langle\psi^{\rm HF}(h)\,|\,H\,|\,\psi^{\rm HF}(h)\rangle \,,$$

with respect to the coefficients $h_{n's',ns}$, is equivalent to variation with respect to the single-particle wave functions in $|\psi^{\rm HF}(h)\rangle$. The variational HF ground state is obtained by minimizing $E^{\rm HF}$ with respect to $h_{n's',ns}$. It is shown in Appendix A that for the Hamiltonian in Eq. (1) it is sufficient to consider the HF Hamiltonian

$$H^{\rm HF}=\sum_{ns} t_n(c^\dagger_{ns}c_{n+1s}+{\rm H.c.}) +2t_0\sum_{ns} x_{ns}c^\dagger_{ns}c_{ns} \,, \tag{4}$$

which depends on the parameters $\vec{t}$ and $\vec{x}$ rather than on the full matrix of parameters $\underset{\sim}{h}$. The minimization condition allows us to express the usual Hartree-Fock self-consistency conditions in a form analogous to Eq. (2):

$$\frac{\delta\langle\psi^{\rm HF}\,|\,H\,|\,\psi^{\rm HF}\rangle}{\delta t_n}=0=\frac{\delta\langle\psi^{\rm HF}\,|\,H\,|\,\psi^{\rm HF}\rangle}{\delta x_{ns}} \,. \tag{5}$$

Because the band is half-filled (commensurability 2), there is a strong tendency for the system to develop a new periodicity with two sites per unit cell. The U term tends to produce an antiferromagnetic spin-density wave while the α term tends to produce bond alternation, or "dimerization." In Appendix A we show that a self-consistent solution to (5) is obtained with

$$t_n=t_0[1+(-1)^n y] \,, \tag{6a}$$

$$x_{ns}=\pm(-1)^n x \,, \tag{6b}$$

where + (−) refers to spin up (down), x is a solution of the equation

$$x=xA_U f_1(1-z^2)/(1+x^2)^{1/2} \,, \tag{6c}$$

$A_U=(U/2t_0\pi)$, and $z^2=(x^2+y^2)/(1+x^2)$. Here y is the dimensionless dimerization

$$y=(-1)^n(2\alpha/t_0)u_n=(2\alpha/t_0)u_0 \,, \tag{7a}$$

and f_1 is the lattice sum defined in Eq. (8) below. If at this point we minimize the energy with respect to y, we obtain the HF value for the ground-state dimerization. Then x and y are simultaneous solutions of Eqs. (6c) and (7b),

$$y=yA_\alpha(1+x^2)^{1/2} \times[f_1(1-z^2)-f_2(1-z^2)]/(1-y^2) \,, \tag{7b}$$

where $A_\alpha=(4\alpha^2/t_0k\pi)$. The functions f_1 and f_2 are the lattice sums

$$f_j(\eta)=\frac{\pi}{N}\sum_{-N/4<n\leq N/4}[1-\eta\sin^2(2\pi n/N)]^{\mp 1/2}\,, \tag{8}$$

where the $-$ ($+$) refers to $j=1$ (2). The normalization has been chosen so that in the limit $N\rightarrow\infty$, f_1 and f_2 become, respectively, the complete eliptic integrals of the first and second kind. The total energy per electron of the system in the HF ground state is

$$\frac{\langle\psi^{\mathrm{HF}}|H|\psi^{\mathrm{HF}}\rangle}{N}=\frac{2t_0}{\pi}\left[\frac{y^2}{A_\alpha}+\frac{x^2}{A_U}-2(1+x^2)^{1/2}f_2(1-z^2)\right]. \tag{9}$$

Finally, the energy gap for charge excitations, that is, the energy required to add an electron to the system minus the energy to add a hole, is

$$E_{\mathrm{gap}}=4t_0(x^2+y^2)^{1/2}\,. \tag{10}$$

Before proceeding to the perturbative calculations, it is interesting to consider some of the properties of the HF ground state. Although, as discussed above, the properties are not correct for the purely one-dimensional model, it has been shown[8(a)] that in anisotropic three-dimensional systems that are not too one-dimensional, the one-dimensional HF results are valid. Thus they are interesting in their own right.

Both x and y are functions of the two dimensionless coupling constants A_U and A_α. In the absence of electron-electron interactions, $A_U=0$, the Peierls or SSH Hamiltonian is recovered from Eq. (1). For $N=\infty$ and $A_U=0$, and $x=0$, the value of y which minimizes Eq. (2) has the asymptotic behavior

$$y(A_\alpha,A_U=0)\sim\begin{cases}4\exp(-1/A_\alpha-1), & A_\alpha\ll 1\\ 1, & A_\alpha\gg 1\,.\end{cases} \tag{11}$$

For $A_\alpha=0$, H in Eq. (1) becomes the Hubbard Hamiltonian, hence $y=0$ and

$$x(A_\alpha=0,A_U)\sim\begin{cases}4\exp(-1/A_U), & A_U\ll 1\\ (\pi/2)A_U, & A_U\gg 1\,.\end{cases} \tag{12}$$

In both cases the order parameter is a monotonically increasing function of the coupling constant and is nonzero for any nonzero value of the coupling constant.

When A_α and A_U are both nonzero, the competition between finite α and finite U effects produces the "Hartree-Fock phase" diagram shown in Fig. 2 for $N=\infty$. This figure describes the nature of the HF ground state in the parameter space spanned by A_U and A_α. Following a vertical line from the A_α axis we find that for small A_U (that is, for weak electron-electron interaction) the HF ground state is the same as for $U=0$, with $x=0$ and $y=y(A_\alpha,0)$. As the strength of the electron-electron repulsion is increased, a coexistence region is crossed in which $0<y<y(A_\alpha,0)$ and $0<x<x(0,A_U)$. In this region both types of interactions play a role in determining the ground state. Finally, as A_U is increased still further, a region in which the electron-phonon interaction is unimportant [$y=0$ and $x=x(0,A_U)$] is encountered. For small A_U the coexistence region is extremely narrow, of order $x(0,A_U)^3$, and the phase diagram can be thought of as having two phases, one in which electron-phonon interactions can be ignored and one in which electron-electron interactions can be ignored. The boundary between the two regions, ignoring corrections of order $x(0,A_U)^3$, is the line

$$A_{U_c}=A_\alpha/(1+A_\alpha)\,. \tag{13}$$

This equation determines a critical Hubbard-interaction strength $U_c(A_\alpha)$ for each value of the

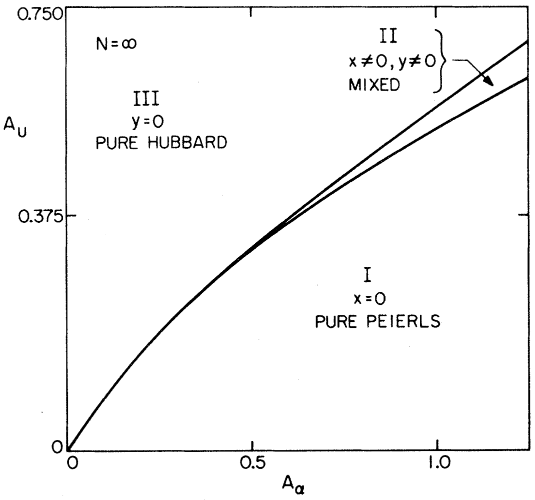

FIG. 2. Hartree-Fock "phase" diagram for an $N=\infty$ ring. The nature of the ground state is plotted in the parameter space spanned by A_U and A_α. In region I, $x=0$ and $y=y(A_\alpha,0)$; in region II, $0<x<x(0,A_U)$ and $0<y<(A_\alpha,0)$; in region III, $x=x(0,A_U)$ and $y=0$.

electron-phonon coupling A_α. For $U < U_c$, the electron-electron interactions have no effect on the HF ground state, and for $U > U_c$ the electron-phonon interaction has no effect on the ground state.

B. Perturbative results

To obtain an improved estimate of the ground-state properties, we will calculate the ground-state energy in second-order Goldstone perturbation theory about the HF ground state. For the pure Hubbard model ($y=0$) perturbation theory is not convergent, even for small $U/2t_0$, due to the presence of vanishing energy denominators. For finite y, there is a gap in the excitation spectrum which insures that the perturbation theory has a finite radius of convergence. In Ref. 3 we will show that perturbation theory is convergent for $U \lesssim \pi t_0/|\ln y|$. Thus for small U and finite y, which is the case of primary interest to us in this paper, our results are, in this sense, rigorous. Even in the pure Hubbard model, an asymptotic expansion for the ground-state energy in powers of $(U/2t_0)$ exists,[9] of which the second-order perturbation theory results are the leading-order term. Thus even in the limit $y \to 0$ we expect the present results to be reasonably reliable.

The second-order corrections to the HF energy [Eq. (9)] are obtained by straightforward calculation

$$\frac{E}{N}=\frac{\langle\psi^{\mathrm{HF}}|H|\psi^{\mathrm{HF}}\rangle}{N}-\frac{U^2}{2t_0}K(x,y)\,, \tag{14}$$

where K is given by Eq. (C5) in Appendix C. Schematically,

$$K(x,y)=\sum_j \frac{|M_i(x,y)|^2}{\Delta E_j(x,y)}\,, \tag{15}$$

where the sum on j runs over all excited states with one particle and one hole of either spin, M_j is the appropriate matrix element, and ΔE_j is the excitation energy. Since we are predominantly interested in the region of parameter space where x is zero, only the y dependence of K concerns us. This dependence is shown in Fig. 3 for various values of N. Notice the divergent nature of K for small y when $N=4n$. As suggested in Eq. (3),

$$K(y,0)=\frac{A_N}{Ny}+\tilde{K}_N(y,0) \tag{16}$$

where $A_N=0$ for $N=4n+2$ and 1 for $N=4n$, and $\tilde{K}$ is well behaved in the limit $y\to 0$. This pathology vanishes as $N\to\infty$.

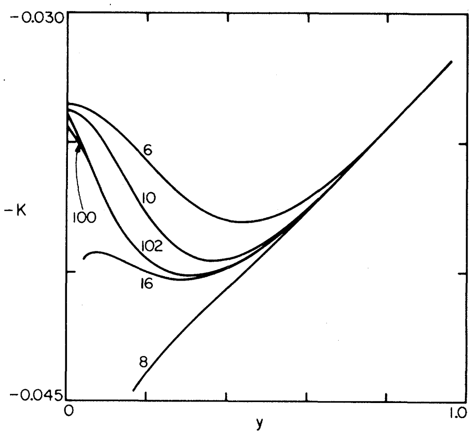

FIG. 3. Correlation energy for various N. Plotted is $-K(y,x=0)$ as defined in Eq. (15). Notice that the curves for $N=4n$ and $4n+2$ bound the asymptotic $N\to\infty$ curve as suggested in Eq. (16).

The most striking result in Fig. 3 is that for small y, K is an increasing function of y. The minus sign in Eq. (14) implies that in the presence of finite U, the Peierls instability (that is, the tendency towards dimerization) is enhanced. This result was obtained previously by Horsch[10] on the basis of a partial summation of the second-order contribution to the ground-state energy. The present treatment is exact to second order, and is hence more accurate (see Sec. III).

The y dependence of K in Fig. 3 results from a competition between two effects. As y is increased, the gap in the excitation spectrum is opened. This tends to increase the energy denominators in Eq. (15), and hence to decrease K. Owing to the short-range nature of the Hubbard interaction, there are substantial contributions to the sum in Eq. (15) from high-lying excited states. Thus for small y the effect on K of the increased energy denominators is small. The other effect of a finite y is to double the unit cell or introduce half-sized reciprocal-lattice vectors. This permits a new class of intermediate states j with total lattice momentum $\pm\pi/a$ (umklapp processes) to enter the sum in Eq. (15). For small y, the umklapp terms dominate the y dependence of K.

We note that for small y and $N\to\infty$, K is approximately linear in y. Although the actual analytic form of K involves logarithms on y, it is simpler for purposes of future calculation to make the approximation

$$K \approx K_0 + |y| K_y \,, \tag{17}$$

where $k_0 = 0.0339\ldots$ and $K_y \approx 0.03$. This approximation form of K is valid for $x=0$ and $y \lesssim 0.2$ as can be seen from Fig. 3.

A final, fortuitous property of K is that for large U it can be shown that $K \sim 1/U^5$. Thus for strong interactions U the second-order corrections to the energy vanish, and the asymptotically correct HF result is recovered.

The second-order corrections to the excited-state energies can also be calculated. This is done explicitly in Appendix C for the lowest-lying excited state. The results can be summarized by the equation

$$E_{\text{gap}} = E_{\text{gap}}^{\text{HF}} \left[1 + \left[\frac{U}{2t_0} \right]^2 \beta(x,y) \right] , \tag{18}$$

where $E_{\text{gap}}^{\text{HF}}$ is given by Eq. (10), and $\beta(x,y)$ is found numerically to be less than 1 for all values of x and y. Thus for small U, where the perturbation results are meaningful, the second-order corrections to the low-lying excitation spectrum are small. In what follows they will be ignored.

We summarize the results of this section in terms of an effective Hamiltonian H^{eff},

$$H^{\text{eff}} = H^{\text{HF}} - \frac{U^2}{2t_0} K(x,y) \,, \tag{19}$$

where H^{HF} is given in Eq. (1), and x is a function of y and U as determined from Eq. (6c), and for small y and $x=0$, K is approximately given by Eq. (18). The equilibrium dimerization y can now be obtained by minimizing the energy in Eq. (19) with respect to y. The self-consistency expression is the same as that for $U=0$ [Eq. (7b)] with A_α replaced by an effective electron-phonon coupling constant,

$$A_\alpha^{\text{eff}} = A_\alpha / [1 - A_\alpha \pi K_y (U/2t_0)^2 (1/y)] \,. \tag{20}$$

The low-lying excitation spectrum of the system can also be determined quite readily from H^{eff}, since it is a one-electron Hamiltonian.

III. EXACT RESULTS

In Sec. II we obtained a simple qualitative picture of the physics of the combined Peierls-Hubbard system. In this section we will consider some exact results, which take full account of correlation effects, so as to test the validity of the perturbative results.

This section is divided into two parts. Part A considers limiting cases in parameter space where exact analytic solutions can be compared to the perturbation calculations and to the finite-ring calculations of part B. Finite-size effects in the ring calculations are discussed. Part B compares, in greater detail, the perturbative results to the results of exact numerical solutions of an six-membered ring and identifies the nature of the correlation effects neglected in HF.

A. Exact analytic results; $N=\infty$

In the limiting $A_\alpha = 0$, Eq. (1) becomes the Hubbard model and has been solved exactly by Lieb and Wu.[7] The exact ground-state energy of the Hubbard model as a function of U is compared with the perturbative results in Fig. 4. In the limit of small U, the exact result for the band gap in the Hubbard model is

$$E_{\text{gap}} = (8/\pi)\sqrt{Ut_0} \exp(-1/A_U) \,. \tag{21}$$

The HF results reproduce this essential singularity exactly [Eqs. (10) and (12)] although the HF prefactor is U independent. For U/t_0 of order 1, this discrepancy is unimportant.

At large U the dimerization vanishes in the HF approximation and becomes vanishingly small in the finite-chain numerical solutions. This almost certainly is not correct in the $N \to \infty$ limit. Nonetheless, for $U \gg t_0$ the dimerization is extremely small and decreases with the $\frac{3}{2}$ power of t_0/U. To see this, we take advantage of the well-known result that for large U/t_0 charge fluctua-

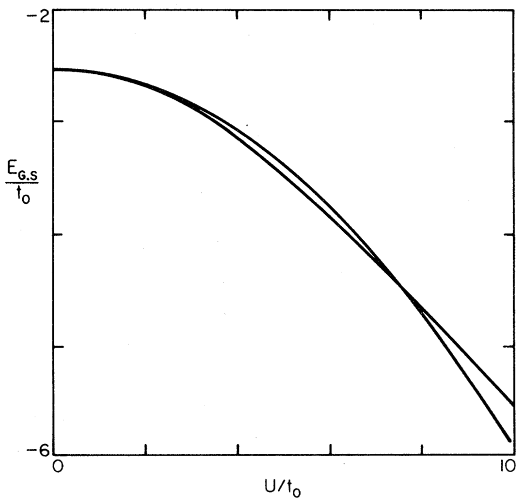

FIG. 4. Ground-state energy E_g/t_0 vs U/t_0 for the $N \to \infty$ Hubbard model. The solid curve is the exact result and the dashed curve is the result of perturbation theory.

tions are suppressed, and the Hubbard chain maps into an antiferromagnetic Heisenberg model with exchange constants

$$J_{n,n+1}=-[t_0+\alpha(u_n-u_{n+1})]^2/U$$
$$\approx-(t_0/U)[t_0+2\alpha(u_n-u_{n+1})]\ .$$

Thus while the stiffness constant k in Eq. (1) is unaffected by U, the electron energies are reduced by a factor of t_0/U. The dimerization is a result of the competition between electronic energy (which favors dimerization) and the elastic energy (which opposes it). A large U reduces the effective coupling constant A_α by a factor of t_0/U. Cross and Fischer[11] have obtained an expression for the energy of the Heisenberg model as a function of the dimerization. In our units, their result translates into the expression

$$\frac{E(y)}{t_0N}=\frac{E(y=0)}{t_0N}-0.12\left[\frac{1}{A_U}\right]y^{4/3}+\frac{y^2}{A_\alpha}\ . \tag{22a}$$

This result is believed[12] to be "exact" for small y except for possible logarithmic corrections. Thus the value of y which minimizes the total energy is found to be

$$y=0.13\left[\frac{A_\alpha}{A_U}\right]^{3/2}\ . \tag{22b}$$

The model in Eq. (1) is also exactly solvable in the unphysical, completely dimerized limit in which $y=1$, where the system breaks up into noninteracting diatomic molecules. The solution is obtained in Appendix B. It is found that the electronic energy of the ground state is given by the expression

$$\frac{E}{N}=-2t_0\left[1+\left[\frac{U}{8t_0}\right]^2\right]^{1/2}, \tag{23}$$

which agrees with the perturbative results

$$\frac{E^{\mathrm{HF}}}{N}=-2t_0\left[1+\frac{1}{2}\left[\frac{U}{8t_0}\right]^2\right],$$

up to corrections of order $(U/8t_0)^4$. We have also performed a stability analysis about this limit by allowing the system to "undimerize" a little, $y=1-\delta$ for small δ. We find that as long as

$$A_\alpha>\frac{4}{\pi}\left[1+\left[\frac{U}{8t_0^2}\right]^2\right]^{1/2},$$

the total energy is an increasing function of δ. As long as $U\ll 4t_0$ this compares favorably to the perturbation theory version of the same criterion,

$$A_\alpha>\frac{4}{\pi}\left[1+\frac{1}{2}\left[\frac{U}{8t_0}\right]^2\right]\ .$$

B. Exact numerical results; $N=6$

Exact numerical solutions[13] have been obtained for six- and eight-membered rings, $N=6$ and 8. We have been limited by computer size to $N\le 8$. Owing to the $4n$ periodicity in the ground-state properties of finite rings, we have not been able to determine the finite-size scaling behavior of our solutions.

The results are best summarized by showing the correlation energy ϵ^{corr} as a function of y for various U's. ϵ^{corr} is, by definition, the difference between the $U=0$ and the finite U ground-state energies for fixed dimerization y,

$$\epsilon^{\mathrm{corr}}(y,U)\equiv[E(y,U)-E(y,0)]/N\ . \tag{24}$$

The exact $N=6$ results for ϵ^{corr} are compared with the perturbative results in Fig. 5. The agreement is

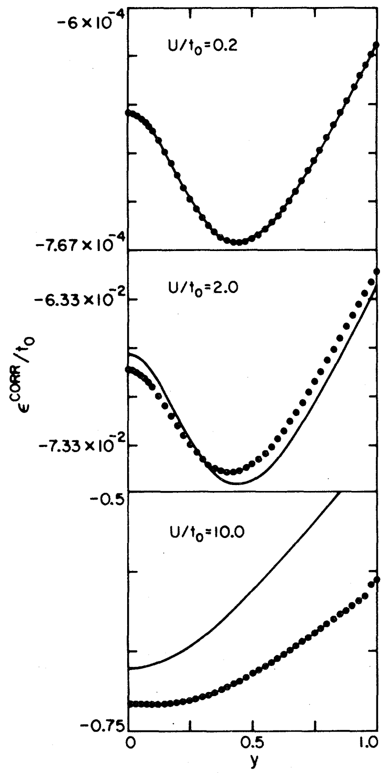

FIG. 5. Correlation energy vs y for $N=6$ and various U/t_0. The circles are the exact numerical results and the solid curves are the perturbative results.

quite good for $U<2t_0$. This is in agreement with the results of Ref. 3, where it is concluded that the perturbative results can be used with confidence for

$$U \lesssim \pi t_0 / |\ln y| \sim 2t_0 \; .$$

For $N=8$ the exact results are also in good agreement with the perturbative results as long as $y > x(U,A_\alpha=0)$. For smaller y serious disagreement occurs. We trace this to the breakdown of perturbation theory due to the degeneracy at the Fermi level. For this reason the results for $N=8$ have not been shown.

IV. THE CASE OF THE SOLITON

SSH predict that soliton excitations, which are boundaries between regions of two different senses of dimerization, $y=+y_0$ and $y=-y_0$, play a central role in determining the properties of $(\mathrm{CH})_x$. In particular, they find that the energy needed to create a charged soliton is less than the energy needed to add an electron (hole) to the conduction (valence) band. They therefore conclude that doping proceeds via the formation of charged solitons. In this section we will examine the effect of finite U on the SSH picture of $(\mathrm{CH})_x$. We will restrict ourselves to the upper right-hand portion of the phase diagram in Fig. 2, where the Hartree-Fock ground state is unaffected by U. We are interested in finding the effect of the electron-electron interactions on the shape and creation energy of charged and neutral solitons. We will do this by calculating the properties of the soliton solution in the Hartree-Fock approximation. Although we have found that order U^2 effects can change the value of the dimerization for a given A_α, in other words change A_α into a larger A_α^{eff}, we also found that the low-lying excitations are treated quite accurately within the HF approximation. Thus we expect the HF results to be valid for small U.

In the presence of a soliton, the Hartree-Fock self-consistency equations (2) and (5) become considerably more complicated than in the uniform case and must be solved numerically. Although this presents no difficulty, it is advantageous to obtain approximate analytic results first so that the structure of the solutions can be studied. Thus we will first examine the soliton solution in the restricted HF approximation.

SSH have shown that there is a localized mid-gap state of each spin associated with a soliton. In the case of a neutral soliton this state is singly occupied, while for the negative and positive solitons it is doubly occupied and unoccupied, respectively. The local electron density of spin s is given by the expression

$$\langle c_{ns}^{\dagger} c_{ns} \rangle = \tfrac{1}{2}[1+\lambda_s |\phi_0(n)|^2] \; , \tag{25}$$

where ϕ_0 is the normalized amplitude of the localized mid-gap state at site n, and $\lambda_s=+1$ or -1 if this state is occupied or unoccupied by an electron of spin s. For a soliton of width l of the form

$$u_n = (-1)^n u_0 \tanh(n/l) \; ,$$

ϕ_0 is given by

$$\phi_0(n) \simeq l^{-1/2} \cos(\pi n/2) \operatorname{sech}(n/l) \; .$$

Since the $U=0$ ground state is a product of one-electron states, the first-order correction to the total energy of the system can be computed easily. If we define ΔE to be the first-order correction in U to the energy of the system, then $\Delta E=0$ for the half-fulfilled, uniformly dimerized chain,

$$\Delta E = -U^{\mathrm{eff}}(l)/4 \tag{26a}$$

for a neutral soliton, and

$$\Delta E = +U^{\mathrm{eff}}(l)/4 \tag{26b}$$

for a charged soliton of either charge, where

$$U^{\mathrm{eff}} = U \sum |\phi_0(n)|^4 \sim U/l \; . \tag{27}$$

For the uniformly dimerized chain with an additional hole or electron, $\Delta E=0$. The charged soliton differs from the neutral one in occupation of the mid-gap state. Thus the energy splitting between the two solitions can be interpreted as the effective Coulomb repulsion $U_{eff}/2$ for electrons in the mid-gap state.

There are two features of these results which warrant attention. The first is the smallness of the effective interaction strength U^{eff} due to the large size of the soliton [$l \sim 7$ for $(\mathrm{CH})_x$]. The second is that the effect of U is to reduce the creation energy of a neutral soliton. The neutral soliton spin polarizes the electron gas in its vicinity which reduces the electron-electron repulsion somewhat.

Since $U^{\mathrm{eff}}(l)$ is a decreasing function of l, the total energy of a neutral soliton is reduced by a slight contraction and the total energy of a charged soliton by a slight expansion. In the absence of U, the energy per soliton as a function of the width l is given by the expression

$$E(l) = E_s + 2t_0 \tfrac{1}{2} k_2 (l-l_0)^2 + \cdots \; , \tag{28}$$

where $E_s \simeq 4t_0 y_0/\pi$ is the soliton-creation energy,

$l_0 \simeq (1/y_0)$ is the $U=0$ soliton width, and k_2 is the dimensionless soliton-stretching stiffness constant (k_2 can be calculated numerically as a function of A_α as in SSH). Thus for small deviations, $|l-l_0| \ll l_0$, the change in the soliton width due to the presence of U is approximately

$$|l-l_0| = U^{\text{eff}}(l_0)/4k_2 l_0 \; . \tag{29}$$

The full, unrestricted Hartree-Fock ground state was found numerically for a 41-atom chain. The topological constraints insure that there must be a soliton in the ground state of any dimerized odd-membered *ring*, and Su[14] has shown that there is also a soliton in the ground state of an odd-membered *chain*. While the absolute formation energy of a soliton cannot be derived by this procedure (since a soliton produces a change in the boundary conditions), the change of shape and energy of the soliton as a function of U can be calculated. Since SSH have already calculated the soliton-creation energy in the $U=0$ limit, the change of soliton energy as a function of U is all that we require. The numerical results are in good general agreement with the results in Eqs. (27) and (29) so long as $A_\alpha > A_U$ [$U < U_c(A_\alpha)$]. For A_U very near A_α, the first-order results break down since the soliton loses its integrity as the phase boundary $A_U \simeq A_\alpha$ is approached. The soliton shape and the spin density is shown in Figs. 6 and 7 for fixed A_α and various $A_U < A_{U_c}$. For calculational convenience, A_α was chosen such that $y(A_\alpha, 0) = 0.25$ rather than the physical $y(A_\alpha, 0) \simeq 0.14$ in $(\mathrm{CH})_x$. Note especially the slight sharpening of the neutral soliton with increasing U, and a slight spreading of the charged soliton.

V. IMPLICATIONS FOR POLYACETYLENE

In this section we will discuss the implications of the above results for interpreting the properties of $(\mathrm{CH})_x$ in terms of the SSH model. We have seen that a good description of the mixed Hubbard-Peierls system can be obtained by replacing A_α by A_α^{eff} [see Eq. (20)] and solving the resulting Hamiltonian [Eq. (1)] in the Hartree-Fock approximation. Therefore, if the parameters appropriate to $(\mathrm{CH})_x$ satisfy the condition

$$U < U_c(A_\alpha) \tag{30}$$

[see Eq. (14)], or, in other words, if $(\mathrm{CH})_x$ falls in the "pure Peierls" region of the parameter space in Fig. 2, then the only major effect of U on the

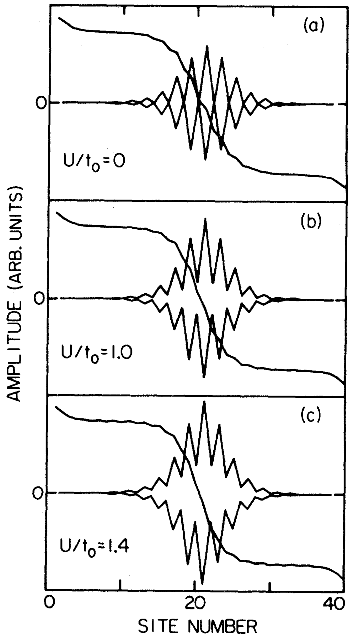

FIG. 6. Profile of a neutral soliton for various U. The tanh-like curve is the staggered ion displacement $\psi(n) = (-1)^n u_n$. The saw-toothed lines are the staggered spin-polarized charge density $G_s(n) = (-1)^n (\langle c_{ns}^\dagger c_{ns} \rangle - \frac{1}{2})$, for spin up (upper) and spin down (lower), respectively. The chain length was $N=41$. Notice the very slight broadening of the soliton.

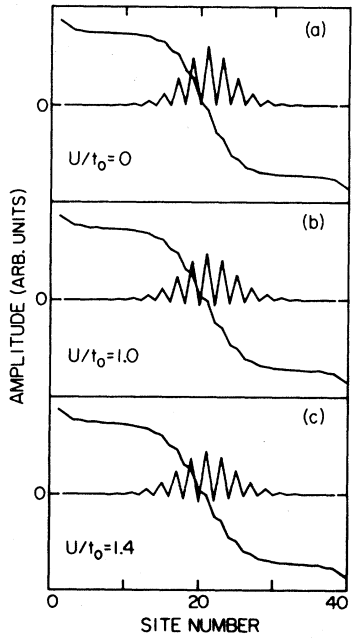

FIG. 7. Profile of a charged soliton for various U. The labeling is as in Fig. 6. The spin-up and spin-down curves coincide. Notice the very slight narrowing of the soliton.

ground-state properties is to renormalize the electron-phonon coupling constant A_α. Recently, the dimerization has been measured in x-ray scattering, and it is found[15] that $u_0 = 0.037 \pm 0.003$ Å. The existence of dimerization is strong indirect evidence that Eq. (30) is satisfied.

Ideally, we would like to estimate the parameters A_α and U from microscopic calculations and verify Eq. (30) directly. There is general agreement that $t_0 \approx 2.5$ eV. However, it is apparently difficult to determine A_α to better than a factor of 2, and estimates of U vary by a factor of 5 or more.[5] Thus the best estimates of these parameters are obtained by indirect means.

The energy gap in $(\mathrm{CH})_x$ has been measured to be $E_{\mathrm{gap}} = 1.4 - 1.8$ eV. From the relation between A_α^{eff} and E_{gap} [see Eqs. (10) and (11)], we infer that A_α^{eff} is in the range $0.41 - 0.45$. Thus Eq. (30) places an upper bound on U, $U < 4.5$ eV. If the value of the bare A_α were known, then U could be determined unambiguously from Eq. (20). From the measured value of u_0, the electron-phonon coupling constant can be determined to be $\alpha = E_{\mathrm{gap}}/8u_0 = 4.5 - 6.0$ eV/Å [see Eqs. (7a) and (10)]. The value of the stiffness constant quoted by SSH is $k = 21$ eV/Å^2. In order that the condition $A_\alpha \leq A_\alpha^{\mathrm{eff}}$ be met, this is roughly a lower bound on k. In order for a value of U near 4.5 eV to be consistent with the observed band gap, it is necessary that $A_\alpha \approx 3/4 A_\alpha^{\mathrm{eff}}$. This then, implies a k in excess of 30 eV/Å^2.

Our conclusions as to the importance of U differ from those of Horsch,[6] which were based on much larger estimates of U obtained from microscopic calculations. We note, however, that even if the observed gap were caused solely by the Hubbard interaction ($A_\alpha = 0$), a value of $U \sim 5$ eV would be deduced from the known dependence of E_{gap} on U. This then, must surely represent an upper bound on U, independent of the validity of any approximation.

For $U < U_c$, which seems to hold for $(\mathrm{CH})_x$, the effects of U on the excitation spectrum are easily obtained. The presence of a finite U of order $2-3$ eV changes the soliton-creation energies by a small amount, $U^{\mathrm{eff}}/4 \sim \pm 0.1$ eV, depending on the charge of the soliton. One of the important conclusions of SSH is that when a small number of electrons (or holes) are added to the system [as in lightly doped $(\mathrm{CH})_x$], they will produce charged solitons rather than remaining in the conduction (valence) band of the perfectly dimerized system. This follows from the fact that the soliton-creation energy in the SSH model is roughly 0.25 eV less than the energy needed to add an electron to the conduction band. As long as $U^{\mathrm{eff}}/4 < 0.25$ eV, this conclusion remains true even in the presence of U. Thus the major effect of U on the results of SSH is to increase the energy and width of a charged soliton slightly and to decrease the energy and width of a neutral soliton. It is also probable that finite U increases the importance of quantum fluctuations of the lattice.

Note. Most of the first-order perturbation-theory results on the effect of U on the soliton energy were first derived by J. R. Schrieffer but never published in a complete form (see Ref. 16). Some of the Hartree-Fock results discussed in this paper were obtained independently and simultaneously by Subbaswamy and Grabowski.[17]

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APPENDIX A: HARTREE-FOCK RESULTS

A simple way of constructing an N-particle Hartree-Fock trial state $|\psi(h)\rangle$ is to consider the N-particle ground state of a general one-electron Hamiltonian

$$H^{\mathrm{HF}} = \sum_{\substack{ns \\ n's'}} h_{ns,n's'} c_{ns}^{\dagger} c_{n's'} \; . \tag{A1}$$

As the Hamiltonian H in Eq. (1) commutes with $\hat{N}_s = \sum_n c_{ns}^{\dagger}$, the number of electrons with spin s, the ground state can be chosen to be an eigenstate of $\hat{N}_\uparrow$ and $\hat{N}_\downarrow$. Thus without loss of generality, the matrix h can be taken to be diagonal in the spin index.

The Hartree-Fock ground state is found by setting the variation of $\langle \psi(h) | H | \psi(h) \rangle$, with respect to h, equal to zero as follows:

$$\frac{\delta \langle \; | H | \psi \rangle}{\delta h_{ns,n's}} = \frac{\delta \langle \psi | H^{\mathrm{HF}} | \psi \rangle}{\delta h_{ns,n's}} + \frac{\delta \langle \psi | (H - H^{\mathrm{HF}}) | \psi \rangle}{\delta h_{ns,n's}} = 0 \; . \tag{A2}$$

The expectation values in Eq. (A2) can be expressed in terms of one-particle correlation functions, since $|\psi\rangle$ is a product state, so that

$$\langle c_{n\uparrow}^{\dagger}c_{n\uparrow}-\tfrac{1}{2})(c_{n\downarrow}^{\dagger}c_{n\downarrow}-\tfrac{1}{2})\rangle=\langle(c_{n\uparrow}^{+}c_{n\uparrow}-\tfrac{1}{2}\rangle\langle(c_{n\downarrow}^{\dagger}c_{n\downarrow}-\tfrac{1}{2})\rangle\ . \tag{A3}$$

Thus the variation in Eq. (A2) produces the following set of minimization conditions on h:

$$\begin{aligned}0=&\sum_{\substack{|m-m'|>1\\ s'}}\frac{\delta\langle c_{ms'}^{\dagger}c_{m's'}\rangle}{\delta h_{ns,n's}}(-h_{ms',m's'})+\sum_{\substack{m\\ s'}}\frac{\delta\langle c_{ms'}^{\dagger}c_{m+1s'}\rangle}{\delta h_{ns,n's}}[t_0+\alpha(u_n-u_{n+1})-h_{ms,m+1s}]\\ &+\sum_{\substack{m\\ s'}}\frac{\delta\langle c_{ms'}^{\dagger}c_{m-1s'}\rangle}{\delta h_{ns,n's}}[t_0+\alpha(u_n-u_{n+1})-h_{ms',m-1s'}]+\sum_{\substack{m\\ s'}}\frac{\delta\langle c_{ms'}^{\dagger}c_{m-1s'}\rangle}{\delta h_{ns,n's}}[U(\langle c_{m\bar{s}'}^{\dagger}c_{m\bar{s}'}\rangle-\tfrac{1}{2})-h_{ms,ms'}]\ .\end{aligned} \tag{A4}$$

Since this equation must be satisfied for all n,n',s, the coefficients of each term should vanish individually. Thus

$$h_{ms,m's}=0 \text{ for } |m-m'|>1\ , \tag{A5a}$$

$$h_{ms,m+1s}=h_{m+1s,ms}=t_0+\alpha(u_n-u_{n+1})\ , \tag{A5b}$$

or, in the notation of the text,

$$t_m\equiv t_0[1+(-1)^m y_m]=t_0+\alpha(u_n-u_{n+1}) \tag{A5c}$$

and

$$h_{ms,ms}=U(\langle c_{ms}^{\dagger}c_{ms}\rangle-\tfrac{1}{2}) \tag{A6a}$$

or, in the notation of the text,

$$x_{ms}=(-1)^m(U/2t_0)(\langle c_{ms}^{\dagger}c_{ms}\rangle-\tfrac{1}{2})\ . \tag{A6b}$$

Thus as promised, we have shown that the Hartree-Fock Hamiltonian in Eq. (3) is sufficiently general to obtain the Hartree-Fock ground state of H.

Care must be taken in using Eq. (2) to find the ionic configuration that minimized the adiabatic potential energy since the Hamiltonian in Eq. (1) is formally unstable with respect to a shrinking of the lattice constant $u_n=(n+1)u_0$. We are only interested in patterns of lattice distortion that do not change the overall length of the system. This constraint is most easily enforced by adding a Lagrange multiplier to H,

$$H\rightarrow H-\lambda\sum_n\alpha(u_n-u_{n+1})\ , \tag{A7}$$

where $\sum_n(u_n-u_{n+1})=\delta L$, the change in length of the system. λ is then chosen such that $\delta L=0$.

With this concern removed, the minimization condition in Eq. (2) can be expressed in terms of one-particle correlation functions in much the same way as the Hartree-Fock conditions were,

$$\frac{\delta\langle H\rangle}{\delta(u_n-u_{n+1})}=0=k(u_n-u_{n+1})+\alpha\left[\sum_s(\langle c_{ns}^{\dagger}c_{n+1s}\rangle+\text{c.c.})-\lambda\right] \tag{A8}$$

or, in terms of

$$y_n=(-1)^n(\alpha/t_0)(u_n-u_{n+1})\ ,$$

$$y_n=-(-1)^n(\alpha^2/t_0k)\times\left[\sum_s(\langle c_{ns}^{\dagger}c_{n+1s}\rangle+\text{c.c.})-\lambda\right]\ . \tag{A9}$$

To ensure $\delta L=0$, we must take

$$\lambda=\sum_{ns}(\langle c_{ns}^{\dagger}c_{n+1s}\rangle+\text{c.c.})/N\ . \tag{A10}$$

To obtain the self-consistent Hartree-Fock ground state for a nontranslationally invariant system, such as the solitons considered in Sec. IV, the Hartree-Fock equations are solved iteratively. First values of $\vec{x}$ and $\vec{t}$ are assumed and the corresponding Hartree-Fock Hamiltonian, H^{HF} in Eq. (3), is constructed. The ground state of this Hamiltonian is obtained and used to calculate new values of the parameters $\vec{x}$ and $\vec{t}$ according to Eqs. (A5c), (A6b), and (A9). This process is repeated until self-consistency is obtained.

For the uniform ring a self-consistent solution of the Hartree-Fock equations can be obtained analytically. In this case the translational symmetry is partially broken by a doubling of the unit cell. This doubling is a consequence of the band being half filled. We let $x_{ns}=(-1)^n x_s$, $x_\uparrow=-x_\downarrow=x$, and $t_n=t_0[1+(-1)^n y]$ in Eq. (3), so that

$$H^{\mathrm{HF}}=t_0\left[\sum_{ns}[1+(-1)^n y](c_{ns}^\dagger c_{n+1s}+\mathrm{H.c.})\right.$$
$$\left.+\sum_n(-1)^n x(c_{n\uparrow}^\dagger c_{n\uparrow}-c_{n\downarrow}^\dagger c_{n\downarrow})\right]. \qquad \text{(A11)}$$

The one-electron eigenstates of H^{HF} are the Bloch states

$$|ks\rangle=\sum_n\frac{e^{i2nk}c_{2ns}^\dagger+e^{i(2n+1)k}\beta_{ks}c_{2n+1s}^\dagger}{[N(1+|\beta_{ks}|^2)/2]^{1/2}}|0\rangle \qquad \text{(A12)}$$

which have energy

$$E_k=\pm 2t_0(x_x^2+\epsilon_k^2)^{1/2}. \qquad \text{(A13)}$$

Here

$$\epsilon_k=[\cos^2(k)+y^2\sin^2(k)]^{1/2}$$

and

$$\beta_{ks}=-\frac{x_s+(x_s^2+\epsilon_k^2)^{1/2}}{[\cos(k)+iy\sin(u)]}. \qquad \text{(A14)}$$

The N-electron ground state is the product state of all the negative-energy Bloch states. The various one-particle correlation functions can be evaluated simply in this state with the results

$$(\langle c_{ns}^\dagger c_{ns}\rangle-\tfrac{1}{2})=-\frac{(-1)^n x_s}{\pi(1+x_s^2)^{1/2}}f_1(1-z^2), \qquad \text{(A15)}$$

$$(\langle c_{ns}^\dagger c_{n+1s}\rangle+\mathrm{H.c.})=-\frac{(1+x^2)^{1/2}}{\pi}\left[\left[\frac{f_2(1-z^2)}{(1-y^2)}-z^2 f_1(1-z^2)\right]+y(-1)^n\left[\frac{f_1(1-z^2)}{(1+x^2)}-f_2(1-z^2)\right]\right], \qquad \text{(A16)}$$

where, as in the text,

$$z^2=(y^2+x^2)/(1+x^2)$$

and the f_j are the lattice sums defined in Eqs. (6c) and (7b). These expressions for the correlation functions can be substituted into the self-consistency Eqs. (A.5c), (A.6b), and (A.9), to obtain Eqs. (6a), (6b), and (7a) in the text.

To become familiar with the behavior of x and y as a function of the coupling constants, we will briefly examine the asymptotic behavior of the self-consistency equations. To do this it is necessary to study f_1 and f_2 in the limits $z \ll 1$ and $(1-z^2)\ll 1$.

For a finite lattice it is easy to show that for $Z^2<1/N$ and for $N=4n$,

$$\begin{aligned} f_1(1-z^2)&\sim\frac{2\pi}{N|z|}+\mathcal{O}(z^2),\\ f_2(1-z^2)&\sim f_2(1)+\frac{2\pi}{N}|z|+\mathcal{O}(z^2), \end{aligned} \qquad \text{(A17)}$$

while for $N=4n+2$,

$$\left.\begin{aligned} &f_1(1-z^2)\\ &[f_2(1-z^2)-f_1(1)] \end{aligned}\right\}\sim\mathcal{O}(z^2). \qquad \text{(A18)}$$

The difference between the $N=4n$ and $N=4n+2$ cases is due to the existence of a zero-energy one-electron state $\cos(k)=0$, for the noninteracting $N=4n$ ring, and the absence of such a state for the $N=4n+2$ ring. Equation (A17) ensures that for a ring of $N=4n$,

$$x_0(A_U)\equiv x(A_\alpha=0,A_U)>0$$

for any nonzero A_U, and

$$y_0(A_\alpha)\equiv y(A_\alpha,A_U=0)>0$$

for any nonzero A_α. However, for $N=4n+2$ there is a threshold value of A_U and A_α below which x_0 and y_0, respectively, vanish. For z near 1, that is, in the strong-coupling limit,

$$f_j(1-z^2)=\frac{\pi}{2}[1\pm(1-z^2)F+\cdots], \qquad \text{(A19)}$$

where $j=1$ corresponds to $+$, $j=2$ corresponds to $-$, and

$$F=\sum_{-N/4<n\le N/4}\frac{\sin^2(2\pi n/N)}{N}. \qquad \text{(A20)}$$

In the limit $N\to\infty$, f_j becomes the complete elliptic integral of the jth kind.

APPENDIX B: THE CASE OF ALMOST COMPLETE DIMERIZATION

In the limit

$$y \equiv (-1)^n \alpha (u_n - u_{n+1})/2t_0 = 1 \, ,$$

the Hamiltonian in Eq. (1) breaks up into an array of completely independent diatomic molecules. Although the assumption of linear electron-phonon coupling implicit in Eq. (1) will break down long before this limit is reached in any physical system, the Hamiltonian is exactly diagonizable in this limit and the results can be compared with the corresponding Hartree-Fock results to obtain some feeling for their range of validity. We will also examine the case of nearly complete dimerization, $y = 1 - \delta$ with $\delta \ll 1$. This allows us to calculate exactly, the range of parameters over which $y = 1$ is the ground-state configuration of Eq. (1) (we impose the constraint $y \leq 1$). This result can be compared with the same stability analysis in the Hartree-Fock approximation.

We start with $y = 1$, in which case we need only solve a two-site Hubbard model:

$$\begin{aligned} H = {} & t_0 \sum_s (c^\dagger_{0s} c_{1s} + \text{H.c.}) \\ & + U \sum_n (c^\dagger_{n\uparrow} c_{n\uparrow} - \tfrac{1}{2})(c^{+}_{n\downarrow} c_{n\downarrow} - \tfrac{1}{2}) \, . \end{aligned} \tag{B1}$$

The two-electron (half-filled) ground state is easily found to be the singlet state

$$\begin{aligned} |\psi\rangle = {} & \frac{1}{\sqrt{2}} [\alpha (a^\dagger_{0\uparrow} a^\dagger_{1\downarrow} + a^\dagger_{1\uparrow} a^\dagger_{0\downarrow}) \\ & + \beta (a^\dagger_{0\uparrow} a^\dagger_{0\downarrow} + a^\dagger_{1\uparrow} a^{+}_{1\downarrow})] | 0 \rangle \end{aligned} \tag{B2}$$

which has electronic energy ϵ_0 per electron,

$$\begin{aligned} \epsilon_0 & = -2t_0 [1 + (U/8t_0)^2]^{1/2} \\ & = 2t_0 [1 + \tfrac{1}{2} (U/8t_0)^2 + \cdots] \, . \end{aligned} \tag{B3}$$

The perturbative result for the ground-state energy is easily found to second order in U,

$$\epsilon^{\text{pert}} = -2t_0 [1 + \tfrac{1}{2} (U/8t_0^2)] \, .$$

As long as U is less than the bandwidth $4t_0$, perturbation theory gives a reasonable estimate of the ground-state energy. α and β in Eq. (B2) are, respectively,

$$\begin{aligned} \alpha & = \left[\frac{1}{2} \right]^{1/2} \left[1 + \frac{U}{4|\epsilon_0|} \right]^{1/2} , \\ \beta & = -\left[\frac{1}{2} \right]^{1/2} \left[1 - \frac{U}{4|\epsilon_0|} \right]^{1/2} . \end{aligned} \tag{B4}$$

For $y = 1 - \delta$ we can write the Hamiltonian in Eq. (1) as an unperturbed perfectly dimerized part,

$$\begin{aligned} H_0 = {} & \sum_{ns} 2t_0 (c^\dagger_{2ns} c_{2n+1s} + \text{H.c.}) \\ & + \sum_n U (c^\dagger_{n\uparrow} c_{n\uparrow} - \tfrac{1}{2})(c^\dagger_{n\downarrow} c_{n\downarrow} - \tfrac{1}{2}) \\ & + (2t_0/\pi A_\alpha) \sum_n (1)^2 \, , \end{aligned} \tag{B4a}$$

and as a δ-dependent perturbation

$$\begin{aligned} H' = {} & -t_0 \sum_{ns} (-1)^n \delta (c^\dagger_{2ns} c_{2n+1s} + \text{H.c.}) \\ & + (2t_0/\pi A_\alpha) \\ & + (2t_0/\pi A_\alpha) \sum_n (-2\delta + \delta^2) \, . \end{aligned} \tag{B4b}$$

The ground state of H_0 is a product of molecular ground states of the form of Eq. (B2). For small δ, the effect of H can be estimated with the use of first-order perturbation theory in δ:

$$\Delta E = 2N \delta t_0 \left[\frac{t_0}{|\epsilon_0|} - \frac{2}{\pi A_\alpha} \right] . \tag{B5}$$

The stability condition $\Delta E > 0$ is thus

$$A_\alpha > (4/\pi)(\epsilon_0/2t_0) \, . \tag{B6}$$

If the same procedure is followed, with the use of the perturbation-theory ground state instead of the actual ground state, the resulting stability condition is

$$A_\alpha > (4/\pi)[1 + \tfrac{1}{2} (U/8t_0)^2] \, . \tag{B7}$$

Again, for U less than the bandwidth, the agreement between Eqs. (B6) and (B7) is good.

APPENDIX C: CORRECTIONS TO HF RESULTS

In this appendix we derive the first perturbation corrections to the HF results. Thus we consider as our unperturbed Hamiltonian, H_0, the HF Hamiltonian in Eq. (A11), and as the perturbation,

$$H' = U\sum_n (c_{n\uparrow}^{\dagger}c_{n\uparrow}-\tfrac{1}{2})(c_{n\downarrow}^{\dagger}c_{n\downarrow}-\tfrac{1}{2}) - \sum_n (-1)^n x(c_{n\uparrow}^{+}c_{n\uparrow}-c_{n\downarrow}^{\dagger}c_{n\downarrow}) \tag{C1}$$

where, since we have added an artificial spin-density wave term into the unperturbed Hamiltonian, we must subtract it out again in H'. Note, however, that $H=H_0+H'$, so we are at least formally justified in this procedure. For now we will treat x as arbitrary although eventually we will require that it satisfy the HF self-consistency condition Equation (6c). The results of ordinary perturbation theory can be obtained by setting $x=0$.

The ground state $|G\rangle$ and all the excited states $|j\rangle$ of H_0 can be obtained as products of the one-electron eigenstates found in Eq. (A.12). The second-order contribution to the energy can be computed from these states according to the usual result of second-order Goldstone perturbation theory

$$E^{(2)}=\sum_{\alpha}\frac{|\langle G|H'|j\rangle|^2}{E_G-E_j}\ . \tag{C2}$$

Two types of intermediate states can, in principle, contribute to the sum in Eq. (C2): (1) those with one electron and one hole with total spin zero, and (2) those with a spin-up electron and a spin-down electron and hole. Note that if $x=0$, only terms of type (2) are possible, for which reason we will refer to the contribution from these states as the "normal" part and to those from states of type (1) as the "anomalous" terms. Both contributions can be found by straightforward algebra:

$$E^{(\mathrm{anom})}=-x^2\left[1-\frac{U}{\pi}\frac{f_1(1-z^2)}{(1+x^2)^{1/2}}\right]^2\frac{\pi}{N}\sum_k\left[\frac{\epsilon_k}{\mathscr{E}_k}\right]^2 \tag{C3}$$

and

$$E^{(\mathrm{norm})}=-\left[\frac{U}{2t_0}\right]^2K(x,y)\ , \tag{C4}$$

where

$$K(x,y)=\frac{1}{2N^3}\sum_{\substack{k_1k_2\\k_3}}\frac{1}{[\mathscr{E}_1+\mathscr{E}_2+\mathscr{E}_3+\mathscr{E}_4]}\frac{1}{[\mathscr{E}_1\mathscr{E}_2\mathscr{E}_3\mathscr{E}_4]} \times(\mathscr{E}_1\mathscr{E}_2\mathscr{E}_3\mathscr{E}_4-2x^2\mathscr{E}_1\mathscr{E}_2+x^4+c_1c_2c_3c_4-2c_1c_2y_3y_4+4c_1c_3y_2y_4+y_1y_2y_3y_4) \tag{C5}$$

and, as in Appendix A, $z^2=(x^2+y^2)/(1+x^2)$, $\epsilon_k=[\cos^2(k)+y^2\sin^2(k)]^{1/2}$, and $\mathscr{E}_k=(x^2+\epsilon_k^2)^{1/2}$. In Eq. (C5) we have adopted the shorthand $\mathscr{E}_{k_j}=\mathscr{E}_j$, $y_j=y\ \sin(k_j)$, and $c_j=\cos(k_j)$, and we have defined $k_4=k_2-k_1-k_3$. Notice that when x is chosen to satisfy the HF self-consistency equation (6c), or if $x=0$, the anomalous contribution to the energy vanishes.

The same procedure can be used to calculate the change in excitation energy of any excited state. To do this we must calculate the second-order change in the excited-state energy and subtract from it the change in the ground-state energy. We consider here the change in the gap energy. Hence, we consider the energy of the spin-zero excited state with an electron and hole with wave numbers $\pi/2a$. Again, "anomalous" terms vanish when x is chosen consistently, leaving only the "normal" term:

$$E_{\mathrm{gap}}^{(2)}=-U^2\beta(x,y)\ , \tag{C6}$$

$$\beta(x,y)=\frac{1}{N^2}\sum_{k_1k_2}\frac{1-\delta_{k_2},k_0}{(\epsilon_0+\epsilon_1+\epsilon_2+\epsilon_3)(\epsilon_0\epsilon_1\epsilon_2\epsilon_3)}\left[2x^2[\epsilon_0(\epsilon_1-\epsilon_2)-\epsilon_1\epsilon_2]+2x^4 + \frac{2\epsilon_0}{\epsilon_1+\epsilon_2+\epsilon_3-\epsilon_0}\{\epsilon_0\epsilon_1\epsilon_2\epsilon_3-x^2[(2\epsilon_1-\epsilon_2)-2\epsilon_1\epsilon_2+\epsilon_1\epsilon_3] - x^4+y(2y_1c_2c_3-y_2c_1c_3+y_1y_2y_3)\}\right]\ , \tag{C7}$$

where $k_0=\pi/2a$ and $k_3=k_0+k_2-k_1$. $\beta(x,y)$ and $K(x,y)$ can be evaluated numerically.

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$$E(U)=E_0+\mathrm{sgn}(U)f\left[\left(\frac{U}{t_0}\right)^2\right],$$

where $f(x)$ is an analytic function about $x=0$, $f=ax+bx^2+\dots$.

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$$x(A_\alpha,A_U)=\frac{U}{2t_0}\left[-\left(\frac{\partial E_q}{\partial U}-\frac{1}{4}\right)\right]^{1/2}.$$

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