Soliton Energetics in Peierls-Hubbard Models

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We study the effect of electron-electron correlations on the energetics of solitons in electron-phonon models of quasi one-dimensional materials. In these combined Peierls-Hubbard models, by use of quantum Monte Carlo techniques, we (1) establish that the ground state of an odd chain, singly charged or neutral, is a soliton; (2) calculate neutral-soliton creation energies; and (3) prove that "soliton doping" persists in the presence of correlations. We discuss the relevance of our results for *trans*-polyacetylene.

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In recent years it has become increasingly clear that both electron-electron and electron-phonon interactions can be important in real quasi one-dimensional materials, such as organic charge transfer salts and conducting polymers. In *trans*-polyacetylene [*trans*-$(CH)_x$], the prototype conducting polymer, for instance, the occurrence of negative spin densities on alternate carbon atoms[1] and the absence of neutral-soliton optical absorption at "midgap"[2] demonstrate the importance of electron correlations. This is further indicated by the ordering of excited states in finite polyenes.[3] Previously, the neglect of electron-electron interactions in models for $(CH)_x$ and related systems was justified by theoretical work that predicted the destruction of ground-state dimerization in the presence of moderate electron correlations.[4]

Recent demonstrations[5,6] that even relatively strong correlations actually *enhance* ground-state dimerization necessitate a thorough reexamination of the predictions of purely electron-phonon models[7,8] for soliton and other excited-state properties. In particular, the occurrence of neutral-soliton absorption near the main optical peak[2] would imply that the optical gap in $(CH)_x$ is dominated by electron correlations rather than by dimerization.[9] For such strong correlations, Hartree-Fock[4,10] and perturbative[10] treatments of soliton energetics are no longer valid,[5,6,9] as these maintain the original one-electron band picture valid in the zero-correlation Su-Schrieffer-Heeger (SSH)[7] limit [and are known[5,6,9] to be qualitatively incorrect in the anticipated region of correlation strengths in $(CH)_x$ [3-5,6,9]]. Exact theories of finite polyene radicals,[9] both within Pariser-Parr-Pople parametrizations and the (Heisenberg) spin Hamiltonian, have examined spin densities, optical gaps, and interactions between neutral-soliton pairs in the spin limit. Limitations of relatively small system size and difficulties associated with the exact diagonalization procedure imply that such exact results can also miss certain key aspects of soliton properties in correlated bands. Thus, for example, the spin Hamiltonian allows calculations on relatively long chains,[9] but both the optical gap and charged solitons are missing.

In the present Letter we report results, based on a quantum Monte Carlo study, on several key issues associated with soliton energetics. Working with relatively large finite-size systems and focusing on the energetics we demonstrate (i) that the ground state of an odd chain is a soliton for *both* neutral and charged chains, although the energetics relative to the neutral and charged dimers are very different for nonzero electron correlations; (ii) the effect of correlations on neutral-soliton creation energies; and (iii) that "soliton doping" persists even at large values of correlation parameters.

We treat explicitly the simplest case of the Peierls-Hubbard Hamiltonian and defer to the conclusion the discussion of the applicability of the model to *trans*-(CH)$_x$. The Hamiltonian is

$$H=\sum_i(p_i^2/2M)+\tfrac{1}{2}K\sum_i(u_i-u_{i+1})^2 + \sum_{i,\sigma}[t_0-\alpha(u_i-u_{i+1})] \times(c_{i,\sigma}^\dagger c_{i+1,\sigma}+c_{i+1,\sigma}^\dagger c_{i,\sigma}) + \tfrac{1}{2}U\sum_{i,\sigma}n_{i,\sigma}n_{i,-\sigma}, \qquad (1)$$

where $n_{i,\sigma}\equiv c_{i,\sigma}^\dagger c_{i,\sigma}$. In the physical context in which H describes *trans*-(CH)$_x$, the displacements (u_i) of the (CH) units along the chain are coupled (with strength α) to the hopping term which transfers π electrons between adjacent sites, and the Hubbard U (>0) models the Coulomb repulsion occurring when two π electrons of opposite spin ($\sigma=\pm\frac{1}{2}$) occupy the same site [i.e., (CH) unit].

For definiteness, we have considered ranges of parameters thought to be appropriate for (CH)$_x$;[4,7,8,10] we have worked in (and near) the half-filled band, and, consistent with previous results[11] that nonadiabatic phonon effects in (CH)$_x$ are small, have taken the Born-Oppenheimer ($M\rightarrow\infty$) limit. This last approximation will, very importantly, allow us to study directly the energetics of *specified* rigid phonon configurations, including single and paired solitons and dimers, without appealing to difficult-to-measure excited-state properties.[12]

To study these energetics we have used an extension[13] to an ensemble of states of the recently proposed "projector Monte Carlo method"[14] and have obtained results with precision (i.e., statistical errors and reproducibility) within a fraction of a percent and accuracy (i.e., systematics) controllable at the same level.

To establish connection with previous results and to illustrate the accuracy of our method, we first report briefly our results on the persistence of dimerization in the presence of U. This persistence is relevant to soliton energetics because dimerization is an essential prerequisite for the existence of (topological) solitons in these systems. Our results, which will be reported in detail elsewhere,[13] were obtained by studying a closed ring system with $N=32$ sites. We fixed the phonon configuration so that sequential transfer integrals alternate between $t_\pm\equiv t_0(1\pm2\delta)$ and then calculated the difference in energy between the undimerized ($\delta=0$) and dimerized ($\delta\neq0$) systems. To measure this difference to about three percent, we measured the individual energies to better than one part in a thousand. As was observed previously,[5,6] we found that up to $U\cong4t_0$ the correlations *increase* this energy difference, proving that they tend to increase dimerization.

We next turn to the numerical "proof" that the ground state of an odd, open chain is a soliton. Previously, this result has been shown only for the SSH model ($U=0$)[15] and within the Hartree-Fock approximation[8,9]; very recently, Hirsch and Grabowski, using a world-line Monte Carlo technique, have extended these results to neutral solitons in the presence of Hubbard U and V terms.[16] To establish this result for solitons of *any* charge we compare energies of $N=21$ chains with (1) a purely dimerized phonon backbone and (2) a "single site" soliton,[10] in which the bond alternation reverses about the central site. The choice of a single-site soliton, although clearly variationally not optimal, and of a $4n+1$ system were made to eliminate the effect of any elastic energy differences.[12] Note that the nonoptimality of our soliton configuration implies that the true soliton will be even more stable relative to the dimer. In Fig. 1 we plot, $|\Delta E_s|$, the *magnitude* of the energy difference between the soli-

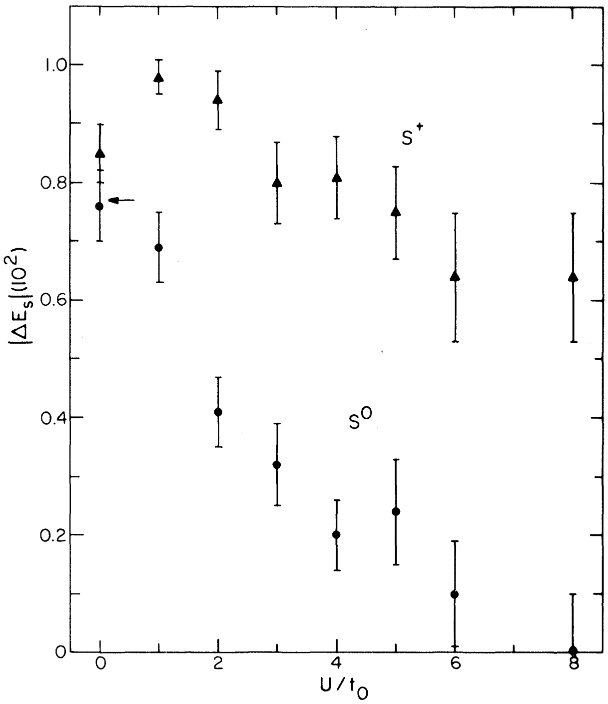

FIG. 1. The magnitude of the energy difference per site, $|\Delta E_s|$, between the soliton and the pure dimer configuration on an open $N=21$ chain vs U. The solitons are always lower in energy. The curve labeled S^+ is for the positively charged soliton, that labeled S^0 is for the neutral soliton. Both are in units of t_0. The arrow marks the exact $|\Delta E_s|$ for $U=0$.

ton (which always has lower energy) and the dimer configuration versus U for both the neutral (labeled S^0) and positively charged (labeled S^+) solitons. The results for negatively charged solitons fall, within errors, on the curve S^+, providing a nontrivial test of our code away from the half-filled band.[17] Note that with increasing U the neutral soliton becomes monotonically less stable relative to the dimer, while the charged soliton first becomes more stable before approaching the dimer energy as $U \rightarrow \infty$. Importantly, note that, as previously observed,[9] our results do *not* say anything about soliton *creation* energies—this is immediately clear since $\Delta E_s < 0$—nor do they indicate that soliton doping persists for $U \neq 0$. To study these effects, we must turn to configurations which parallel the physical situations of soliton creation and doping. Before discussing these calculations let us make two final remarks concerning the odd open chains. First, we note that apart from finite-size effects, in our EPMC method[13] systematic errors can arise from the finite time slice $\Delta\tau$[14] and from the (limited) number of states, N_E, in the ensemble. The curves in Fig. 1 were made with $\Delta\tau = 1/(8t_0)$ and $N_E \cong 1500\text{–}2500$,[13] and all measurements were made after projecting for $\beta = 2.5/t_0$ imaginary time units to bring the system into the ground state.[13,14] Extensive studies have shown that, for systems of this size, these choices were sufficient to obtain $|\Delta E_s|$ to about one percent. Again the individual energies were measured to better than one part per thousand. Second, both the charge-density profile for the charged soliton and the spin-density profile (which exhibits negative spin densities for $U > 0$) for the neutral soliton extend well beyond the single site on which the bond alternation defect is localized. Comparison with exact $U = 0$ results shows that for $N_E \cong 1500\text{–}2500$, the actual densities, while qualitatively correct, are not quantitatively accurate. This is (unfortunately) consistent with the result familiar from variational calculations that it is easier to obtain accurate energies than accurate wave functions.[13]

Since topology requires that solitons be made in $S\bar{S}$ pairs and we want to know the creation energy relative to the ground state, we consider the difference between the total energy ($E_{S\bar{S}}$) of a large finite system with an $S\bar{S}$ pair and the total energy (E_D) of the same size system purely dimerized. To conserve overall length,[12] we take the transfer integrals adjacent to the single-site solitons to be $t_s \equiv 1 - \delta$.[9] We define the soliton creation energy[18] as $E_{\text{cr}} = [E_{\bar{S}S} - E_D]/2$. On the basis of observed spin- and charge-density profiles, our results show that, for any finite U, the lowest-energy configuration is the neutral $S^0\bar{S}^0$ pair. In Fig. 2(a) we plot the creation energy, $2E^0_{\text{cr}}$, for a pair of neutral solitons calculated in the above manner for fixed dimerization $\delta = 0.1$ versus U. We have chosen an $N = 34$ open chain because the chain avoids the "image" soliton effects associated with closed rings.[13] Results for $N = 18$ and 26 show the same behavior: namely, a relatively flat region for $U \lesssim 2t_0$ and then a steady decrease as U gets very large.

We turn next to the problem of "soliton doping." Considering again the actual physical situation, we conclude that for finite systems the correct procedure is, in a system of $N - 2$ electrons on N sites, for example, to compare the $S^+\bar{S}^+$ configuration with the doubly positively charged dimer (D^{++}). Although for small finite systems remov-

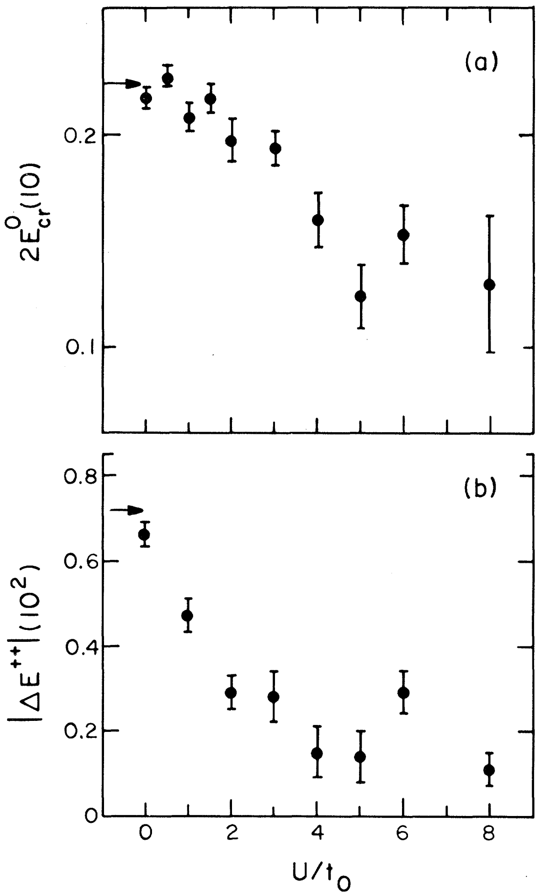

FIG. 2. (a) The creation energy of a pair of neutral solitons, $2E^0_{\text{cr}}$, vs U. (b) The energy difference, $|\Delta E^{++}|$, between the $\bar{S}^+S^+$ and the D^{++} configurations. The $\bar{S}^+S^+$ configuration is lower in energy. All energies are in units of t_0. The arrows mark the exact energy differences for $U = 0$.

ing two electrons can take one relatively far from the half-filled band, we do *not* compare to the energies of phonon configurations corresponding to either the metallic phase ($\delta = 0$) or to an incommensurate bond order wave [corresponding to band filling $\rho = (N-2)/N$] because our extrapolation in N is for $N-2$ electrons on N sites, *not for fixed* ρ, and hence neither of these potential phases will occur. Thus we consider $\Delta E^{++} \equiv E_{\bar{S}^+S^+} - E_{D^{++}}$; establishing that $\Delta E^{++} < 0$ proves soliton doping. Since ΔE^{++} is both quite small and a $1/N$ effect, we study an open chain of length $N = 18$ with bond alternation pattern as in the previous $S\bar{S}$ case. In Fig. 2(b) we plot ΔE^{++} versus U. The uniform decrease of ΔE^{++} with increasing U shows that the $\bar{S}^+S^+$ configuration becomes relatively less favored as U becomes large, but at least for $U \lesssim 6t_0$, our results clearly establish that soliton doping occurs in this Peierls-Hubbard model.

To conclude let us consider the applicability of the model (1) to *trans*-$(CH)_x$. To obtain quantitative agreement with experiment, at least a nearest-neighbor interaction $V\sum n_l n_{l+1}$ has to be included.[16] However, negative spin densities,[1] excited-state orderings,[3] and the absence of a "midgap" neutral-soliton absorption[2] can all be *qualitatively* described by U alone. Further, for our present results, the effects of V can be anticipated from the real space picture.[5] First, it has been demonstrated that dimerization is further enhanced by V (for $V \leq \frac{1}{2}U$).[5,6] Second, for the neutral odd chain, a positive V (for any fixed U) *enhances* the stability of the soliton, since the "ionic" configurations[5] that favor the soliton are *less* suppressed by V than are those that favor the dimer. Third, in the case of the charged odd chain, there is an *additional* effect of V that stabilizes the soliton configuration further: for the soliton there are two excitations at $U-2V$,[19] whereas in the dimer there is only one such excitation. Similarly, soliton doping also becomes stronger for $V > 0$, as now the $S^+\bar{S}^+$ has four excitations at $U-2V$, compared to two in the doubly charged dimer. Thus by examining a region of correlations where soliton doping is *least* favored, we have established that it will persist for any realistic correlation parameters. Finally, however, note that for even a qualitative study of photo-excited species, inclusion of V is crucial, as it can lead to exciton formation instead of $S^+\bar{S}^-$ pairs. Photogeneration requires a study of the excited states, and we are currently pursuing this question.

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