

Renormalization-group studies of the Hubbard-Peierls Hamiltonian for finite polyenes

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We have applied a numerical renormalization-group technique to study the Hubbard-Peierls model for $(\text{CH})_x$. The method provides accurate many-body wave functions and energies for the ground and low-lying excited states of finite polyenes. We report tests of the method for finite chains ($N=16$) which show that the technique accurately reproduces known results in the noninteracting particle limit ($U=0$) and in the highly correlated limit ($U/4t \gg 1$) and agrees well with Monte Carlo data where available for intermediate U . The model is applied to study correlation effects on the ground-state dimerization amplitude and to the ordering of the low-lying excited states of the rigid-lattice spectrum. Extension of the method to even longer systems appears to be quite practical.

Over the past several years there has been considerable interest in the effects of the electron-electron interaction on the ground- and excited-state properties of polyenes. Results of mean-field theory calculations show that the dimerization amplitude in the ground state decreases when an on-site Coulomb interaction is introduced. However, several authors using various many-body techniques have found that the ground-state dimerization amplitude is enhanced when a weak Coulomb interaction is included in the Hubbard-Peierls Hamiltonian. To reproduce the observed spectra of short polyenes, Schulten, Ohmine, and Karplus¹ found that doubly excited configurations and higher-order configuration interaction was necessary. In addition, these authors found that the introduction of electron-electron interaction leads to an interchange in the ordering of the excited states so that a 1A_g (dipole-forbidden) state lies lower than the 1B_u (dipole-allowed) state anticipated in a one-electron theory. The experimental evidence in support of a 1A_g first excited state has been briefly reviewed by Hudson and Kohler.² Our previous study³ of the Hubbard-Peierls Hamiltonian on a six-atom ring demonstrated that the excited-state ordering depends strongly on competition between the electron-electron interaction and the electron-phonon coupling. We were therefore interested in developing a method for examining the effects of both electron correlation and electron-phonon coupling in the excited states of longer chains.

A number of methods have been applied to study interaction effects in polyenes. Mean-field theory has been used by Kivelson and Heim⁴ to study the ground state of $(\text{CH})_x$ in the limit of small electron-electron interaction. The Monte Carlo method^{5,6} has been productively applied to study ground-state properties of finite chains, but it is difficult to apply this method to excited states. A Gutzwiller ansatz for the ground state, applicable for small electron-electron interaction has been applied by Baeriswyl and Maki to $(\text{CH})_x$.⁷ Excited states have been studied using configuration-interaction (CI) methods¹ and valence-band methods,^{8,9} but are limited to about 12 or so atoms because of the rapidly expanding size of the basis set.

One way to get around the basis size problem is to use scaling methods. Hirsch¹⁰ applied the renormalization group (RG) to the ground state of the Hubbard model on an infinite chain, keeping only the lowest energy state in each cell.¹¹ Here we apply a different renormalization scheme which has been applied by Bray and Chui¹² to the one-dimensional Hubbard model. This method retains a much larger number of states in each cell, thus allowing more variational freedom in the basis set. It provides a diagonalization of the many-body Hamiltonian, efficiently providing eigenvalues and eigenvectors of the low-lying states for long but not infinite chains. Here we present results of tests of the method on a 16-atom chain, showing that it works well at small $U/4t$, reproducing structural relaxation energies, and at high $U/4t$, reproducing the low-lying eigenstates. At intermediate $U/4t$ we find an enhanced dimerization amplitude in the ground state. We also study the rigid-lattice excitation spectrum at the equilibrium dimerization amplitude over the range of $U/4t$. We find that the dipole-allowed first excited state is pushed up above a dipole-forbidden second excited state as U is increased, and that the Coulomb repulsion is responsible for a significant portion of the optical gap.

In this work we use the Hubbard-Peierls Hamiltonian, which includes the Su-Schrieffer-Heeger (SSH) Hamiltonian and an on-site electron-electron repulsion term,

$$H = \sum_{i,\sigma} [t_0 + \alpha(x_{i+1} - x_i)] c_{i+1}^\dagger c_i + \text{H.c.} \\ + \frac{1}{2} \sum_i K(x_{i+1} - x_i)^2 + \frac{1}{2} \sum_{i,\sigma} U n_{i,\sigma} n_{i,-\sigma},$$

where $c_{i\sigma}$ and $c_{i\sigma}^\dagger$ are the electron creation and annihilation operators for site i and spin σ , x_i are the ion coordinates away from a reference equal bond-length structure, $n_{i\sigma}$ are the electron number operators, and K is the effective spring constant.

The method of solving this Hamiltonian for the first few electronic states on a finite chain consists of constructing larger generalized sites from smaller ones, where generalized sites are several atom subsets of the full chain. On the smaller "sites," we diagonalize all the required

blocks of the Hamiltonian specified by the good quantum numbers of the problem, electron number N , spin S^2 , and the z -component of spin S_z . We diagonalize as many as 15 blocks of various N and S^2 . There may be several different S_z 's for a given S^2 , but the basis set can be conveniently arranged so that the eigenvalues are the same for each, permitting the diagonalization of one representative block of given N and S^2 . Then we construct product states from neighboring "sites," coupling to good N , S^2 , and S_z for the combined "site." The Hamiltonian for the new generalized site consists of a diagonal part containing the sum of the left and right "site" eigenvalues from the previous level and the off-diagonal hopping term for the link between the left and right "sites." It is convenient to work in the site representation at each level, since the Coulomb terms are already diagonal in this representation and the hopping matrix elements are easy to identify. At each level of the construction it is only necessary to store c matrix elements between pairs of "right-" or "left-" hand eigenfunctions, since $c^\dagger c$ elements can be factored into a product of c^\dagger and c , and c^\dagger elements can be obtained from c elements. The other large storage requirement in the linking program is for information connecting the basis set for each pair of levels.

This method would provide an exact diagonalization of the Hamiltonian if all the basis states could be retained. However, the number of basis states increases quite rapidly as a function of the number of electrons. For example, the complete singlet basis set contains 20 states for 4 atoms and 4 electrons, 1764 for 8 atoms and 8 electrons, and about 35 million for the 16-atom chain with 16 electrons. So it is necessary to restrict the number of basis functions to be included, and this is done using an energy cutoff. The lowest-lying 100–200 states are kept in each manifold, and 2000 or so states are included using Lowdin perturbation theory.¹³ At high $U/4t$ the states split into narrow bands labeled by the number of doubly occupied (or empty) sites. In this case, the states in the lowest band (neutral states), are connected in second order through a subset of the singly ionic band. Our method does not pick out the subset automatically, so it is necessary to go beyond 2000 states, using random sampling to capture as many as possible of the important singly ionic states. The method of constructing generalized sites works well because the low-lying eigenvectors at the lower levels of the construction provide a good guide to the low-lying states at higher levels when the added hopping terms linking the "sites" are a small perturbation. (In one dimension there is only one link added in going from level to level. In two or three dimensions there are several links involved, and unless they are weak, this method would not be expected to perform as well.)

It is important to know how much accuracy has been obtained by including a particular number of states in the basis set at each level. A convenient check can be made by eliminating the two-body interaction term in the Hamiltonian by setting $U=0$, and comparing the results to those obtained by directly diagonalizing the SSH Hamiltonian. In Fig. 1 we have plotted the electronic plus elastic energy relative to the undimerized structure versus dimerization amplitude (alternating displacement field) for

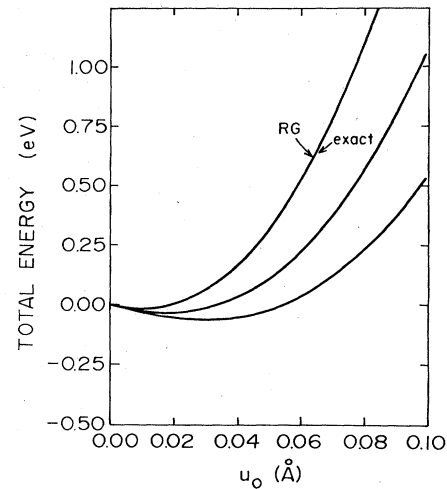


FIG. 1. Total energy as a function of dimerization amplitude for three values of the spring constant on a 16-atom chain. The results from the RG method and by direct diagonalization of the SSH Hamiltonian lie on top of each other to within the width of the line.

three values of the spring constant. The results of our method lie on top of the one-electron results to within the width of the line, thus providing a good check on the energy changes during ion coordinate relaxation in the ground state. In Fig. 2 we have plotted the first electronic excited state relative to the ground state as a function of dimerization amplitude. This energy corresponds to the direct gap in the SSH model. Odd bonds on the dimerized finite chain are weak compared with their neighbors and such bonds link generalized sites. The agreement improves with increasing dimerization amplitude because these weak links between generalized sites are getting

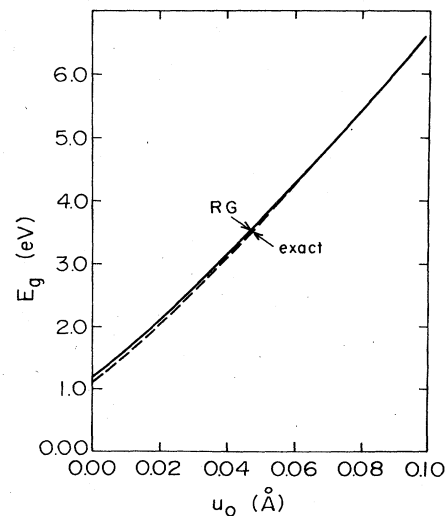


FIG. 2. Optical gap as a function of dimerization amplitude, from the RG method and by direct diagonalization of the SSH Hamiltonian, on a 16-atom chain.

weaker and are thus providing a smaller perturbation. Each diagonalization to obtain points for Figs. 1 and 2 took about seven minutes on an IBM 3081 using 200 16-atom basis states improved by 2000 states in perturbation theory.

We have also compared our results for $U/4t \gg 1$ to results in the literature. Though we found no eigenvalues on the 16-atom chain in this limit to compare with, a diagonalization of the spin- $\frac{1}{2}$ Heisenberg Hamiltonian on an eight-atom chain exists.¹⁴ For an undimerized chain with spin coupling $J=0.1$, Orbach obtained a singlet gap of 0.206 eV compared with our 0.190 eV and a singlet-triplet gap of 0.080 eV compared with our 0.104 eV. Some of the discrepancy in the latter value is due to the Lowdin perturbation method, which independently shifts the origin of the energy scale in each manifold by a small amount. We have calculated the nearest-neighbor spin-spin correlation function $4\langle S_{zi}S_{zi+1} \rangle$ for each pair of sites by building up the correlation function through each level in a similar way to the construction of the Hamiltonian. We can compare Orbach's value of -0.600 (Ref. 15) averaged over N sites to our values of -0.708 for 4 atoms, -0.633 for 8 atoms, and 0.605 for 16 atoms.

A good internal test of the method is to be certain that correlation functions, such as the spin-spin correlation function or bond order across the center link in the chain are similar to those on other even links. This is the last bond to be added, and if not enough degrees of freedom are included, the correlation function across this link can be considerably different from that of its next-nearest neighbor. We have included a sufficient number of states to satisfy this test to within 10%.

Having tested the accuracy of the method at both ends of the $U/4t$ range, we now examine the equilibrium dimerization amplitude in the ground state as a function of $U/4t$. In Fig. 3 we present data for three different values

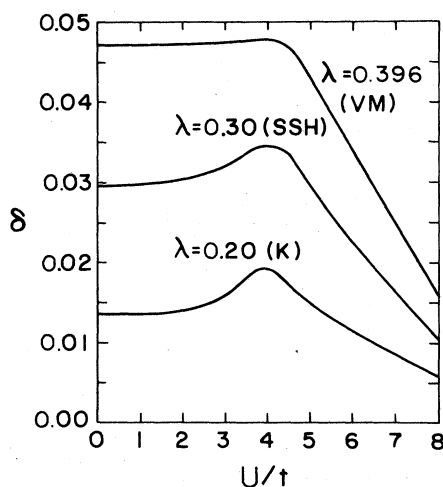


FIG. 3. Dimensionless dimerization amplitude versus strength of the on-site Coulomb term for three values of dimensionless electron-phonon coupling constants [K denotes Kakitani (Ref. 16) and VM Vanderbilt and Mele (Ref. 17)] on a 16-atom chain.

of the electron-phonon coupling constant $\lambda=(2\alpha)^2/\pi t_0 K$ corresponding to SSH parameters, parameters used by Kakitani,¹⁶ and parameters used by Vanderbilt and Mele.¹⁷ We have plotted the dimensionless dimerization amplitude $\delta=\alpha u/t_0$ for convenience to separate the three curves. We see that the dimerization amplitude is enhanced with increasing U in all three cases, and that the enhancement decreases with increasing λ , in agreement with the results of Baeriswyl and Maki, using the Gutzwiller ansatz on an infinite chain. The maximum enhancement occurs near $U/4t=1$, the canonical crossover point from the Peierls ($U/4t \ll 1$) limit to the spin-Peierls ($U/4t \gg 1$) limit. We can also compare the enhancement in the dimerization amplitude at $\lambda=0.30$ to that found by Baeriswyl and Maki⁷ and Hirsch⁵ (using Monte Carlo on a longer chain with periodic boundary conditions). Hirsch obtains a 26% enhancement, Baeriswyl and Maki a 9% enhancement, and we obtain a 20% enhancement.

It is interesting to examine the rigid-lattice excitation spectrum at the equilibrium dimerization amplitude for the ground state. In Fig. 4 we have plotted the first two excited states relative to the ground state as a function of $U/4t$. As small $U/4t$ the dipole-allowed 1B_u state is the first excited state and corresponds to excitation across the Peierls gap for the infinite chain. However, as $U/4t$ is increased, the 1B_u state is pushed up above the $2{}^1A_g$ state, leading to a dipole-forbidden first excited state at higher $U/4t$. We are currently studying the structurally relaxed excited states to see if the ordering is maintained after relaxation. Another interesting observation to be made concerning Fig. 4 is that the Coulomb interaction is responsible for as much as 40% of the optical gap. This is much smaller than the estimates from Monte Carlo data.⁵ The Monte Carlo study follows the decay of the current-current correlation function in imaginary time and concludes that the Coulomb gap dominates the "lattice gap" in this system for intermediate values of the repulsion strength.

In conclusion we have tested a numerical

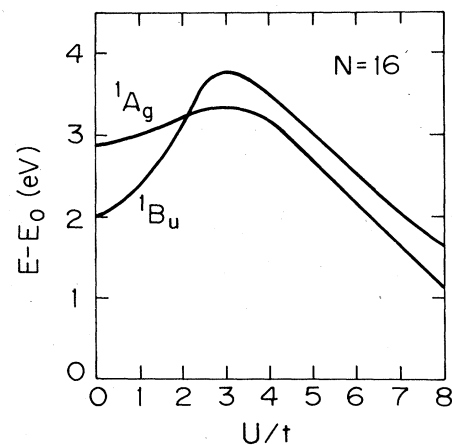


FIG. 4. Energy of the first two excited states relative to the ground state as a function of the strength of an on-site Coulomb term on a 16-atom chain.

renormalization-group method of obtaining low-lying states of the Hubbard-Peierls Hamiltonian on a 16-atom chain over the full range of on-site electron-electron correlation. We have demonstrated that the method can produce information about these states quickly and accurately. In addition, we find, in agreement with other authors, that an on-site electron-electron repulsion tends to enhance the dimerization amplitude in the ground state. In examining the rigid-lattice spectrum, we have found that the 1B_u and $2\ {}^1A_g$ excited states cross over at intermediate $U/4t$, resulting in a dipole-forbidden 1A_g first excited state at higher $U/4t$. We also note that the Coulomb contribution to the optical gap is quite significant for the 16-atom chain in the $U/4t$ region of physical

interest. We are currently conducting further studies of the excited states, examining the bond orders and spin-spin correlation functions in structurally relaxed configurations. We expect to be able to extend the method to longer chains and rings and to be able to add off-site Coulomb terms to the Hamiltonian.

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