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Correlation effects on electronic and optical properties of a C_{60} molecule: A variational Monte Carlo study

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The electronic and optical properties of the neutral C_{60} molecule are investigated in the extended Su-Schrieffer-Heeger model including a Hubbard-type on-site interaction by the variational Monte Carlo (VMC) method. The optical energy gap E_g of the molecule and the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been calculated as functions of the Hubbard interaction strength U divided by the hopping constant t. It is found that the energy of both the HOMO and LUMO levels increase almost equally with increase of U/t, so that the Hubbard term U/t has only a weak effect on E_g for intermediate interaction strengths $(U/t<5)$. This is significantly different from the situation in conducting polymers. Pair-binding energies in the singlet and triplet states have also been calculated by the VMC method for nondimerized molecules, and a comparison has been made with the results obtained by perturbation theory. [S0163-1829(96)06443-0]

It is a widely accepted view that in pure and doped C_{60} systems the electron correlation is important.[1–10] This is due to the observation that superconductivity with rather high critical temperature T_c exists in alkali-metal ion-doped C_{60} crystals ($T_c=28$ K for Rb_3C_{60}),[11] and the C_{60} tetrakis dimethylamino ethylene (TDAE) complexes show soft ferromagnetism.[10] In addition to the traditional electron-phonon mechanism for superconductivity,[12,13] the Cooper pairing induced by electronic correlation effects within a single C_{60} molecule[1–4] has also been proposed to explain the superconductivity in the doped C_{60} system.

Using the Hubbard model, Chakravarty *et al.* (CGK),[1] found that an effective attraction between two electrons on the same C_{60} molecule may arise from the undressed repulsive electron-electron interaction in a second-order perturbation theory. Later, it had been shown[2] that the long range Coulomb interaction does not destroy the effective pairing if the frequency-dependent screening, which exists in a molecular metal such as C_{60}, is included. These authors found that the results obtained from the Hubbard model could be almost reproduced by using a frequency-dependent screened Coulomb interaction. Their argument can also be used to evoke the possibility of ferromagnetism in the fullerenes,[1] which cannot be explained by a single electron theory. For certain ranges of the parameters, the theory predicts that two electrons on the same molecule will have a lower energy in the triplet state than in the singlet state, and this may give rise to itinerant ferromagnetism.

Electron correlations also have an important influence on the optical band gap E_g, as has been demonstrated in the case of conducting polymers.[14] E_g can be determined directly by optical absorption[7] and other experiments.[15,16] Whether the optical energy gap is increased or decreased by electron-electron interaction was one of the most controversial questions concerning conducting polymers.[17]

The experimental data for E_g in C_{60} systems are rather ambiguous because they yield values scattered over a wide range (from 1.5 to 2.3 eV). For example, the low-energy electron-energy-loss spectrum[15] of solid C_{60} gives $E_g=1.55$ eV, while the photoemission and inverse photoemission spectra[7] of C_{60} lead to $E_g=2.3$ eV. Finally, by using the microwave absorption method,[16] $E_g=1.86$ eV has been obtained. Theoretically, the band-structure calculations in the local density approximation (LDA) give $E_g=1.5$ eV,[18] at the lower limit of the range of experimental data. Can this theoretical result for E_g be improved when the electron correlation is included? Shirley and Louie[19] used an *ab initio* quasiparticle method [i.e., the so-called Gutzwiller (GW) approximation] to calculate the quasiparticle energy gap (or the optical gap) in undoped solid C_{60}, and found a band gap of 2.15 eV, which is in good agreement with experiment and is a good improvement on the LDA calculation result. This GW calculation showed that there is a sizable many-body correction to the band gap. Therefore, an investigation of the effect of the electron correlation on the optical gap of the C_{60} system is of great interest. Does the electron correlation

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have as strong an effect on the optical energy gap of the C_{60} system as it has on conducting polymers? Does the correlation increase or decrease E_g of a C_{60} molecule? All these questions are important for the understanding of the electronic and optical properties of C_{60} systems.

By definition, the optical energy gap of a system, E_g, is the same as the sum of the energies required for adding and for removing an electron to the system; that is,

$$E_g = E_0(N+1) - E_0(N) + E_0(N-1) - E_0(N), \tag{1}$$

where E_0 is the ground-state energy for a system of N electrons (for a *fixed* lattice configuration).[20] There are different theoretical methods of finding the ground-state energy of an interacting many-body system. For example, analytical calculations include the mean field treatments, perturbational expansion, and Gutzwiller variational method with the Gutzwiller approximation,[21] etc. Among the numerical methods that may seem applicable to find the ground-state energy of the C_{60} molecule, we mention exact diagonalization[22] and the quantum Monte Carlo (QMC)[9,23] and variational Monte Carlo (VMC) methods.[24] The exact diagonalization method is not practical because C_{60} has too many sites. The QMC calculation cannot be applied at too low a temperature due to its intrinsic limitations. In this paper, therefore, we use the VMC method to calculate the optical energy gap E_g as defined in Eq. (1).

The VMC method is a combination of variational theory and the numerical Monte Carlo technique. It has been demonstrated to be applicable, in principle, to the whole range of weak to strong electron correlations. It is flexible enough to be used with different trial wave functions to incorporate important features of different physical systems. It has been successfully used in the study of high-T_c superconductivity,[25] of low-dimensional strongly correlated electron systems,[24] and also of the C_{60} molecule in other systems.[26,27] In particular, the usual finite-size effect is not a problem here, because the C_{60} molecule is a truncated icosahedron of fixed size.

This truncated icosahedron has 60 sites on which 60 carbon atoms are situated. Each carbon atom contributes one delocalized π electron, and so the C_{60} molecule has a total of 60 π electrons. As is the case in conducting polymers, these more delocalized π electrons play an important role in the electronic, magnetic, and optical properties of the C_{60} system, since the electron correlation is quite important for the π electrons.

The electronic and optical properties of pure and doped C_{60} systems have been investigated[28–30] by the Su-Schrieffer-Heeger (SSH) model without electron correlation. This model was originally proposed for polyacetylene and has been applied successfully in the study of conducting polymers over the past decade.[31]

Including the electron correlation, the model Hamiltonian for the C_{60} molecule can be written as the sum of the extended SSH Hamiltonian and the Hubbard interaction term,[28–30] i.e.,

$$H = H_{\mathrm{SSH}} + U\sum_i n_{i,\uparrow} n_{i,\downarrow}, \tag{2a}$$

$$H_{\mathrm{SSH}} = -\sum_{\langle i,j\rangle,s} [t + \alpha y_{i,j}](C^\dagger_{i,s} C_{j,s} + \mathrm{H.c.}) + K/2 \sum_{\langle i,j\rangle} y^2_{i,j}, \tag{2b}$$

where H_{SSH} is the SSH Hamiltonian, $C^\dagger_{i,s}$ ($C_{i,s}$) is the creation (annihilation) operator of a π electron with spin s at the ith carbon atom, t is the hopping integral of the undimerized system, α describes the influence of the change $y_{i,j}$ of the bond length between the ith and jth atom on the hopping.[28] The sum over $\langle i,j\rangle$ is taken for nearest-neighbor pair sites $\langle i,j\rangle$ and K is the "spring constant." The last term in Eq. (2a) represents the Hubbard interaction with U as the on-site Coulomb repulsion energy, and $n_{i,s} = C^\dagger_{i,s} C_{i,s}$.

It is well known that for a three-dimensional system such as the C_{60} molecule, it is impossible to obtain an exact solution of the Hamiltonian H given by Eq. (2a) analytically. Thus, we used the VMC method to investigate the effect of electron correlation on the optical energy gap E_g for the neutral C_{60} molecule with or without the dimerization. We did not try to obtain a precise value of E_g which could be compared quantitatively with the experimental data, but searched for a qualitative result from which we can understand what actual effect the electron correlation has on E_g in the C_{60} system. Besides, the ferromagnetism in C_{60} complexes and the pairing possibility due to pure repulsive interaction between two electrons on the same C_{60} molecule have also been investigated in the case of intermediate values of $U/t \sim 3$ to 6, which are estimated to be suitable for the C_{60} system. In this region of the parameter U/t, conclusions from the second-order perturbation theory seem to be questionable.

A Gutzwiller-type variational wave function is chosen as usual:

$$|\Psi\rangle = \prod_i [1 - (1-g) n_{i,\uparrow} n_{i,\downarrow}] |\Phi\rangle, \tag{3}$$

where g is the Gutzwiller variational parameter ($0 \leqslant g \leqslant 1$), and $|\Phi\rangle$ is the ground-state wave function of the noninteracting electron system ($U=0$). It is a product of two Slater determinants of electrons with up- and down-spins, respectively, in the ground state, hence

$$|\Phi\rangle = \det[Z_{k,\uparrow}(i)] \det[Z_{k,\downarrow}(i)], \tag{4}$$

where $Z_{k,s}(i)$ is the one-electron wave function on site i, the kth eigenstate.

From our model Hamiltonian, Eq. (2b), we obtain a set of self-consistent equations,

$$\varepsilon_k Z_{k,s}(i) = -\sum_{\langle i,j\rangle} (t + \alpha y_{i,j}) Z_{k,s}(j), \tag{5a}$$

$$y_{i,j} = \frac{2\alpha}{K} {\sum_{k,s}}' Z_{k,s}(i) Z_{k,s}(j) - \Delta y, \tag{5b}$$

$$\Delta y = \frac{1}{N_b} \sum_{\langle i,j\rangle} \frac{2\alpha}{K} {\sum_{k,s}}' Z_{k,s}(i) Z_{k,s}(j), \tag{5c}$$

where ε_k is the eigenvalue of the kth eigenstate and $N_b(=90)$ is the number of π bonds in the C_{60} molecule. For fixed α, t, and k the coupled equations (5a)–(5c) can be solved iteratively, $Z_{k,s}(j)$ and $y_{i,j}$ and the final result should be independent of the choice of the initial values of the set $y_{i,j}$.

When $Z_{k,s}$ has been found, the ground-state energy $E_0(N,g)$ of the C_{60} molecule with N electrons can then be found as

$$E_0(N,g)=\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle. \qquad (6)$$

Finally, the value of the variational parameter g is determined by minimizing the total energy $E_0(N,g)$ for each fixed electron number N, and a set of values of U.

The VMC calculation has been performed by the standard Metropolis algorithm, and a large number of samples has been taken in order to reduce the error due to statistical fluctuation. In our VMC calculation, we performed 3×10^5 to 4×10^5 MC steps for each value of g .

For the case of no dimerization, the electron-phonon coupling constant α in Eq. (2) is chosen as zero ($\alpha=0$), and thus all 90 bonds have the same lengths. In the case with dimerization, $\alpha\neq0$, and the three parameters t,α,K in the SSH model are chosen as follows:[28,30] $t=2.5$ eV, $\alpha=6.31$ eV/Å, $K=49.7$ eV/Å^2.

The results of the VMC calculation for E_g and the LUMO, HOMO levels are shown in Fig. 1 and Fig. 2. From these diagrams the following conclusions can be drawn.

(1) For both cases, i.e., with and without dimerization, the variations of E_g with U/t are almost the same. Below $U/t\sim4.0$, E_g is hardly changed when U/t is increased. Above this value, however, E_g increases gradually with U/t.

(2) In Fig. 2, the upper and lower curves correspond, respectively, to the LUMO $[E_0(61)-E_0(60)]$ and HOMO $[E_0(60)-E_0(59)]$ levels. Below $U/t\sim4.0$, an increase in U/t causes the LUMO and HOMO levels to rise almost equally, so that E_g remains approximately constant. However, above $U/t\sim4.0$, increasing U/t raises the LUMO level faster than the HOMO level, and thus E_g increases with U/t.

(3) Since the value of U/t is estimated to be $3\sim6$ for the real C_{60} system, it can be seen that E_g is not much affected by the electron-electron interaction. It is possible that the electron-phonon interaction affects E_g more strongly than the electron-electron interaction does.

(4) The variation of E_g with U/t is markedly different from that in conducting polymers, where E_g increases with U/t for the Hubbard model.[14]

We wish to point out that the optical gap of an isolated C_{60} molecule is different from that of a solid C_{60} system because each single energy level in the isolated C_{60} molecule forms its own energy band in the solid C_{60} and it is the energy band broadening that makes the optical gap smaller.

In the case without dimerization (i.e., $\alpha=0$), we have also calculated the two-particle pairing energy E_{pair} in the singlet ($L=0$, $S=0$) and triplet ($L=1$, $S=1$) states for the neutral C_{60} molecule following the definition of Chakravarty *et al.*[1] of E_{pair}:

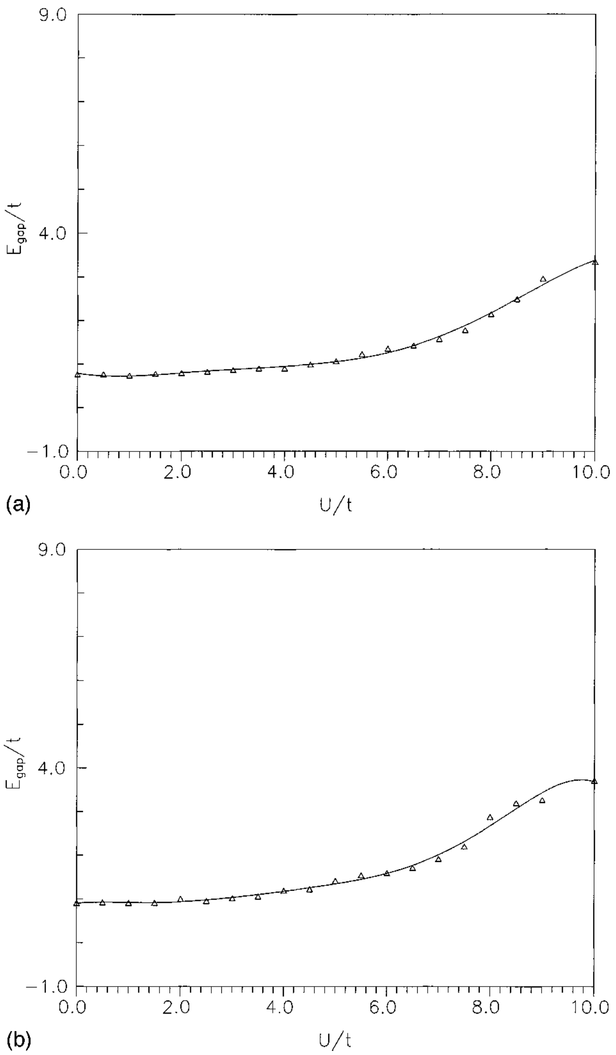

FIG. 1. Optical energy gap E_{gap} in a neutral C_{60} molecule versus U/t. U, Hubbard interaction strength; t, electron hopping matrix element. (a) Without dimerization; (b) with dimerization.

$$E_{\text{pair}}=2E_0(61)-E_0(60)-E_0(62). \qquad (7)$$

Here, L and S represent the total angular momentum and spin of the C_{60}^{n-} molecule ion with n extra electrons. Note that according to this definition, a positive E_{pair} will imply favoring a two-electron pairing state. The electron pair, localized on the same ion, may be in a singlet or triplet state. The splitting between the triplet and singlet state is $\Delta_{\text{FM}}=E_0^s(62)-E_0^t(62)=E_{\text{pair}}^t-E_{\text{pair}}^s$ where the superscripts t and s represent the triplet and singlet states, respectively. If $\Delta_{\text{FM}}>0$, this means that the triplet state is more stable than the singlet state, and the possibility of ferromagnetism exists.

The results of the calculation of E_{pair} are shown in Fig. 3, from which we can see that for $U/t<5.5$, no transition of E_{pair}^s from a negative to a positive value takes place. This is completely different from the results of the perturbational calculation,[1] which showed that E_{pair}^s became positive for $U/t>\sim3$. Our VMC result is quite consistent with that of Krivnov *et al.*[27] who treated the case with dimerization.

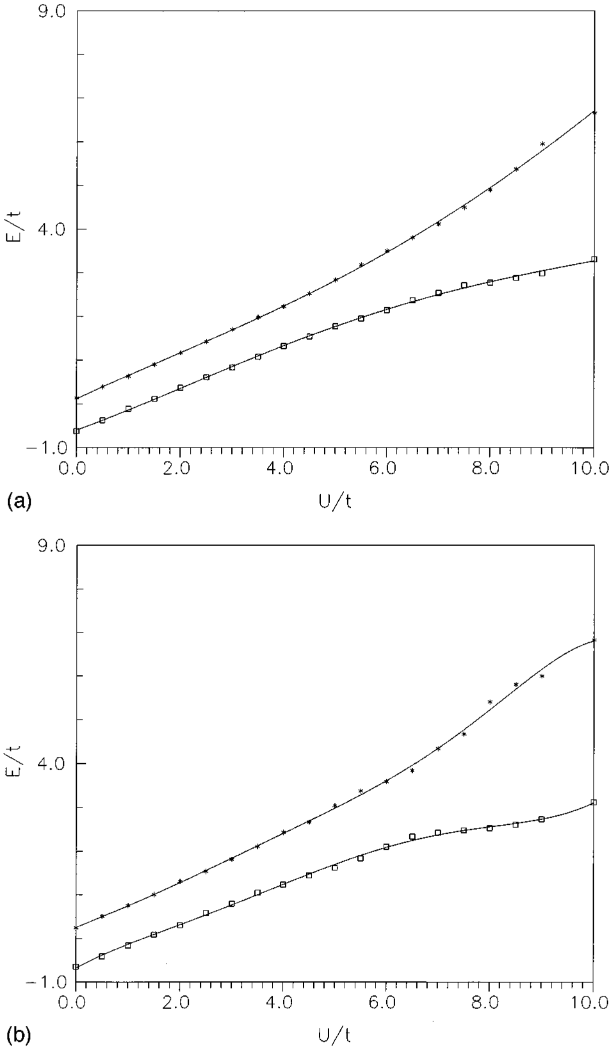

FIG. 2. Both the LUMO (*) and HOMO (□) levels in a neutral C_{60} molecule as functions of U/t. (a) Without dimerization; (b) with dimerization.

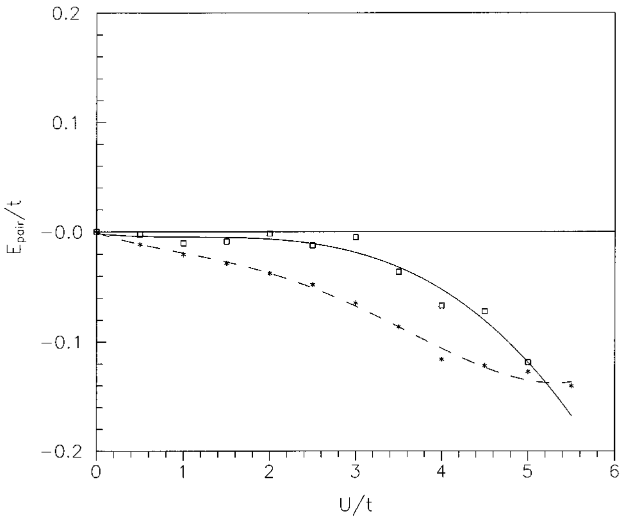

FIG. 3. The C_{60} singlet (*) and triplet (□) pair binding energies $E_{\text{pair}/t}$ as functions of U/t for the case without dimerization.

Since the pairing energies are negative and decrease with U/t, it seems likely that this tendency will continue even for values of $U/t>5.5$.

We conclude that no pair binding can occur, if one believes the results obtained from a VMC treatment of a simple Hubbard interaction with Gutzwiller-type trial wave function. Of course, we do not know what would happen if we went beyond the limitations of a Gutzwiller wave function and select a more complicated electron-electron interaction, e.g., a frequency-dependent Coulomb interaction. It should be remarked that our VMC calculation of E_{pair} in the triplet state simply reproduces CGK's result obtained by a perturbation calculation up to second order: E^{t}_{pair} decreases as U/t increases. Combining the results for E^{s}_{pair} and E^{t}_{pair}, we can see that, for $U/t<5$ one has $\Delta_{\text{FM}}>0$. Thus, a doubly charged C_{60} molecule (C_{60}^{2-}) favors the triplet state rather than the singlet state, which demonstrates the possibility of the existence of ferromagnetism in C_{60} complexes. This result is qualitatively consistent with that of perturbation theory, but yields a greater range of values of the interaction parameter U/t (now $U/t<5$, instead of 3 as in the perturbation calculation) for which the triplet state has a lower energy than the singlet state. This is so because, in our VMC results, E^{s}_{pair} decreases with increasing U/t, but in the perturbation treatment, E^{s}_{pair} first decreases as U/t increases, and then, when $U/t>2$, E^{s}_{pair} increases with U/t.

Physically, in the framework of the Hubbard model, the effect of electron-electron interaction on the electronic properties of a system could be quite different for different dimensions (e.g., one dimension or two dimensions). In a one-dimensional system such as polyacetylene, an electron can only hop in one of two directions. Thus, in order to arrive at its next-nearest neighbor, it has to hop over its nearest-neighbor site, and in this case, the on-site Hubbard interaction term plays a decisive role in determining the electron motion. However, in two dimensions, an electron can go around a given occupied nearest-neighbor site and can arrive at its next-nearest-neighbor sites by many paths. Therefore, the on-site Hubbard interaction term has a lesser effect on the physical properties of the system than it does in the one-dimensional situation.

To conclude, starting from the extended SSH model with the Hubbard interaction included, we have presented a VMC analysis for the electron correlation effect on the optical energy gap. It has been found that the Hubbard interaction has merely a weak effect on E_g in realistic C_{60} systems. We have also calculated pair binding energies in the singlet and triplet states, and compared our results with those obtained from the perturbation theory.

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