Quantum Monte Carlo calculation of the electronic binding energy in a C_{60} molecule

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(Received 16 November 2004; published 27 April 2005)

Electronic energies are calculated for a Hubbard model on the C_{60} molecule using projector quantum Monte Carlo (QMC) methods. The calculations are performed to an accuracy high enough to determine the pair-binding energy for two electrons added to neutral C_{60}. The method itself is checked against a variety of other quantum Monte Carlo methods as well as the exact diagonalization for smaller molecules. The conclusion is that the ground state with two extra electrons on one C_{60} molecule is a triplet, and, over the range of parameters where QMC is reliable, it has a slightly higher energy than the state with electrons on two separate molecules, so that the pair is unbound.

DOI: 10.1103/PhysRevB.71.165436 PACS number(s): 74.70.Wz, 71.10.Li, 02.70.Ss

I. INTRODUCTION

The discovery of superconductivity in the alkali-metal-doped bulk fullerenes K_3C_{60} and Rb_3C_{60} (Refs. 1,2) sparked intense interest in fullerene-based materials, leading to extensive experimental and theoretical studies (for a review see Ref. 3). The theoretical calculations to explain the insulating and superconducting properties of bulk fullerene materials fall into two major categories: molecular-level calculations which determine the effective interactions of intramolecular electrons[4–11] and lattice-level calculations based on an effective Hamiltonian in which the intramolecular degrees of freedom have been integrated out.[12–14]

Although much of the work has focused on the phonon mechanism for superconductivity in the alkali-C_{60}'s, some authors have proposed a purely electronic mechanism. In particular, it was argued by Chakravarty, Kivelson, and coworkers (CK) that electronic interactions within a single C_{60} molecule can lead to an effective attraction between charge carriers.[4,5,15–17] This argument was supported by perturbative calculations of the electronic binding energies of the conventional one-band Hubbard model on the C_{60} structure. The results of the CK calculation suggest that electrons have a tendency to form paired states in a single fullerene molecule, rather than remaining separate. This tendency could be the origin of the attractive interaction which is an essential ingredient of the BCS theory of superconductivity.

However, one might doubt the applicability of perturbation theory to this problem. First, the Hubbard repulsion U in the CK calculation is approximately 75% of the bandwidth, so it is hardly a small parameter. Also, the binding energy is typically a small quantity, calculated from the difference of the large internal energies of the C_{60} molecule at different electron dopings. Low-order perturbation theory estimates of such subtle energy differences may be unreliable. Thus it is interesting to repeat the calculation using different methods, which might lend support to or cast doubt upon the perturbation theory results.

In this paper we use quantum Monte Carlo (QMC) calculations to estimate the binding energy of pairs of electrons on a single C_{60} Hubbard molecule. In order to establish a high level of confidence in our results, we use a number of complementary QMC methods, including auxiliary field QMC for both real and imaginary chemical potentials[18,19] and stochastic series expansion (SSE) at a finite temperature T and projector QMC (PQMC) at $T=0$, on a series of Hubbard molecules, with the number of sites ranging from 4 to 60. In addition, a comparison is made to the results of exact diagonalization (ED) for systems of up to 12 sites. Our main result, shown in Fig. 1, is a comparison of the pair-binding energy (see below for a definition) for two electrons added to a neutral C_{60} molecule to the perturbation calculations of CK. All energies are measured in units of the hopping parameter t. In contrast to perturbation theory, which finds that the ground state is a singlet for $U/t>3$, we find, in agreement with Hund's rule, that the ground state remains a triplet state over the entire range of U studied. In particular, there is no indication of the attractive singlet ground state which perturbation theory finds for U/t greater than about 3.3. Our QMC studies find small positive binding energies for $U/t \leqslant 4.5$, indicating that two separate molecules, each with one extra electron, have lower energy than one molecule with two extra electrons. The largest value of U we are able to study is $4.5t$, since the sign problem discussed below becomes unmanageable for larger values of U. Due to this restriction, we cannot exclude a singlet-triplet energy crossing for the C_{60} molecule with two electron dopings for $U/t > 4.5$.

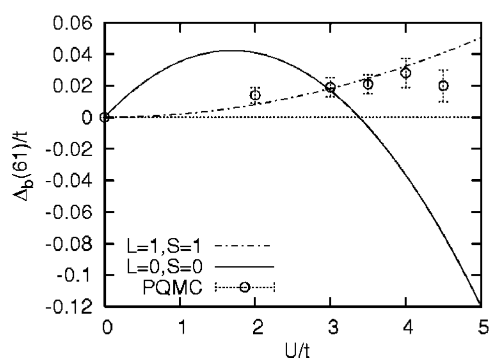

FIG. 1. Comparison of electronic pair binding energies $\Delta_b(61)/t$, defined in Eq. (2), obtained from perturbation theory in different spin sectors (solid and dash-dot lines)[4,5,20] and PQMC calculations on a C_{60} molecule. PQMC finds $S=1$ for ground states with 62 electrons.

TABLE I. Comparison of exact diagonalization and PQMC calculations on the truncated tetrahedron (12 sites) at $U=2t$. PQMC simulation parameters: $\beta=10/t$, $\Delta\tau=0.05/t$, $N_m=10^7$. $E_n(S_z)$ is the energy of a system with n electrons and a z component of total spin S_z. $\Delta_{n,m}$ is the energy difference $E_{12+n}(S_z^n)-E_{12+m}(S_z^m)$ with (S_z^n,S_z^m) given in the second column. For binding energies $\Delta_b(n)$ the second column shows $(S_z^{n+1},S_z^{n-1},S_z^n)$ the S_z values for the three states involved in its calculation, in the order of appearance in Eq. (2).

	S_z	ED	PQMC	sign
E_{10}	0	−14.506219	−14.397(3)	0.47
E_{10}	1	−14.506219	−14.504(2)	1.00
E_{11}	1/2	−13.623187	−13.620(3)	0.81
E_{11}	3/2	−12.876242	−12.880(4)	0.57
E_{12}	0	−12.697340	−12.698(2)	1.00
E_{12}	1	−11.874844	−11.856(3)	0.52
E_{13}	1/2	−10.701320	−10.698(3)	0.58
E_{13}	3/2	−9.982385	−9.969(3)	0.46
E_{14}	0	−8.725294	−8.681(4)	0.30
E_{14}	1	−8.645244	−8.643(4)	0.54
$\Delta_{1,0}$	(1/2,0)	0.996021	1.000(3)	
$\Delta_{1,0}$	(3/2,0)	1.714956	1.729(3)	
$\Delta_{-1,0}$	(1/2,0)	0.074154	0.078(3)	
$\Delta_{-1,0}$	(3/2,0)	0.821099	0.818(4)	
$\Delta_b(13)$	(0,0,1/2)	−0.019995	0.017(4)	
$\Delta_b(11)$	(0,1,1/2)	0.042813	0.038(3)	

The paper is organized as follows. In the next section we introduce the model and the QMC methods used in our simulations. We then proceed to present the tests of QMC codes on smaller molecules (truncated tetrahedron, etc.), where exact analytical or exact diagonalization results are available. Then the results for the C_{60} molecule are presented and analyzed. Finally, a conclusion based on our numerical results is drawn and the reliability of the method is discussed.

II. METHODOLOGY

Following CK, we consider a one-band Hubbard model with the Hamiltonian $H=H_0+H_1$, defined on a C_{60} molecule by

$$H_0 = -\sum_{\langle ij\rangle\sigma} t_{ij}(c_{i\sigma}^\dagger c_{j\sigma} + \mathrm{H.c.}) - \mu\sum_{i\sigma} n_{i\sigma},$$

$$H_1 = U\sum_i n_{i\uparrow}n_{i\downarrow} - \frac{U}{2}\sum_{i\sigma} n_{i\sigma}. \tag{1}$$

Here H_0 contains the standard kinetic energy and chemical potential term. The summation in the kinetic energy term is performed over all nearest-neighbor pairs on a C_{60} molecule. The hopping constants t_{ij} are chosen to be equal to t for the single bonds connecting a pentagon and a hexagon, and to $t'=1.2t$ for the double bonds between two hexagons. H_1 is a sum of the on-site Coulomb repulsion (Hubbard) term and a diagonal term, added to make the model particle-hole symmetric around $\mu=0$ on bipartite lattices. Clearly, this additional term does not affect the value of the electronic binding energy, which we choose to define as

$$\Delta_b(n) = E_{n+1} + E_{n-1} - 2E_n, \tag{2}$$

where E_n is the internal energy of a molecule with n electrons. Note that this definition has the opposite sign, compared to that of CK. In our case the tendency of the electrons to bind into pairs is indicated by a negative value of the binding energy Δ_b.

TABLE II. Comparison of the density n, total internal energy E and average sign S between exact analytical results ($U=0$), SSE ($U=4t$) and AFQMC on a C_{60} molecule. Simulation parameters: $\beta=0.5/t$, $\Delta\tau=0.05/t$, $N_m=10^5$. In the SSE run 10^7 measurements, separated by a full diagonal and directed loop update (Refs. 34,35) were performed. At lower temperatures SSE is unreliable due to the severe sign problem.

	$U=0$		
μ	−1	0	1
n_{exact}	0.7959095	1.0001765	1.2043146
E_{exact}	−44.2672020	−46.3708440	−44.3478000
n_{AFQMC}	0.7959095	1.0001765	1.2043146
E_{AFQMC}	−44.2672020	−46.3708440	−44.3478000
S_{AFQMC}	1.0	1.0	1.0
	$U=4t$		
μ	−1	0	1
n_{SSE}	0.873(1)	1.0005(2)	1.126(1)
E_{SSE}	−16.5(2)	−4.0(2)	13.9(1)
S_{SSE}	0.955	0.957	0.960
n_{AFQMC}	0.8734(2)	1.000078(1)	1.1266(2)
E_{AFQMC}	−16.61(2)	−4.13(4)	13.74(6)
S_{AFQMC}	1.0	1.0	1.0

The determinant or auxiliary field QMC (AFQMC) has been widely used in model Hamiltonian simulations since its introduction by Blankenbecler *et al.*[21,22] and its further development by Hirsch[23,24] and White *et al.*[25] The application of this technique to the one-band Hubbard model starts with the Suzuki-Trotter discretization of the imaginary time in the grand canonical partition function,[26]

$$Z_{\mathrm{GC}} = \mathrm{Tr}\, e^{-\beta H} = \mathrm{Tr}\, e^{-\beta(H_0+H_1)} = \mathrm{Tr}\prod_{i=1}^{L} e^{-\Delta\tau(H_0+H_1)}, \tag{3}$$

where $\beta=1/(k_BT)$ is the inverse temperature, discretized in such a way that $\beta=\Delta\tau L$. After the application of the Hubbard-Stratonovich transformation[27,28] the fermionic degrees of freedom in Eq. (3) may be traced out, and we arrive at

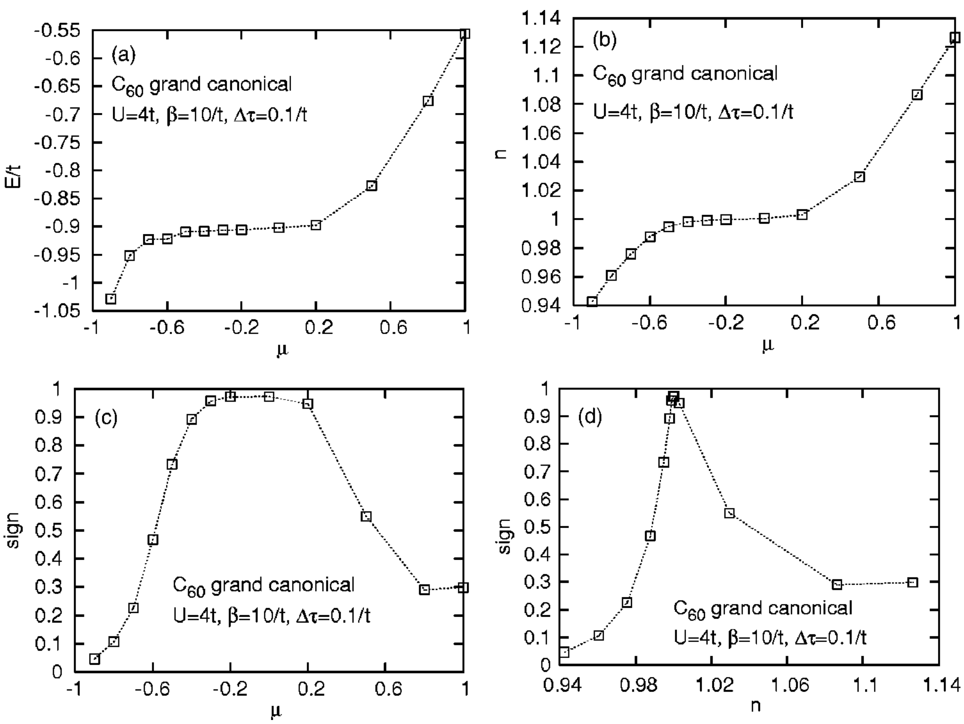

FIG. 2. Grand canonical simulation of a C_{60} molecule at various chemical potentials. Simulation parameters: $U=4t$, $\beta=10/t$, $\Delta\tau=0.1/t$, $N_t=10^3$, $N_m=10^5$. We are interested only in the qualitative behavior of the system around half filling, so the statistical errors are not estimated. (a) Energy per site vs chemical potential. (b) Electron density vs chemical potential. (c) Average sign as a function of chemical potential. (d) Average sign as a function of electron density. Curves connecting the points are guides to the eye.

$$Z_{\mathrm{GC}} = \sum_{\{\sigma\}} \prod_{\alpha} \det[1 + B_L(\alpha)B_{L-1}(\alpha)\cdots B_1(\alpha)]$$
$$= \sum_{\{\sigma\}} \det O(\{\sigma\},\mu)_{\uparrow} \det O(\{\sigma\},\mu)_{\downarrow}. \quad (4)$$

The B_l matrices are defined as

$$B_l(\alpha) = e^{-\Delta\tau K/2} e^{V^{\alpha}(l)} e^{-\Delta\tau K/2}, \quad (5)$$

$$(K)_{ij} = \begin{cases} -t_{ij} \text{ for } i,j & \text{nearest neighbours}, \\ 0 & \text{otherwise}, \end{cases} \quad (6)$$

$$V_{ij}^{\alpha}(l) = \delta_{ij}[\lambda\alpha\sigma_i(l) + \mu\Delta\tau], \quad (7)$$

where $\sigma_i(l)=\pm 1$ is the auxiliary Ising spin coupled with the electrons at lattice site i and time $l\Delta\tau$, and $\alpha=\pm 1$ corresponds to the $\uparrow$ or $\downarrow$ in Eq. (4). In Eq. (5) we have used a symmetric decomposition of the partition function, which produces a much smaller Trotter error[29,30] compared to the nonsymmetric decomposition.[21–23,25] The Monte Carlo (MC) weight P is then given by the product of two determinants in Eq. (4), which is always positive for bipartite lattices at half filling.[24] At low temperatures we use QR factorization to stabilize the matrix multiplications and inversions.[25,32] A version (projector QMC or PQMC) of the above procedure can be used to directly project the ground state properties from an initial trial wave function (see Ref. 25 for details).

Unless indicated otherwise, PQMC and AFQMC calculations were performed at the projection factor or temperature fixed by $\beta=10/t$, with an imaginary time discretization of $\Delta\tau=0.05/t$. The system was first brought to thermal equilibrium by performing N_t thermalization sweeps $S2$, followed by N_m measurements with a single sweep $S1$ (Ref. 36) performed between them.

Since we are interested in nonbipartite molecules such as C_{60}, the MC weights in general are not always positive. In the case of the negative weight P, we associate a probability value $|P|$ with it and include a sign $S=P/|P|$ in the average: $\langle E\rangle=\langle ES\rangle/\langle S\rangle$. Now the average $\langle\cdots\rangle$ is with respect to the probability distribution $|P|$.

Finally, we note that in estimating the statistical error for a composite quantity $X=X_1+X_2+\cdots+X_n$, we use the standard formula $\delta X=(\delta X_1^2+\delta X_2^2+\cdots+\delta X_n^2)^{1/2}$, where δX_i's are estimated by the Jackknife method.[31]

III. APPLICATION

A. Comparison to other methods

In this section, we check our QMC programs against the ED and SSE results.[33–35] Table I lists the energies and binding energies from both ED and PQMC for a truncated tetrahedron, which has 12 lattice sites and 3 nearest neighbors for each site. For energies at different dopings, good agreement is obtained between the two methods. The largest deviation of PQMC from ED is found for $n=10$ ($S_z=0$) (about 0.7% deviation), which might be due to the relatively low value of the average sign and the incomplete projection of a nearby singlet excitation. The energy differences between two different dopings (e.g., $\Delta_{1,0}$) are in good agreement for the two methods. However, the inaccuracies are magnified when pair-binding energies are extracted from two already small energy differences, although some of these energies are still in good agreement for the two methods within error bounds, e.g., $\Delta_{\mathrm{b}}(11)$. The difficulty of extracting $\Delta_{\mathrm{b}}(13)$ from the PQMC is possibly because the ground state with 14 electrons lies in the spin singlet sector (as confirmed by ED), and it is difficult for the PQMC to completely project out the nearby spin triplet state (the first excited state). There is no such

TABLE III. PQMC calculations on a C_{60} molecule. Part *A* of the table shows the total internal energy $E_n(S_z)$ of a C_{60} molecule with n electrons and a z component of total spin S_z. The parameters used in the simulations are $t'=1.2t$ $\beta=10/t$, $\Delta\tau=0.0625/t$ (for $U=4t$), $\Delta\tau=0.05/t$ (for other U values), $N_m=10^7$. N_m data were divided into ten bins for error estimation. For $n=60,61,62$, we have collected more data (between 4×10^7 and 8×10^7 measurements) for a more accurate comparison between PQMC and the perturbative results. Part *B* shows the electron- (hole-) binding energies $\Delta_b(n)$. As before, the S_z column in this case lists the S_z values of the three states involved in the calculation of the binding energy, in the order of appearance in Eq. (2). For example, $\Delta_b(58)$ with $S_z=(1/2,3/2,1)$ denotes $E_{59}(S_z=1/2)+E_{57}(3/2)-2E_{58}(1)$. The data points marked with * were calculated using a nonsymmetric decomposition in Eq. (5). Only limited results were obtained for $U=4.5t$ because of the long averaging times required.

	Part *A*	$U=2t$		$U=3t$		$U=4t$		$U=4.5t$	
n	S_z	$E_n(S_z)$	sign	$E_n(S_z)$	sign	$E_n(S_z)$	sign	$E_n(S_z)$	sign
57	1/2	−74.535(5)	0.69	−64.72(2)	0.15	−56.6(6)*	0.02		
57	3/2	−74.574(4)	0.81	−64.79(2)	0.25	−57.1(1)*	0.04		
58	0	−74.290(3)	0.75	−64.06(2)	0.25	−55.82(8)*	0.04		
58	1	−74.322(4)	0.82	−64.098(9)	0.32	−55.95(5)*	0.07		
59	1/2	−74.080(4)	0.89	−63.366(8)	0.51	−54.74(2)*	0.22		
59	3/2	−73.104(4)	0.83	−62.475(7)	0.31	−54.06(4)*	0.06		
60	0	−73.810(3)	1.00	−62.633(3)	1.00	−53.091(2)	0.98	−48.969(3)	0.94
60	1	−72.885(4)*	0.92	−61.83(1)*	0.44	−52.30(2)*	0.29		
61	1/2	−72.448(2)	0.98	−60.704(3)	0.82	−50.542(5)	0.47	−46.080(5)	0.32
61	3/2	−71.547(3)*	0.89	−59.957(7)*	0.46	−50.21(3)*	0.13		
62	0	−71.043(4)	0.95	−58.728(6)	0.63	−47.92(1)	0.22	−43.15(4)	0.10
62	1	−71.072(2)	0.98	−58.756(3)	0.77	−47.965(6)	0.35	−43.175(9)	0.18
63	1/2	−69.649(3)	0.96	−56.760(5)	0.60	−45.34(2)	0.17		
63	3/2	−69.688(4)	1.00	−56.802(3)	0.88	−45.360(8)	0.40		
64	0	−68.227(3)	0.95	−54.735(8)	0.54	−42.67(5)	0.12		
64	1	−68.252(4)	0.98	−54.743(5)	0.71	−42.69(2)	0.20		
65	1/2	−66.801(3)	0.98	−52.719(7)	0.70	−39.96(3)	0.17		
65	3/2	−66.587(5)	0.96	−52.505(8)	0.61	−39.85(2)	0.15		
66	0	−65.337(4)	1.00	−50.638(4)	0.81	−37.26(2)	0.21		
66	1	−65.115(3)	0.95	−50.419(9)	0.58	−37.07(4)	0.13		
	Part *B*								
		$\Delta_b(n)$		$\Delta_b(n)$		$\Delta_b(n)$		$\Delta_b(n)$	
58	(1/2,3/2,1)	−0.010(8)		0.04(3)		0.1(2)*			
59	(0,1,1/2)	0.028(8)		0.00(1)		−0.06(5)*			
60	(1/2,1/2,0)	1.092(6)		1.20(1)		1.42(2)*			
61	(1,0,1/2)	0.014(5)		0.019(6)		0.028(9)		0.02(1)	
62	(3/2,1/2,1)	0.008(5)		0.006(6)		0.03(1)			
63	(1,1,3/2)	0.052(7)		0.105(7)		0.07(2)			
64	(1/2,3/2,1)	0.015(8)		−0.04(1)		0.05(4)			
65	(0,1,1/2)	0.013(7)		0.06(1)		−0.03(5)			

problem if the ground state for two-electron doping is a spin triplet, which, as we will see below, is exactly the case for C_{60}. From the good agreement between ED and the PQMC, we conclude that the discretization error caused by $\Delta\tau=0.05/t$ is sufficiently small. We also find that the projection factor $\beta=10/t$ is large enough to project out the ground state from an initial trial state. We will use these values of $\Delta\tau$ and β in our AFQMC and PQMC simulations of the C_{60} molecule.

In Table II, we check our grand canonical simulation program (AFQMC), against ED (at $U=0$) and SSE (at $U=4t$) on a C_{60} molecule. Again we see good agreement in both the density n and energy E calculations among these methods. For $U=0$, the AFQMC results are exactly the same as the exact diagonalization results. This is because at $U=0$, there is no coupling between the electrons and the auxiliary Ising field; the Ising field is wiped out completely and the electrons cannot feel the existence of the Ising spins. The simulation at $U=0$ also shows that the discretization error is absent in AFQMC. In both $U=0$ and $U=4t$, we have set the temperature $T=2t$ to avoid a severe sign problem in the SSE simulation. Because the SSE does not suffer from the discretization error, we again confirm that $\Delta\tau=0.05/t$ in the

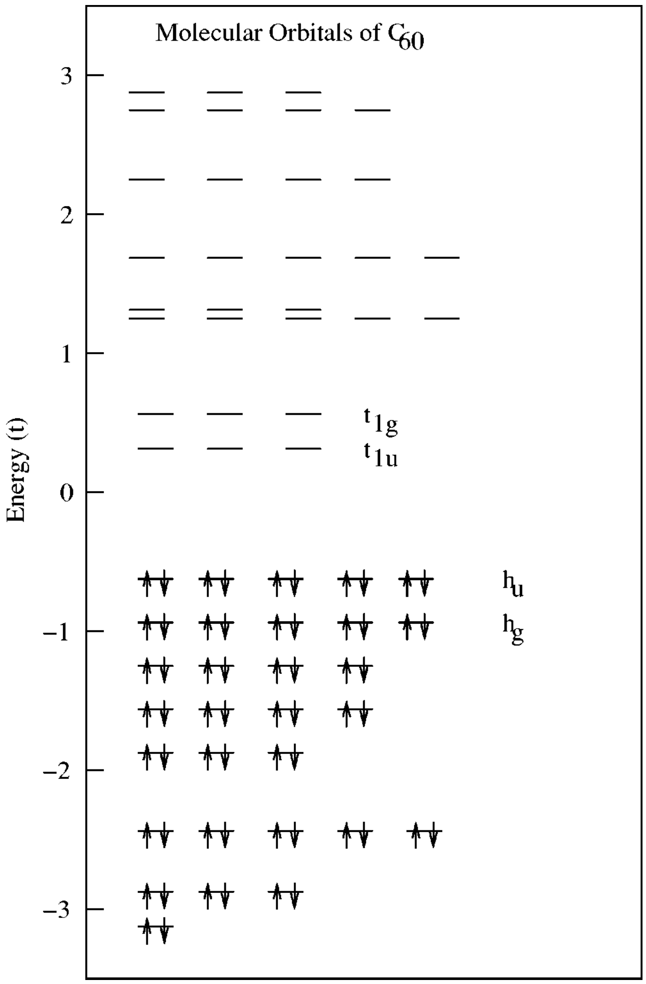

FIG. 3. Huckel energy-level diagram for the neutral C_{60} molecule. The lowest 30 levels are doubly occupied. The energy level scale is drawn according to the exact diagonalization of the noninteracting on-site Hubbard Hamiltonian, i.e., $U=0$. The energy level labels are from those of the icosahedral group, which is the symmetry group of a C_{60} molecule. The LUMO band is labelled by t_{1u}, and HOMO by h_u. We will consider the doping of LUMO and HOMO for a discussion of Hund's rule.

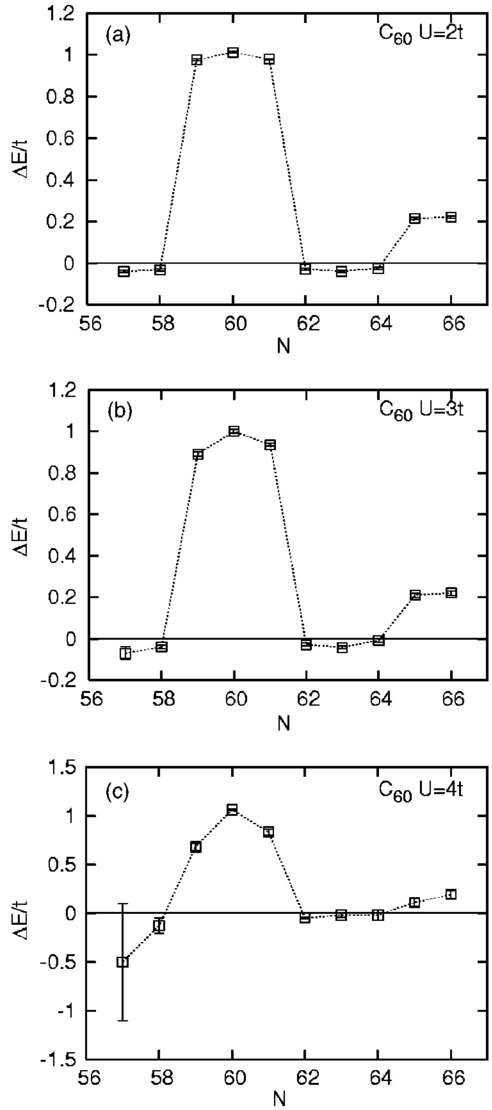

FIG. 4. Comparison of the PQMC spin configuration of a C_{60} molecule at various dopings with Hund's rule. ΔE is defined as the energy difference between two total spin z component sectors, e.g., $\Delta E(60)=E_{60}(S_z=1)-E_{60}(S_z=0)$ for the neutral molecule and $\Delta E(61)=E_{61}(S_z=3/2)-E_{61}(S_z=1/2)$ for one-electron doping. A positive ΔE at fillings $n=59$, 60, 61 can be understood in the noninteracting picture in Fig. 3, and a negative ΔE at fillings $n=57$, 58, 62, 63, 64 is in agreement with Hund's rule. $n=65$, 66 can again be explained with Fig. 3. See the text for discussions. The dotted lines connecting the MC points are only guides to the eye.

AFQMC is sufficiently small to avoid any systematic discrepancy.

The results in Table I for the simulations on a truncated tetrahedron molecule show that the PQMC results are in good agreement with ED. The systematic discretization error caused by $\Delta\tau$ is reasonably small; thus the extrapolation to $\Delta\tau=0$ is unnecessary.

B. Application to the C_{60} molecule

In this section, we discuss the QMC results for a C_{60} molecule. Figure 2 shows the results of an AFQMC simulation of the Hubbard model on a C_{60} molecule at various chemical potentials μ. At half filling, unlike the bipartite two-dimensional (2D) square lattice, the QMC simulation has a slight sign problem due to the pentagon frustration in the C_{60} geometry; see figs. 2(c) and 2(d). From Figs. 2(c) and 2(d) we also see that hole dopings have a worse sign problem than electron dopings. As expected, the compressibility[37] $\kappa \equiv (1/n^2)(dn/d\mu) \sim 0$ around $\mu=0$.

Table III lists the PQMC results for $2 \leqslant U/t \leqslant 4.5$ for the C_{60} molecule. It can be seen that hole doping causes a more severe sign problem than the electron doping, which is consistent with the behavior in Fig. 2. In part A of the table we see that reasonably accurate results can be obtained for $U=2t$, $3t$, and $4t$. The sign problem quickly becomes severe for $U>4t$, as is evident in the data presented for $U=4.5t$, where the average sign is only 0.18 for 62 electrons. For $U=5t$ and 62 electrons, the average sign is 0.08, and it is not possible to extract a reliable binding energy.

From Table III, part *A* we can calculate the energy difference between different total spin sectors at the same doping to compare the ground state-spin configuration with Hund's rule. Let us first discuss the noninteracting single electron energy levels of a C_{60} molecule. At half filling, 60 electrons move independently in "π" molecular orbitals formed from the 60 p_z atomic orbitals of the 60 carbon atoms. An exact diagonalization of the noninteracting Hamiltonian gives 60 energy levels, of which the lowest 30 levels are occupied at half filling. The lowest unoccupied molecular orbitals (LUMO) are threefold degenerate. The highest occupied molecular orbitals (HOMO) are fivefold degenerate. The detailed energy levels of the neutral C_{60} molecule are shown in Fig. 3. The energy gap between HOMO and LUMO is $1.04t$ from this exact diagonalization for the noninteracting neutral C_{60}.

We calculate the energy difference ΔE of different total S_z values at the same filling as shown in Fig. 4. At $n=59$, 60, and 61, ΔE is positive, which can be explained by the noninteracting energy levels in Fig. 3. For example, for $n=59$ and total spin $S_z=1/2$, we need to flip one electron from spin down to spin up in order to get $S_z=3/2$, which means we need to excite one spin-down electron from the HOMO band to the LUMO band, with an energy cost of $1.04t$. The same explanation applies to $n=60$ and 61. At $n=57$, 58, 62, 63, 64, ΔE is close to zero, which means that the two different values of S_z are part of the same multiplet. For these cases, in agreement with Hund's rule, the electrons tend to occupy the degenerate HOMO or LUMO in a way that maximizes the total spin.

Note that the small differences in energy for fixed n and different S_z within a multiplet must result from small admixtures of excited states. For example, if the ground state is a triplet, as for $n=62$, and if the first excited state is a singlet, then the $S_z=0$ state may contain a small admixture of the excited singlet state, while the $S_z=1$ state will not. This will result in the $S_z=0$ state having a slightly higher energy than the $S_z=1$ state, providing a measure of the effectiveness of the projection within this multiplet.

At $n=65$, 66, the positive ΔE can again be explained by the single electron picture. A spin-down electron in the t_{1u} band must flip its spin and be excited to the t_{1g} band, with an energy cost of $0.2603t$ for the noninteracting Hamiltonian. This is consistent with Fig. 4 for $n=65$ and 66.

In Table III, part *B*, we calculate the pair-binding energy $\Delta_b(n)$ at various dopings. In these calculation, we have used the lowest energy of the different total spin *z* states for a given *n*. Figure 1 shows a comparison between the perturbation calculations of Refs. 4 and 5 and the PQMC calculations. There is no indication from the PQMC calculations of a bound singlet state for $U>3.3t$, as suggested by perturbation theory and represented by the solid line in Fig. 1. Instead, the ground state for 62 electrons is a triplet over the entire range of parameters studied, in agreement with Hund's rule. Furthermore, we find that this triplet state is unbound for $U/t\leqslant 4.5$. Unfortunately, the sign problem precludes us from studying larger values of *U* using the PQMC. We have also checked the energy difference obtained from the PQMC with the results from imaginary chemical potential simulations, which shows good agreement and is presented elsewhere.[19]

IV. CONCLUSIONS

We have performed extensive QMC simulations on a single C_{60} molecule. The PQMC simulation calculates internal energies at various fillings and shows that Hund's rule is well obeyed. In contradiction to the perturbation theory result,[4,5,20] we find no singlet pair binding [i.e., no negative $\Delta_b(n)$] for the parameter ranges explored ($U=2t$, $3t, 3.5t, 4t, 4.5t$, $t'=1.2t$). Therefore, a purely electronic attractive interaction, originating from the one-band Hubbard model with the on-site Coulomb interaction, seems unlikely. This main result is presented in Fig. 1. However, due to the sign problem, we cannot exclude a singlet-triplet energy crossing for the C_{60} molecule with two-electron doping at larger U/t ($U/t>4.5$) than those studied.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of this project by the Natural Sciences and Engineering Research Council (Canada), The Canadian Institute for Advanced Research (CIAR), CFI, and SHARCNET. All the calculations were carried out at the SHARCNET supercomputing facilities at McMaster University.

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