QMC Calculation of the Electronic Binding Energy in a $C_{60}$ Molecule

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(Dated: March 23, 2022)

Electronic energies are calculated for a Hubbard model on the $C_{60}$ molecule using projector quantum Monte Carlo (QMC). Calculations are performed to 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 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, has a slightly higher energy than the state with electrons on two separate molecules, so that the pair is unbound.

PACS numbers: 74.70.Wz, 71.10.Li, 02.70.Ss

I. INTRODUCTION

The discovery of superconductivity in the alkali-metal-doped bulk fulleranes $K_3C_{60}$ and $Rb_3C_{60}$ sparked intense interest in fullerene-based materials, leading to extensive experimental and theoretical studies (for a review see Ref. 3). 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, and lattice level calculations based on an effective Hamiltonian in which the intramolecular degrees of freedom have been integrated out.

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 co-workers (CK) that electronic interactions within a single $C_{60}$ molecule can lead to an effective attraction between charge carriers. This argument was supported by perturbative calculations of the electronic binding energies of the conventional one band Hubbard model, on the $C_{60}$ structure. Results of the CK calculation suggest that electrons have a tendency to form paired states in a single fullerene molecule, rather than remain 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 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, and stochastic series expansion (SSE) at 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, comparison is made to the results of exact diagonalization (ED) for systems of up to 12 sites. Our main result, shown in Figure 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 $U/t \leq 4.5$, indicating that two
TABLE I: Comparison of exact diagonalization and PQMC calculations on the truncated tetrahedron (12 sites) at \( U = 2t \). PQMC simulation parameters: \( \beta = 10/t, \Delta \tau = 0.05/t, N_m = 10^7 \). \( E_{\text{ex}}(S_z) \) is the energy of a system with \( n \) electrons and \( z \)-component of total spin \( S_z \). \( \Delta_n, m \) is the energy difference \( E_{12+n}(S_z^m) - E_{12+n}(S_z^0) \) with \( (S_z^m, S_z^m) \) given in the second column. For binding energies \( \Delta_n(n) \) the second column shows \( (S_z^{n+1}, S_z^{n-1}, S_z^n) \) – the \( S_z \) values for 3 states involved in its calculation, in the order of appearance in Eq. 4.

| \( n \) | \( S_z \) | ED | PQMC | sign |
|---|---|---|---|---|
| \( 1 \) | 0 | \(-14.506219\) | \(-14.397(3)\) | 0.47 |
| \( 1 \) | 1 | \(-14.506219\) | \(-14.504(2)\) | 1.00 |
| \( 1 \) | \( 1/2 \) | \(-13.623187\) | \(-13.620(3)\) | 0.81 |
| \( 1 \) | \( 3/2 \) | \(-12.876242\) | \(-12.880(4)\) | 0.57 |
| \( 1 \) | \( 2 \) | \(-12.697340\) | \(-12.698(2)\) | 1.00 |
| \( 1 \) | \( 1 \) | \(-11.874844\) | \(-11.856(3)\) | 0.52 |
| \( 1 \) | \( 1/2 \) | \(-10.701320\) | \(-10.698(3)\) | 0.58 |
| \( 1 \) | \( 3/2 \) | \(-9.982385\) | \(-9.969(3)\) | 0.46 |
| \( 2 \) | \( 0 \) | \(-8.762594\) | \(-8.681(4)\) | 0.30 |
| \( 2 \) | \( 1 \) | \(-8.645244\) | \(-8.643(4)\) | 0.54 |
| \( \Delta_{1,0} \) | \( 1(2,0) \) | \( 0.996021 \) | \( 1.000(3) \) |
| \( \Delta_{1,0} \) | \( 3(2,0) \) | \( 1.714956 \) | \( 1.729(3) \) |
| \( \Delta_{-1,0} \) | \( 1(2,0) \) | \( 0.074154 \) | \( 0.078(3) \) |
| \( \Delta_{-1,0} \) | \( 3(2,0) \) | \( 0.821099 \) | \( 0.818(4) \) |
| \( \Delta_n(3) \) | \( 0(0.1/2) \) | \(-0.019995 \) | \( 0.017(4) \) |
| \( \Delta_n(11) \) | \( 0(0.1/2) \) | \( 0.042813 \) | \( 0.038(3) \) |

The largest value of \( U \) we are able to study is 4.5\( t \), since the sign problem discussed below becomes unmanageable for larger values of \( U \).

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

\[
H_0 = - \sum_{\langle ij \rangle \sigma} t_{ij} c_i^\dagger c_j + \text{h.c.} - \mu \sum_{i \sigma} n_{i \sigma},
\]

\[
H_1 = U \sum_i n_{i \uparrow} n_{i \downarrow} - \frac{U}{2} \sum_{i \sigma} n_{i \sigma}.
\]

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

\[
\Delta_n(n) = E_{n+1} + E_{n-1} - 2E_n,
\]

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 \( \Delta_n \).

Determinant or auxiliary field QMC (AFQMC) has been widely used in model Hamiltonian simulations since its introduction by Blankenbecler et al.\textsuperscript{22,23} and its further development by Hirsch\textsuperscript{24,25} and White et al.\textsuperscript{26} 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\textsuperscript{27,28}

\[
Z_{\text{GC}} = \text{Tr} e^{-\beta H} = \text{Tr} e^{-\beta (H_0 + H_1)} = \text{Tr} \prod_{i=1}^L e^{-\Delta \tau (H_0 + H_1)},
\]

where \( \beta = 1/(k_B T) \) is the inverse temperature, discretized in such a way that \( \beta = \Delta \tau L \). After the application of the Hubbard-Stratonovich transformation\textsuperscript{29,30} the
FIG. 2: Grand canonical simulation of a C$_{60}$ molecule at various chemical potentials. Simulation parameters: $U \times 4t$, $\beta \times 10/t$, $\Delta \tau = 0.1/t$. We are only interested 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. Curves connecting the points are guides to the eye.

fermionic degrees of freedom in Eq. (3) may be traced out, and we arrive at

$$Z_{GC} = \prod_{\alpha} \prod_{\sigma} \det[1 + B_L(\alpha)B_{L-1}(\alpha) \cdots B_1(\alpha)]$$

$$= \prod_{\alpha} \prod_{\sigma} \det O(\sigma, \mu) \det O(\sigma, \mu).$$

The $B_l$ matrices are defined as

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

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

$$V'_{ij}(\lambda) = \delta_{ij}[\lambda \sigma_i(l) + \mu \Delta \tau],$$

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 $\uparrow$ or $\downarrow$ in Eq. (3). In Eq. (4) we have used a symmetric decomposition of the partition function, which produces a much smaller Trotter error compared to the non-symmetric decomposition.

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. At low temperatures we use QR factorization to stabilize the matrix multiplications and inversions. A version (projector QMC or PQMC) of the above procedure can be used to directly project out the ground state properties from an initial trial wave function; see Ref. 26 for details.

Unless indicated otherwise, PQMC and AFQMC calculations were performed at the temperature fixed by $\beta = 10/t$, with imaginary time discretization $\Delta \tau = 0.05/t$. The system was first brought to thermal equilibrium by performing $N_t$ thermalizations sweeps $S^2$, followed by $N_m$ measurements with a single sweep $S^1$, performed between them.

Since we are interested in non-bipartite molecules such as C$_{60}$, the MC weights in general are not always positive. In the case of 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 $\langle \ldots \rangle$ is with respect to the probability distribution $|P|$.

Finally, we note that in estimating the statistical error for a composite quantity $X = X_1 + X_2 + \ldots + X_n$, we use the standard formula $\delta X = (\delta X_1^2 + \delta X_2^2 + \ldots + \delta X_n^2)^{1/2}$, where $\delta X_i$’s are estimated by the Jackknife method.
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 $z$-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), $N_m = 10^5$. $N_m$ data were divided into 10 bins for error estimation. For $n = 60, 61, 62$, we have collected more data (between $4 \times 10^7$ and $8 \times 10^7$ measurements) for a more accurate comparison between PQMC and perturbative results. Part B shows electron (hole) binding energies $\Delta_b(n)$. As before, the $S_z$ column in this case lists the $S_z$ values of three states, involved in the calculation of the binding energy, in the order of appearance in Eq. (4). For example, $\Delta_b(58)$ with $S_z = (1/2, 3/2, 1)$ denotes $E_{59}(S_z = 1/2) + E_{59}(3/2) - 2E_{59}(1)$. The data points marked with * were calculated using a non-symmetric decomposition in Eq. (5). Only limited results were obtained for $U = 4.5t$ because of the long averaging times required.

### III. APPLICATION

#### A. Comparison to other methods

In this section, we check our QMC programs against ED and SSE results.\(^{14,35,38}\) Table I lists 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. 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., $\Delta_{b}(11)$. The difficulty of extracting $\Delta_{b}(13)$ from PQMC is possibly because the ground state with 14 electrons lies out the ground state from an initial trial state. We will use these values of $\Delta \tau$ and $\beta$ in our AFQMC and PQMC simulations of the $C_{60}$ molecule.
In Table IV, 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 electrons and the auxiliary Ising field; the Ising field is wiped out completely and the electrons cannot feel the existence of 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 SSE does not suffer from the discretization error, we again confirm that $\Delta \tau = 0.05/t$ in AFQMC is sufficiently small to avoid any systematic discrepancy.

The results in Table IV for simulations on a truncated tetrahedron molecule show that 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 $C_{60}$ 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 $\mu$. At half-filling, unlike the bipartite 2D square lattice, the QMC simulation has a slight sign problem due to the pentagon frustration in the $C_{60}$ geometry; see panels (c) and (d) in Figure 4. From (c) and (d) we also see that hole dopings have a worse sign problem than electron dopings. As expected, the compressibility $\kappa \equiv \frac{1}{\rho} \frac{\partial E}{\partial \rho}$ is reasonably small; thus the extrapolation to $\Delta \tau = 0$ is unnecessary.

Table IV lists the PQMC results for $2 \leq U/t \leq 4.5$ 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 Figure 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 IV, 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 non-interacting single electron energy levels of a $C_{60}$ molecule. At half-filling, 60 electrons move independently in “$\pi$” molecular orbitals formed from the 60 $p_z$ atomic orbitals of the 60 carbon atoms. An exact diagonalization of the non-interacting Hamiltonian gives 60 energy levels, of which the lowest 30 levels are occupied at half filling. The lowest unoccupied molecular orbitals (LUMO) are 3-fold degenerate. The highest occupied molecular orbitals (HOMO) are 5-fold degenerate. The detailed energy levels of the neutral $C_{60}$ molecule are shown in Figure 3. The energy gap between HOMO and LUMO is 1.04$t$ from this exact diagonalization for non-interacting neutral $C_{60}$.

We calculate the energy difference $\Delta E$ of different total $S_z$ values at the same filling as shown in Figure 4. As a severe sign problem occurs for $U = 5t$, the statistical errors are too large for a definite discussion of Hund’s rule. Thus, we mainly discuss results in Figure 4(a)-(c). At $n = 59, 60$ and 61, $\Delta E$ is positive, which can be explained by the non-interacting energy levels in Figure 4. 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 1.04$t$. The same explanation applies to $n = 60$ and 61. At $n = 57, 58, 62, 63, 64$, $\Delta E$ 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 \( \Delta E \) 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 0.2603\( t \) for the
non-interacting Hamiltonian. This is consistent with Figure
4 for \( n = 65 \) and 66.

In Table IV we calculate the pair binding energy
\( \Delta \delta(n) \) at various dopings. In these calculation, we have
used the lowest energy of the different spin \( z \) states for a
given \( n \). Figure IV shows a comparison between the
perturbation calculations of Refs. 4, 5 and PQMC calculations.
There is no indication from the PQMC calculations of a bound
singlet state for \( U > 3.3t \) as suggested by perturbation theory, represented by the solid
line in Figure IV. 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 \( U/t \leq 4.5 \).
Unfortunately, the sign problem precludes us from studying
larger values of \( U \) using PQMC. We have also checked the
energy difference obtained from PQMC with the results
from imaginary chemical potential simulations, which
shows good agreement and will be presented elsewhere. 19

IV. CONCLUSIONS

We have performed extensive QMC simulations on a
single \( C_{60} \) molecule. The PQMC simulation calculates in-
ternal energies at various fillings, and shows that Hund’s
rule is well obeyed. In contradiction to the perturbation theory result, we find no singlet pair binding (i.e.,
no negative \( \Delta \delta(n) \)) 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 on-site Coulomb interaction,
seems unlikely. This main result is presented in Figure

Acknowledgments

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