Nonperturbative approach to the Hubbard model in \( C_{60} \) cluster

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(May 11, 2017)

We propose a computational scheme for the Hubbard model in the \( C_{60} \) cluster in which the interaction with the Fermi sea of charges added to the neutral molecule is switched on sequentially. This is applied to the calculation of the balance of charging energies, within a low-energy truncation of the space of states which produces moderate errors for an intermediate range of the interaction strength.

\[ 36.40, 71.10 \]

The description of the electronic properties of alkali-doped fullerene crystals poses a challenge to the traditional methods of condensed matter physics, as the properties of these systems depend on the conjunction of the large scale structure of the crystal with the small scale effects inside each fullerene. This conjunction is probably responsible for some of the exotic phenomena observed in these materials, the most important of which is the relatively high-\( T_c \) superconductivity of the \( A_3C_{60} \) compounds, \( A \) being an alkaline metal. It is worth to remind that the transition temperatures attained in some of the compounds are above the 40 K, while other carbon based materials like the intercalated compounds of graphite are superconducting up to \( \sim 1 \) K. Most part of the theoretical frameworks proposed for the explanation of the high-\( T_c \) superconductivity rely on specific properties of the electron-phonon interaction or the electron interaction inside the \( C_{60} \) cluster.

In this paper we undertake a formal study of the electronic interaction in the \( C_{60} \) molecule, which is perhaps the worst understood from the phenomenological as well as from the theoretical point of view. In the first place, it seems that, even taking into account screening effects due to the polarization of neighboring molecules, the Coulomb interaction should give rise to a significant repulsion (\( \sim 1 \) eV) between added charges in the \( C_{60} \) molecule. There have been some attempts to explain that, in spite of the bare strong repulsive interaction, the effective interaction between charges over the whole cluster could have a completely different character, because of strong dressing effects or the existence of selection rules for the transitions between different charged states. From the theoretical point of view, the properties of the \( C_{60} \) cluster are difficult to describe since the molecule has an intermediate scale which renders rather useless the standard many-body methods while a numerical diagonalization approach is still unfeasible. In the present paper we deal with a Hubbard model for the electron interaction and propose an alternative to perturbation theory for the same, which may also give the correct physical picture in the strong coupling regime.

The nonperturbative approach we propose is based on the idea of dealing with a reduced Fermi sea comprised of states down the highest unoccupied molecular orbital, up to a given level. One introduces in this process a truncation of the whole set of one-particle occupied orbitals and the way to get under control this approximation has two steps. The first consists of enlarging the set of states in the Fermi sea by adding orbitals of lower energy, up to a point in which the observables considered get stabilized. In practice this happens when the many-body system has reached a too large number of states to admit an exact diagonalization of the Hamiltonian. Then one has to introduce an approximation method which still renders the problem numerically solvable while producing accurate enough results. We implement in this paper an iteration in the number of allowed particle-hole excitations from the reduced Fermi sea. Thus we may be dealing with a Fermi sea made of \( 28 \) states, for instance, and considering an iteration \( n = 0, 1, 2, \ldots \) of respective many-body spaces of states with up to \( n \) particle-hole excitations from the 28 occupied orbitals. The first terms of the succession still lead to a truncated space of states in which the interaction can be numerically solved, but the important point is that the convergence of quantities like the ground state of the system is exponential with regard to \( n \). In any event, the error introduced by stopping the iteration at a given number \( n \) can be estimated. Comparing this computational method with perturbation theory, it turns out that diagonalizing the system with up to \( n \) particle-hole excitations already accounts for a partial sum of the usual perturbative series, since it amounts to consider all the diagrams which can be cut in two parts showing up to \( 2n \) internal electron lines.

The crucial point in our computational scheme lies on the progressive enlargement of the Fermi sea and the possibility of keeping under control the variations of the observables computed. In this sense, our nonperturbative approach is particularly well-suited in the calculation of quantities which do not depend extensively on the size of the Fermi sea, as is the case of the balance of charging energies or correlation functions in the molecule. In the present situation we focus on the evaluation of the energy needed to place a pair of electrons over a neutral \( C_{60} \) cluster, measured with
neutral, singly and doubly charged molecules are given in Table II. The respective differences still gives rise to a manageable space of states. The ground state energies computed in this approximation for the sea considered before. The empirical law (2) enables then to estimate the error produced by stopping at allowed particle-hole excitations. Again these effects are enhanced for even values of \( n \), however, the screening effects of the enlarged Fermi sea by constraining the maximum number of one-particle energy levels in the free theory has the well-known pattern shown in Fig. [4]. In the neutral \( C_{60} \) molecule, all the levels are filled up to the quintuplet right below zero energy. The charged states of the molecule correspond to filling the positive energy levels, starting from the first triplet above zero energy, the states in the triplet transform under spatial rotations as those of an \( l = 1 \) angular momentum representation. Thus, the \( C_{60} \) molecule with one added charge must have a six-fold degenerate ground state, corresponding to spin \( s = 1/2 \) and angular momentum \( l = 1 \) quantum numbers. This degeneracy remains unchanged in the interacting theory, since both quantities are conserved in the Hubbard model [4]. In the same fashion, the \( C_{60}^- \) anion would have in the free theory a 15-fold degenerate ground state, comprising a multiplet with total spin \( s = 1 \) and total angular momentum \( l = 1 \), another with \( s = 0 \), \( l = 2 \), and a singlet state with \( s = 0 \), \( l = 0 \). The degeneracy between these multiplets is removed, though, in the interacting theory.

The parameters which may apply to the actual description of the \( C_{60} \) cluster are \( t \sim 2 \) eV and \( U \sim 5 - 10 \) eV. It seems adequate to consider the interaction between the states in the triplet as the starting point of our computation, since the energy difference with respect to the lower one-particle multiplets is more than 1.5 eV. Thus, neglecting the interaction with the rest of occupied levels below the triplet, the multiplet with \( l = 1 \), \( s = 1 \) would have the lowest energy and \( E_{\text{pair}} = 0 \), as it is possible to place the two electrons with parallel spins without feeling the on-site repulsion. For the above range of parameters it is easy to check that the hybridization with higher unoccupied levels is insignificant, except for the states of the second triplet above zero energy. Therefore, level crossing involving the ground state of the doubly charged molecule and a negative value of \( E_{\text{pair}} \) can only be due to the mixing between the two triplets and the interaction with the negative energy levels. We will consider these as our Fermi sea, whose dynamics we want to include progressively.

As a first step we consider a many-body space of states in which the two triplets above zero energy hybridize and only particle-hole excitations from the quintuplet right below zero energy are included. In this case, the dimension of the space of states for the different anions is small enough that the respective ground states can be obtained by numerical diagonalization. The results are summarized in Table III and plotted in Fig. 2, for \( t = 1.8 \) eV and an on-site repulsion ranging from 2.5 eV to 10.0 eV. For the \( C_{60}^- \) anion we give the energy corresponding to the singlet \( l = 0 \), \( s = 0 \), as well as that of the level with quantum numbers \( l = 1 \), \( s = 1 \). In all the instances it can be seen that the latter has the lowest energy, keeping \( E_{\text{pair}} = E^{(2)} + E^{(0)} - 2E^{(1)} \) well below 0.01 eV—the maximum value we find is for \( U = 10.0 \) eV, \( E_{\text{pair}} \approx 0.001 \) eV. The results for \( E_{\text{pair}} \) match at small \( U \) with those from perturbation theory, which predicts for the singlet a slope equal to 1/20 at the origin [4]. Our fit of the points in the figure gives in turn \( \approx 0.0499 \). It is also instructive, for later use, to check the convergence to the correct ground state energies as the space of states is constrained each time to contain states with a number of particle-hole excitations \( \leq n = 1, 2, 3, \ldots \), up to the total number of particles in the Fermi sea. The screening due to these polarization effects is enhanced at even values of \( n \), but the excitation of two additional particles produces a much weaker effect as \( n \) increases. If we call \( E(n) \) the approximation to the ground state energy \( E_{\infty} \) when taking into account states with up to \( n \) particle-hole excitations, we find that the \( n \)-dependence may be reasonably fitted by

\[
E(n) = E_{\infty} + be^{-an}
\]

with \( a \sim O(1) \). We conjecture that the value of \( a \) does not depend significantly on the size of the Fermi sea, while it certainly is a decreasing function of \( U/t \).

Next we proceed to enlarge the Fermi sea by allowing also particle-hole excitations from the multiplet below the quintuplet considered before. The many-particle space of states we are dealing with now is built out of the two hybridized triplets and particle-hole excitations from the 5-fold and 9-fold degenerated multiplets below zero energy. This space has such a large dimension that makes unfeasible the numerical diagonalization of the hamiltonian. We may estimate, however, the screening effects of the enlarged Fermi sea by constraining the maximum number \( n \) of allowed particle-hole excitations. Again these effects are enhanced for even values of \( n \), and the truncation at \( n = 2 \) still gives rise to a manageable space of states. The ground state energies computed in this approximation for the neutral, singly and doubly charged molecules are given in Table III. The respective differences \( E(n = 2) - E(n = 0) \) can be evaluated, showing that the value of \( b \) in (3) is now between 4 and 4.5 times greater than for the smaller Fermi sea considered before. The empirical law (3) enables then to estimate the error produced by stopping at \( n = 2 \). This
is anyhow a systematic error which goes in the same direction for $E^{(0)}, E^{(1)}$ and $E^{(2)}$, propagating with a weaker influence to a quantity like $E_{\text{pair}}$. The approximated values of $E_{\text{pair}}$ from the above truncation together with the error estimates are plotted in Fig. 2. The fit of the points in the figure gives a slope at the origin $\approx 0.053$, in good agreement with perturbation theory.

The inspection of the respective curves of $E_{\text{pair}}$ in Fig. 2 for the Fermi sea with 10 states and for that with 28 states (including spin) shows a clear stabilization of the results in the second case. One should not expect a significant modification of the curves by the inclusion of lower energy multiplets in the Fermi sea since, moreover, particle-hole excitations from the low one-particle levels would require higher energy. It is therefore plausible that the physical picture which emerges from Fig. 2 is essentially correct. The screening effects which take place within the $C_{60}$ molecule turn out to be very efficient reducing the bare electronic repulsion between added charges in the $s = 1$ multiplet. This repulsion is appreciably smaller, already at intermediate values of $U/t$, than that estimated by perturbation theory. The doubly charged state with $s = 0$ seems to be always an excited state, opposite to what happens in smaller clusters like the truncated tetrahedron.

The reason for this different behaviour is that, switching off the interaction with the Fermi sea in the $C_{60}$ cluster, the interaction in the partially occupied triplet already places the singlet state at a fair energy above the $s = 1$ multiplet and the screening effects are not able to modify this trend. In the cluster of the truncated tetrahedron, the interaction within the triplet keeps the $s = 1$ level degenerated with a $s = 0$ doublet, which is driven at a lower energy by the particle-hole excitations. It would be interesting to understand the factors which may alter the relative position of the levels. In this sense, a most interesting proposal has been made in ref. 10 considering the frequency dependence of the screening effects, which may favor energetically the $s = 0$ singlet state. The nonperturbative framework presented in this paper may be useful in the study of these problems, as well as in the study of other effects like charge and spin correlations.

We want to thank F. Guinea for encouragement and useful discussions during the development of this work.

FIG. 1. One-particle spectrum of the $C_{60}$ cluster. Energy eigenvalues are plotted in the horizontal axis and the multiplet degeneracy is given along the vertical direction.

FIG. 2. Plot of the values of $E_{\text{pair}} = E^{(0)} + E^{(2)} - 2E^{(1)}$ corresponding to the data in Table 1 (points over the solid lines) and to those in Table 2 (points over the dashed lines). The latter are affected by the error bars mentioned in the text.
| $U$ (eV) | $E^{(0)}$ (eV) | $E^{(1)}$ (eV) | $E^{(2)}$ (eV) | $E^{(2)}$ (eV) |
|----------|----------------|----------------|----------------|----------------|
| 2.5      | 1.021          | 2.593          | 4.166          | 4.266          |
| 5.0      | 2.007          | 3.795          | 5.583          | 5.744          |
| 7.5      | 2.963          | 4.970          | 6.977          | 7.170          |
| 10.0     | 3.894          | 6.121          | 8.349          | 8.558          |

**TABLE I.** Respective ground state energies of the neutral, singly and doubly charged $C_{60}$ molecule, computed with a Fermi sea of 10 states. The origin of energies is taken at the highest occupied one-particle level of the neutral molecule.
TABLE II. Respective ground state energies of the neutral, singly and doubly charged $C_{60}$ molecule, computed with a Fermi sea of 28 states and the approximation mentioned in the text. The origin of energies is as in the preceding table.

| $U$ (eV) | $E^{(0)}$ (eV) | $E^{(1)}$ (eV) | $E^{(2)}$ (eV) | $E^{(2)}$ (eV) |
|----------|----------------|----------------|----------------|----------------|
|          | $s = 1$        | $s = 0$        |                 |                 |
| 2.5      | −4.308         | −2.352         | −0.394         | −0.300         |
| 5.0      | 3.621          | 6.191          | 8.765          | 8.909          |
| 7.5      | 11.451         | 14.643         | 17.846         | 18.018         |
| 10.0     | 19.218         | 23.036         | 26.872         | 27.060         |
