Variational approach to the Hubbard model in a C_{60} cluster

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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.

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.¹ It is worth remembering 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 ~ 1 K. Most of the theoretical frameworks proposed for the explanation of the high- T_c superconductivity rely on specific properties of the electron-phonon interaction²⁻⁶ or the electron interaction⁷⁻⁹ 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 (~ 1 eV) between added charges in the C_{60} molecule.^{10,11} 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 effects⁷ or the existence of selection rules for the transitions between different charged states.¹² 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 this approximation under control 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 $n=0,1,2,\dots$ 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 respect to a configuration of a single electron in each of two different molecules. This is what has been called E_{pair} in Ref. 7, and it has been linked to the signature of a purely electronic mechanism for the superconductivity in the alkali-doped materials.

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. The thick lines correspond to filled levels in the noninteracting neutral molecule.

For the sake of simplicity we will consider a Hubbard model of interaction for the 60 π orbitals of the C_{60} cluster,

$$H = -t \sum_{i,j,\sigma} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad \sigma = \uparrow, \downarrow, \quad (1)$$

where the first sum is over nearest neighbors i, j and n_i is the electron number operator at site i . The spectrum of one-particle energy levels in the free theory has the well-known pattern shown in Fig. 1.¹³ 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.¹⁴ Thus, the C_{60} molecule with one added charge must have a sixfold-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 (1). In the same fashion, the C_{60}^{2-} 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 three 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_{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

TABLE I. Respective ground state energies of the neutral, singly, and doubly charged C_{60} molecule, computed with a Fermi sea of ten states. The origin of energies is taken at the highest-occupied one-particle level of the neutral molecule.

U (eV)	$E^{(0)}$ (eV)	$E^{(1)}$ (eV)	$E^{(2)}$ (eV)	$E^{(2)}$ (eV)
			$s=1$	$s=0$
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

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 I 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}^{2-} 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_{pair} match at small U with those from perturbation theory, which predicts for the singlet a slope equal to $1/20$ at the origin.⁷ Our fit of the points in the figure gives in turn ≈ 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 $\leq n=1, 2, 3, \dots$, 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

FIG. 2. Plot of the values of $E_{\text{pair}} = E^{(0)} + E^{(2)} - 2E^{(1)}$ corresponding to the data in Table I (points over the solid lines), to those in Table II (points over the dashed lines, affected by the error bars mentioned in the text), and to data obtained after addition of the renormalization shown in Table III (points over the dotted lines).

FIG. 3. Plot of the values of $E_{\text{pair}} = E^{(0)} + E^{(2)} - 2E^{(1)}$ corresponding to the system with a reduced Fermi sea of ten states and up to two particle-hole excitations to the first two unoccupied triplets (points over the solid lines) and to the first unoccupied quintuplet in addition (points over the dashed lines, that for $s=1$ being superposed to the corresponding solid line).

much weaker effect as n increases. If we call $E(n)$ the approximation to the ground state energy E_{∞} when taking into account states with up to n particle-hole excitations, we find that the n dependence may be reasonably fitted by

$$E(n) = E_{\infty} + b e^{-an}, \quad (2)$$

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 .

We may pause at this point to check the influence on the screening effects of the unoccupied states above the two triplets. For this purpose we enlarge the previous space of states by considering also particle-hole excitations to the first unoccupied quintuplet in the spectrum. This represents a more symmetric truncation of the one-particle basis, as this is made now of the two triplets and the two quintuplets closer to zero energy in the diagram of Fig. 1. Within the huge many-body space of states thus generated we are able to find the ground state for the different charged molecules among the states with up to two particle-hole excitations. According to our previous experience, this already provides a very good approximation (within several meV) to the ground state energy. We have plotted in Fig. 3 the curves of the pair-binding energies in the present situation compared to those obtained in the smaller many-body space of states considered before, with a similar restriction on the maximum number (2) of particle-hole excitations. The deviation between the two instances is only appreciable in the case of the singlet $s=0$, though it becomes clear that the enhancement of the screening due to higher unoccupied states is rather small and cannot produce by itself a qualitative change of the picture for E_{pair} .

Bearing the above consideration in mind, we focus on the screening of the interaction within the lowest two unoccu-

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)	
			$s=1$	$s=0$
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

pled triplets and proceed next to enlarge the Fermi sea by allowing also particle-hole excitations from the multiplet below the occupied 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 fivefold- and ninefold-degenerate 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 II. The respective differences $E(n=2) - E(n=0)$ can be evaluated, showing that the value of b in (2) is now between 4 and 4.5 times greater than for the smaller Fermi sea considered before. The empirical law (2) enables one 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_{pair} . The approximated values of E_{pair} from the above truncation together with the error estimates are plotted in Fig. 2. The fit of the points for the singlet gives a slope at the origin ≈ 0.053 , in good agreement with perturbation theory.

The inspection of the respective curves of E_{pair} in Fig. 2 for the Fermi sea with 10 states and for that with 28 states (including spin) shows a tendency to the stabilization of the results in the second case. One should not expect a qualitative 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 require higher energy. An estimate of the effect of the lower orbitals not taken yet into account can be obtained by studying the way in which these renormalize the energy of the states over the Fermi sea. We have followed this approach by diagonalizing the interaction within the two unoccupied triplets, including this time up to two particle-hole excitations only from the multiplets in the lowest part of the spectrum in Fig. 1, corresponding to the representations **1**, **3**, **5**, and **7** (broken to **3** + **4**) of the rotation group. In the many-body space of states thus generated (without particle-hole excitations from the two highest occupied levels already considered before) the ground state energies of the neutral, singly, and doubly charged systems get shifted by values $\Delta E^{(0)}$, $\Delta E^{(1)}$, and

TABLE III. Renormalization of the level of zero energy ($\Delta E^{(0)}$), of the energy of one particle ($\Delta E^{(1)}$) and of the energy of two particles ($\Delta E^{(2)}$) due to the interaction with the orbitals deep in the Fermi sea of Fig. 1, as explained in the text.

U (eV)	$E^{(0)}$ (eV)	$E^{(1)}$ (eV)	$E^{(2)}$ (eV)	
			$s=1$	$s=0$
2.5	-0.055	-0.046	-0.037	-0.044
5.0	-0.210	-0.177	-0.142	-0.160
7.5	-0.445	-0.377	-0.304	-0.330
10.0	-0.746	-0.634	-0.513	-0.544

$\Delta E^{(2)}$, respectively, with respect to the case in which the Fermi sea is absent. What we are measuring in this way is the redefinition of the level of zero energy, of the energy of one particle, and of the energy of two particles over the Fermi level, due exclusively to the interaction with the orbitals deep in the Fermi sea. The values we have obtained for $\Delta E^{(0)}$, $\Delta E^{(1)}$, and $\Delta E^{(2)}$ are shown in Table III. These shifts can be consistently taken into account in the determination of the pair-binding energy, by adding them, respectively, to our previous results for $E^{(0)}$, $E^{(1)}$, and $E^{(2)}$. The curves of E_{pair} corrected in this way are shown in Fig. 2 and Fig. 4. The final picture that we obtain with our variational computation is qualitatively different to that obtained in perturbation theory, as shown in Fig. 4, but is very close otherwise to that arising from the result of the sum of ladder diagrams (see Fig. 7 in Ref. 9). The fair agreement between that non-perturbative computation and our variational approach makes plausible that the physical picture which emerges from Fig. 2 is essentially correct.

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.¹⁵ The reason for this different behavior 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 degenerate 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. 16 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.

FIG. 4. Plot of the renormalized values of E_{pair} (same dotted lines as in Fig. 2) and of the same quantity obtained to second order in perturbation theory (dashed lines).

On the other hand, 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. As can be seen in Fig. 4, this repulsion is appreciably smaller, throughout the range of U/t considered, than that estimated by perturbation theory. It has been pointed out that, in the description of the interactions within the C_{60} molecule by means of a model Hamiltonian like (1), the appropriate value of U/t is ≈ 2 .¹⁷ For this value, the effective repulsion between electrons in the present situation of one charge per C_{60} should be very small (only a few meV), according to our results. The estimate of this repulsion is an important ingredient in the phenomenological description of the superconductivity,¹⁸ as there has been some controversy about the form in which the required value of the pseudopotential μ^* may arise from the bare electronic interaction.¹⁹ Our results seem to agree with the conclusions of Ref. 19, where screening effects are considered in the random-phase approximation (RPA) while the renormalization of μ is studied by means of a sum of ladder diagrams. Our variational approach implements a different kind of approximation but is able to deal simultaneously with both types of quantum corrections. It would be worthwhile therefore to extend our treatment, together with the analysis of the electron-phonon interaction, to produce a precise picture of the superconductivity mechanism of the A_3C_{60} compounds.

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