PHYSICAL REVIEW B VOLUME 45, NUMBER 20 15 MAY 1992-II

Application of the Gutzwiller method to neutral and ionic C_{60} aggregates

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(Received 16 July 1991; revised manuscript received 6 February 1992)

We use the Gutzwiller method for studying various characteristic energies of C_{60} in the free state (first and second ionization energy, electron affinity, and singlet and triplet excitation energies). We improve a previous description by adding a term that takes into account the noncompensation of the overall nuclear and electronic charges in ionic species. Our results are in good agreement with experiment. We also study $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$, which are nonstable in the free state but can be produced in solution. By including a polarization term and by using the electron affinities calculated in the free state, we evaluate the reduction potentials in solution for the reactions $C_{60}{}^{Z-}\rightarrow C_{60}{}^{(Z+1)-}$ $(Z=0,1,2)$ and compare them with recent experimental data.

I. INTRODUCTION

The recent discovery of a method for producing C_{60} molecules[1] has been the start of a very active field of research. Many experimental techniques have been applied to either pure C_{60} or alkali-metal-alloyed solid phases: x-ray diffraction,[2,3] infrared absorption,[4–6] ultraviolet absorption,[4] photoemission,[7] nuclear magnetic resonance,[8] electron spin resonance,[5] magnetic susceptibility study,[9,10] etc. One of the most interesting observations is that K_xC_{60} and Rb_xC_{60} $(x\sim 3)$ exhibit a superconducting transition at, respectively, $T_c=18$ and 28 K.[11,12]

For understanding these results a good knowledge of the individual C_{60} molecule is required. The first purpose of this paper is to study various excitation energies of free C_{60} aggregates (ionization potentials, electronic affinities, excitation energies). The last section will be devoted to a discussion of the reduction potentials of C_{60} in solution for which experimental values have recently been published.[5]

II. THE MODEL

A. Description of the system

We will suppose that C_{60} has a truncated icosahedral shape. This is a slightly distorted sp^2 structure and then two kinds of bands appear: a σ-bonding band which is complete and a half-filled π band with 60 electrons (1π electron per atom). As it is usually done, we will limit ourselves to the study of the highest π electronic levels.

In a first step, let us pay some attention to the Hückel-type calculations.[13–16] They show that C_{60} is very stable since the π energy per atom, 1.553β, is close to the graphite value, 1.576β (β is the Hückel hopping energy). Unfortunately, the Hückel method, which gives the main trends in some problems, is not sufficient here. One of the reasons is that we intend to evaluate energy differences between systems which do not have the same number of electrons. So in this case, the correlation energy plays an important part and must be taken into account.

Following numerous authors, such as, for instance, Lee,[17,18] we will limit ourselves to intra-atomic correlation, then the Hamiltonian takes the Hubbard form:

$$H_{\rm Hub}=\beta \sum_{\substack{i,j\ \text{neighbors}\\ \sigma}} c^{\dagger}_{1\sigma}c_{j\sigma}+U\sum_{i} n_{i\uparrow}n_{i\downarrow}\ .$$

The first term is the one-electron Hückel part, the second the correlation term where U is the intra-atomic correlation energy. In some studies the Heisenberg Hamiltonian, which is the limit form of $H_{\rm Hub}$ for very large $U/|\beta|$, is also used.[19,20]

Here, we will adopt the values $\beta=-2.35$ eV and $U=5.5$ eV as in a previous calculation.[21] These parameters describe a system which is intermediate between the two limits: $U\sim 0$ (Hückel theory) or $U\sim\infty$ (Heisenberg Hamiltonian). In this range of $U/|\beta|$ value, the Gutzwiller approximation gives a good approximate solution of $H_{\rm Hub}$.

B. The Gutzwiller method

We will not give a complete description of the Gutzwiller method[22] and will only briefly recall its basic principles. The determinant Ψ_0 which represents the solution of the Hückel Hamiltonian is projected on the basis of the atomic determinants Φ_k:

$$\Psi_0=\sum_k c_k\Phi_k\ .$$

Then a new wave function Ψ is built by multiplying the weights c_k by a factor η^{ν_k} $(\eta\le 1)$:

$$\Psi=\sum_k c_k\eta^{\nu_k}\Phi_k\ ,$$

where ν_k is the number of doubly occupied sites in Φ_k and η is a variational parameter. This last parameter is fixed by minimizing:

$$\varepsilon(\eta)=\frac{\langle\Psi|H_{\mathrm{Hub}}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$

and the electronic energy E_{el} is the minimum of $\varepsilon(\eta)$.

For systems with a relatively large number of electrons (larger than about ten) a simplification of the calculation is obtained by replacing η by another variational parameter ν (which physically gives the number of doubly occupied sites). Then, if we introduce the total number of electrons and sites, respectively, N and L, the energy to be minimized is simply written, for $N \leq L$,

$$\varepsilon(\nu)=NE_{\mathrm{at}}+Q(\nu)E^H+\nu U ,$$

where

$$Q(\nu)=\frac{(N_\uparrow-\nu)}{N_\uparrow(L-N_\downarrow)}\left[(L-N_\uparrow-N_\downarrow+\nu)^{1/2}+\nu^{1/2}\left[\frac{N_\downarrow-\nu}{N_\uparrow-\nu}\right]^{1/2}\right]^2 ,$$

E^H is the Hückel energy, $N_\uparrow$ and $N_\downarrow$ the total number of $\uparrow$ and $\downarrow$ spins, and

$$0\leq\nu\leq\frac{N_\uparrow N_\downarrow}{L} .$$

When $N>L$

$$\varepsilon(\nu)=NE_{\mathrm{at}}+Q'(\nu)E^H+(N-L)U+\nu U ,$$

where $Q'(\nu)$ is obtained from $Q(\nu)$ by replacing $N_\uparrow$ and $N_\downarrow$ by $(L-N_\uparrow)$ and $(L-N_\downarrow)$ and

$$0\leq\nu\leq\frac{(L-N_\uparrow)(L-N_\downarrow)}{L} .$$

Originally, the Gutzwiller method was proposed for studying bulk systems with equivalent atoms but its extension to finite systems has been made. This extension has been checked by a comparison with the exact solutions of H_{Hub}.[23,24] In Ref. 21, we have applied this method for analyzing the existence of a triplet ground state in some polyenes with six or eight carbon atoms. We also studied the evolution of the ionization energy of some aromatic polyenes with $6 \leq L \leq 34$ and various experimental characteristics were well reproduced, such as, for example, the global decrease with L of the ionization energies. The main point to be improved is that the ionization energy decreases too slowly with L. This discrepancy is due to the fact that we did not take into account a capacitive R^{-1} term[25] which destabilizes the ions with small sizes. The physical origin of this term is the noncompensation between positive nuclear and negative electronic charges in charged aggregates.

Here, we will add this energy, that we will denote $C(Z)$, and we then write the total energy as

$$E=E_{\mathrm{el}}+C(Z)$$

with

$$C(Z)=\alpha_Z\frac{(Ze)^2}{4\pi\epsilon_0 R} ,$$

where $\alpha_Z=\frac{3}{8}(Z>0)$; $\alpha_Z=\frac{5}{8}(Z<0)$ and where R is an average radius of the π molecular orbital. We have used the same R value ($R=4.5$ Å) for all the calculations on C_{60} (neutral and ionic).

As we add a new term in the energy we have to change the energy origin E_{at}. We fix it by adjustment with experiment (ionization energy of the aromatic polyene containing 34 atoms studied in Ref. 21). We then obtain $E_{\mathrm{at}}=7.32$ eV. Our result for the benzene ionization energy (theory: 9.62 eV; experiment: 9.25 eV) shows that the method can be applied over a wide range of L values.

III. RESULTS FOR FREE C_{60}

We give in Table I the values of I_1 and I_2, the ionization energies involved in $C_{60}\rightarrow C_{60}{}^{+}$ and $C_{60}^{+}\rightarrow C_{60}{}^{2+}$ reactions. The I_1 value, 7.2 eV, is smaller than the experimental value, 7.61 eV.[26–30] If we consider the approximate character of our model a difference of some tenth of eV is not surprising. Better calculations should, for instance, allow a variation of the shapes of the various C_{60} species. We observe that the double ionization energy $I_1+I_2=16.88$ eV ($C_{60}\rightarrow C_{60}{}^{2+}$) agrees with the experimental results. It is also the case of the electronic affinity $E_{A1}(C_{60}\rightarrow C_{60}{}^{-})$. The E_{A2} and E_{A3} energies, involved in $C_{60}{}^{-}\rightarrow C_{60}{}^{2-}$ and $C_{60}{}^{2-}\rightarrow C_{60}{}^{3-}$ reactions, are negative which means that, as it is likely, free $C_{60}{}^{2-}$ and $C_{60}{}^{3-}$ are not stable. These results will be used in the next section.

The method also allows the determination of excitation energies of neutral C_{60}. If we consider the where HOMO→LUMO (where HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital), HOMO→LUMO+1, and HOMO−1→LUMO transitions, we obtain the energies $E_{S1}=1.74$ eV; $E_{S2}=2.29$ eV; $E_{S3}=2.60$ eV for a singlet excited state and $E_{T1}=1.67$ eV; $E_{T2}=2.22$ eV; $E_{T3}=2.53$ eV for a triplet excited state. Our values are comparable with the results of other calculations,[33–35] for example, $E_{S2}=3.2$ (equal bond case, Ref. 33) and 2.5 eV.[35] The

TABLE I. Calculated and experimental values (eV) of the ionization energies I, and of the electron affinity E_A, in the free state for the following reactions: I_1 ($C_{60}\rightarrow C_{60}{}^{+}$), I_2 ($C_{60}{}^{+}\rightarrow C_{60}{}^{2+}$), E_{A1} ($C_{60}\rightarrow C_{60}{}^{-}$), E_{A2} ($C_{60}{}^{-}\rightarrow C_{60}{}^{2-}$), E_{A3} ($C_{60}{}^{2-}\rightarrow C_{60}{}^{3-}$). We also give a theoretical value for I_1 (Ref. 30), obtained recently with a local-density-functional method.

	Theory	Experiment
		7.6 (Ref. 26)
I_1	7.2	7.61±0.11 (Ref. 27)
		7.61±0.2 (Refs. 28 and 29)
	7.6 (Ref. 30)	7.5–7.72 (Ref. 31)
I_2	9.68	
I_1+I_2	16.88	>16 (Ref. 8)
		<18 (Ref. 5)
E_{A1}	2.23	2.6–2.8 (Ref. 32)
E_{A2}	−1.86	
E_{A3}	−5.87	

comparison with experiment is difficult because one must take into account the oscillator strength of each transition and some transitions, though optically active, have a very small oscillator strength and are thus difficult to observe.[33] Let us mention that the energy difference between the lowest triplet state and the fundamental state of C_{60} (which corresponds to E_{T1}) has been measured by uv photoelectron spectroscopy of $C_{60}{}^-$ and gives 1.7 eV,[36] in close agreement with our result.

IV. REDUCTION POTENTIALS IN SOLUTION

When the ionization takes place in a solution the phenomenon becomes more complex. However, a recent study on silver [Ag, Ag_2, Ag_4 (Ref. 37)] has shown that the redox potential can be related to the ionization energy in the free state. By adapting the same ideas to the negative ionizations of C_{60} we will write that the electronic affinity in solution $E_{A_{\mathrm{sol}}}$ is given by adding to the electronic affinity in the free state a polarization energy ΔG_{sol} due to the screening of the charge by the solvent:

$$E_{A_{\mathrm{sol}}} = E_A + \Delta G_{\mathrm{sol}} .$$

The energy $E_{A_{\mathrm{sol}}}$ does not directly give the redox energy $|e|P_R$ (where P_R is the measured redox potential); one must introduce a shift E_{shift} characteristic of the type of electrodes. Therefore we have

$$|e|P_R = E_{A_{\mathrm{sol}}} + E_{\mathrm{shift}} = E_A + \Delta G_{\mathrm{sol}} + E_{\mathrm{shift}} . \tag{1}$$

By using the reduction potentials given in Ref. 5 and our values of Table I three equations can be written (in eV):

$$C_{60} \rightarrow C_{60}{}^-:\ -0.51 = 2.23 + \Delta G^1_{\mathrm{sol}} + E_{\mathrm{shift}} , \tag{2}$$

$$C_{60}{}^- \rightarrow C_{60}{}^{2-}:\ -0.9 = -1.86 + \Delta G^2_{\mathrm{sol}} - \Delta G^1_{\mathrm{sol}} + E_{\mathrm{shift}} , \tag{3}$$

$$C_{60}{}^{2-} \rightarrow C_{60}{}^{3-}:\ -1.38 = -5.87 + \Delta G^3_{\mathrm{sol}} - \Delta G^2_{\mathrm{sol}} + E_{\mathrm{shift}} , \tag{4}$$

where $\Delta G^Z_{\mathrm{sol}}$ ($Z=1,2,3$) is the polarization energy of the $C_{60}{}^{Z-}$ ion in the solvent. The system of equations can be simplified if we consider that, as $\Delta G^Z_{\mathrm{sol}}$ is a polarization energy, it will mainly depend on Z^2, the square of the charge:

$$\Delta G^Z_{\mathrm{sol}} = Z^2 \Delta G^1_{\mathrm{sol}} . \tag{5}$$

This assumption, which would be questionable in other cases, is likely here because all the electrons are added on the same LUMO degenerate molecular orbital. By inserting relation (5) in Eqs. (2)–(4) we obtain a set of three equations depending only on $\Delta G^1_{\mathrm{sol}}$ and E_{shift}.

By solving the system of Eqs. (2) and (3), where Eq. (3) is now written

$$-0.9 = -1.86 + 3\Delta G^1_{\mathrm{sol}} + E_{\mathrm{shift}}$$

we obtain

$$\Delta G^1_{\mathrm{sol}} = 1.85 \text{ eV}, \quad E_{\mathrm{shift}} = -4.59 \text{ eV} . \tag{6}$$

Let us first discuss these two values. The order of magnitude of $\Delta G^1_{\mathrm{sol}}$ seems correct if we compare it with the value obtained for Ag^+ [$\Delta G_{\mathrm{sol}} \sim 4.9$ eV (Ref. 37)]. The reduction from Ag^+ to $C_{60}{}^-$ can be explained by the radius of the particles (1.26 and 4.5 Å) since a decrease roughly proportional to R^{β}, with $\beta \sim -1$, is expected. The value of E_{shift} is not too far from -4.26 eV, the value given by tables, which corresponds to the electrode used in the experiments (SCE: standard calomel electrode). As all our parameters are fixed, Eq. (4) can be used as a control of the method. By using (5) this equation is written

$$-1.38 = -5.87 + 5\Delta G^1_{\mathrm{sol}} + E_{\mathrm{shift}} .$$

Then, by inserting the values (6) we obtain for the second member -1.21 eV which is close to the first member value -1.38 eV.

Then, one sees that this simple description gives results which agree with experiment. It is noteworthy that the rapid decrease of E^Z_A with the degree of ionization Z is mainly due to the $C(Z)$ term, not to the E_{el} term since the three electrons are added on the same LUMO level. However, this E_A decrease does not lead to a strong P_R variation because the increase of $\Delta G^Z_{\mathrm{sol}}$ nearly compensates the $C(Z)$ effect (both vary as Z^2).

In conclusion, one may say that this work has shown that the Gutzwiller method is a simple useful tool which can be used as a first step for understanding experimental data on C_{60} systems. Another possible application is the study of $C_{60}X_3$ solid phases[38] (X=K, Rb, Cs), where the electronic affinities of C_{60} play a large part.

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