The exchange coupling between the valence electrons of the fullerene cage and the electrons of the N atoms in N@C_{60}^{-1,3}

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**Abstract**

MCSCF calculations are performed in order to determine the exchange coupling between the 2p electrons of the N atom and the LUMOs of the fullerene cage in the case of mono- and tri- anions of N@C_{60}. The exchange coupling resulted by our calculations is large compared to the hyperfine interaction. The strong coupling can explain the missing EPR signal of the nitrogen in paramagnetic anions.

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I. INTRODUCTION

Since the discovery of the first endohedral fullerene a lot of interests have been attracted by this area of the nanotechnology. Many metal atom can be encapsulated by using discharge techniques or ion implantation. In all the cases the metal atom interacts strongly with the fullerene and acts as an electron donor occupying an ‘off-centered’ position inside the cage. In contrast the nitrogen in N@C$_{60}$ is situated at the center of the molecule and retains its S=3/2 spin quartet atomic state. This amazing property of the encapsulated N atom triggered several research on its possible application in quantum computing and spin labeling. Several publications studied the promise and limitations of using endohedral fullerenes as quantum information carriers. Mehring et al. recently pointed out experimentally the entanglement of the nuclear spin and the electronic spin of the encaged N atom.

The changes of the characteristic EPR signal of the quartet electronic spin of the N atom makes it an ideal probe for monitoring chemical reactions of C$_{60}$. During the last decade a great deal of excitement has been brought by the discovery of the superconductivity of the alkali-doped fullerenes. In this type of fullerene compounds the valence electrons of the ionized alkali atoms partially occupy the bands formed by the LUMOs of the C$_{60}$ molecules. The applicability of the quartet atomic state of the N atom as a spin label depends on the strength of the interaction between the 2p electrons of the N atom and the valence electron of the fullerene cage. An interaction which is small compared to the hyper-fine interaction, results in a line width effect of the EPR signal and the N@C$_{60}$ is a good candidate for a spin labeling agent. In the case of strong coupling the EPR signal of the system is completely changed and the lines corresponding to the valence electrons of the N atom are hard to identify in the signal of the paramagnetic system.

The interaction between the 2p electrons of the N atom and the valence electrons of the C$_{60}$ can be described by a Heisenberg like effective Hamiltonian $H_{int} = J S_N S_{C_{60}}$ where $S_N$ and $S_{C_{60}}$ denote the spin operator for the valence electrons of the N atom and the C$_{60}$, respectively, and J is the exchange coupling characterizing the strength of the interaction. The aim of the present paper is to determine theoretically the exchange coupling of the effective Hamiltonian. The exchange coupling has importance not only for EPR measurements but it plays essential role in the description of the transport through magnetic molecules which is particularly interesting from the point of view of spintronics.
II. COMPUTATIONAL DETAILS

The calculations have been performed using the Gamess quantum chemical program package. The proper description of the open-shell N@C$_{60}^-$ and N@C$_{60}^-$ anions requires multi-determinant wave functions. The restricted open-shell (ROHF) calculations in the Gamess package are accessible via the generalized valence bond (GVB) or the multi-configurational self-consistent field (MCSCF) methods using an appropriate active space. The energy of the anions of N@C$_{60}$ with different multiplicity has been determined by means of CAS SCF calculations where the active space is confined to the 2p orbitals of the nitrogen atom and the three fold degenerate LUMOs of the fullerene molecule. For the clear interpretation of the results the excitations from the orbitals of the nitrogen to the LUMOs of the cage, and vice versa, were excluded from the active space applying the occupation restricted multiple active space technique. The MCSCF treatment of the open-shell systems using such a small active space is practically equivalent to the ROHF level of calculations. The calculation has been performed using split valence 631g basis on the carbon atoms. For the better description of the week interaction between the encapsulated atom and the fullerene molecule the basis on the N atom is extended by additional diffuse p orbitals and two d polarization functions (631+g(dd)). It is well known that in order to describe the electronic structure of negatively charged species application of diffuse basis functions is necessary. In our case the excess charge is distributed uniformly among the 60 carbon atoms and the lack of the diffuse basis on the carbon atoms does not affect dramatically our results. However, in order to check the sensitivity of the exchange coupling to the applied basis the calculations have also been performed with the Dunning’s double zeta and the split valence 631+g basis sets on the carbon atoms. The geometry of the N@C$_{60}^-$ molecule in the S=1 state and the N@C$_{60}^-$ in the high spin S=3 state have been optimized at ROHF level and it is retained during the calculations of the energy of the systems with different multiplicity.

III. RESULTS AND DISCUSSIONS

It has been shown experimentally that in the highly reduced states of the N@C$_{60}$ the excess electrons occupy the LUMOs of the fullerene and the N atom inside the cage remains in spin quartet state. In order to check the consistency of our calculations to the experimental
findings we performed a set of ROHF calculations on the mono- and tri-anions populating at first the 2p orbitals of the nitrogen and then populating the LUMOs of the C\textsubscript{60}. The results are summarized in Table I. The valence electrons of the nitrogen referred as N2p in Table II occupy the 7t\textsubscript{1u} orbitals of the endohedral complex between the 6h\textsubscript{u} HOMO and 8t\textsubscript{1u} LUMO of the C\textsubscript{60} in agreement with the result of ref\textsuperscript{15}. Rather different value for the one-electron energy of the N2p orbitals is reported by Greer\textsuperscript{16}. This discrepancy is originated from the different treatment of the open-shell problem as it is discussed in ref\textsuperscript{17}. In the case of the mono-anion the energy of the two triplet states were compared while in the case of the triply ionized molecule the energy of the singlet state with fully occupied valence orbitals of N was compared to the high spin state of the N@C\textsubscript{60}\textsuperscript{3-}. For both ions the system with intact N atom were energetically more favorable in agreement with the EPR measurements\textsuperscript{13}.

The interaction between the electrons of the nitrogen atom and the valence electrons on the C\textsubscript{60} anion is described by a Heisenberg-like effective Hamiltonian:

\[ H_{int} = J S_N S_{c_{60}} \]  

(1)

where J is the coupling constant, S\textsubscript{N} and S\textsubscript{c\textsubscript{60}} are the spin of the nitrogen atom and the C\textsubscript{60} anion, respectively. The square of the total spin operator S\textsuperscript{2} = (S\textsubscript{N} + S\textsubscript{c\textsubscript{60}}\textsuperscript{2}) commutes with the Hamiltonian of the full system H = H\textsubscript{N} + H\textsubscript{C\textsubscript{60}} + H\textsubscript{int} and, consequently, its eigenvalue is a good quantum number. Expressing the interaction in terms of the spin of the subsystems and the spin of the whole molecule:

\[ H_{int} = \frac{1}{2} J (S^2 - S_N^2 - S_{c_{60}}^2) \]  

(2)

the energy can be simply given as:

\[ E_S = E_0 + \frac{1}{2} JS(S + 1) \]  

(3)

where E\textsubscript{0} denotes the energy of the separated systems and the subscript S indicates the explicit dependence of the energy on the multiplicity. Since our interaction Hamiltonian can describe only such processes in which S\textsubscript{N} and S\textsubscript{c\textsubscript{60}} are unchanged the excitations altering the spin of the subsystems, namely the hole and the particle are on different species, has to be excluded from the configuration space. In the case of N@C\textsubscript{60}\textsuperscript{1} S\textsubscript{N} = 3/2 and S\textsubscript{C\textsubscript{60}} = 1/2 spanning an 8 dimensional direct product space. The total spin can have the values of S = 1 or S = 2 with the corresponding energies

\[ E_{S=1} = E_0 + J \]  
\[ E_{S=2} = E_0 + 3J \]  

(4)
Comparing the energy of the triplet and quintet state one can easily extract the exchange coupling as:

\[ J = \frac{1}{2} (E_{S=2} - E_{S=1}) \]  

(5)

The results of the MCSCF calculations using 631g and DH basis are summarized in Table II. Although the application of the double zeta basis resulted in considerably deeper total energy the deviation of the exchange couplings is small.

In the case of the triply ionized N@C\textsubscript{60} the valence electrons form a \( S_{C_{60}} = 3/2 \) state on the LUMOs of the fullerene molecule according to the Hund’s rule. From the two quartet states, \( S_N, S_{C_{60}} \), four eigenstate of the \( S^2 \) operator can be constructed with the spin of \( S = 0, 1, 2, 3 \), respectively. The corresponding energies as a function of \( S \) must be on a parabola according to Eq. 3. The results provided by the MCSCF calculations using three different basis sets are shown by Fig. 1. The energies can nicely be fitted by the parabola given by Eq. 3. The exchange couplings obtained by using the split valence basis with and without diffuse \( p \) orbitals are practically the same. The inclusion of the diffuse basis functions on the carbon atoms resulted in negligible change. Although the magnitude of the exchange coupling corresponding to the double zeta basis is somewhat smaller than those provided by the split valence basis the agreement between them is satisfactory.

Ferromagnetic exchange couplings between the \( 2p \) orbitals of the N atom and the valence electrons of the fullerene molecule have been found in both anions. The exchange coupling of approximately 1 meV provided by our calculations for both systems is within the range of those found in organic ferromagnets\textsuperscript{14}. This relatively strong coupling between the valence electrons of the nitrogen and the valence electrons of the fullerene cage could be responsible for the disappearance of the nitrogen lines in the EPR spectrum of N@C\textsubscript{60} anions with partially filled LUMOs\textsuperscript{13}.

IV. CONCLUSIONS

In conclusion, ROHF and MCSF calculations have been performed on singly and triply ionized anions of N@C\textsubscript{60} in order to determine the effective exchange coupling between the valence electrons of the encapsulated N atom and the fullerene cage. In agreement with experiments we found that the excess electrons occupy the LUMOs of the fullerene molecule and the entrapped atom keeps its atomic character. The interaction between the valence
electrons of the N atom and the LUMOs of the C$_{60}$ can be well described by a Heisenberg like Hamiltonian. The size of the exchange couplings obtained by our calculations are much larger than the hyperfine interaction and can explain the results of EPR measurements on radical anions of N@C$_{60}$.

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| Configuration         | $E_{\text{total}}$ (Hartree) | $\Delta E$ (eV) |
|-----------------------|-----------------------------|-----------------|
| N@C$_{60}^{-1}$       | -2325.30365                 | (a)             |
| $N_2p^3C_{60}8t_{1u}^0$ | -2325.37155                 | -1.84           |
| N@C$_{60}^{-3}$       | -2324.74514                 | (a)             |
| $N_2p^3C_{60}8t_{1u}^3$ | -2325.10707                 | -9.84           |

TABLE I: Energies of N@C$_{60}^{-1}$ and N@C$_{60}^{-3}$ with excess electron(s) occupying the 2p orbitals of the N atom (a) and the LUMOs of the C$_{60}$ molecule (b).

| basis $E_{S=1}$ (Hartree) | $E_{S=2}$ (Hartree) | $J$ (meV) |
|---------------------------|---------------------|-----------|
| 631g                      | -2325.371558        | -2325.371673 | -1.56    |
| DH                        | -2325.515025        | -2325.515134 | -1.49    |

TABLE II: Energy of the N@C$_{60}^{-3}$ resulted by MCSCF calculations using split valence (631g) and double zeta (DH) basis on the carbon atoms and the exchange coupling extracted from the energies.

FIG. 1: Energies of N@C$_{60}^{-3}$ corresponding to different multiplicity and the parabola fitted to the data points. The energy $E_0$ independent of spin is subtracted.