7-3-2006

Structural and Electronic Properties of Gd@C$_{60}$: All-Electron Relativistic Total-Energy Study

Jing Lu
University of Nebraska - Lincoln

Wai-Ning Mei
University of Nebraska-Lincoln, physmei@unomaha.edu

Yi Gao
University of Nebraska - Lincoln, ygao3@Unl.edu

Xiao Cheng Zeng
University of Nebraska - Lincoln, xzeng1@unl.edu

Mingwei Jing
Peking University

See next page for additional authors

Lu, Jing; Mei, Wai-Ning; Gao, Yi; Zeng, Xiao Cheng; Jing, Mingwei; Li, Guangping; Sabirianov, Renat F.; Gao, Zhengxiang; You, Liping; Xu, Jun; Yu, Dapeng; and Ye, Hengqiang, "Structural and Electronic Properties of Gd@C$_{60}$: All-Electron Relativistic Total-Energy Study" (2006). *Xiao Cheng Zeng Publications*. 89.
http://digitalcommons.unl.edu/chemzeng/89

Authors

Jing Lu, Wai-Ning Mei, Yi Gao, Xiao Cheng Zeng, Mingwei Jing, Guangping Li, Renat F. Sabirianov, Zhengxiang Gao, Liping You, Jun Xu, Dapeng Yu, and Hengqiang Ye

Structural and electronic properties of Gd@C$_{60}$: All-electron relativistic total-energy study

Jing Lu,[1, 2] W. N. Mei,[1] Yi Gao,[3] Xiaocheng Zeng,[3] Mingwei Jing,[2] Guangping Li,[1]

Renat Sabirianov,[1] Zhengxiang Gao,[2] Liping You,[2] Jun Xu,[2] Dapeng Yu,[2] and Hengqiang Ye [2]

1. Department of Physics, University of Nebraska—Omaha, Omaha, NE 68182-0266, USA
2. Mesoscopic Physics Laboratory, Department of Physics, Peking University, Number 209, Chengfu Road, Beijing 100871, China
3. Department of Chemistry, University of Nebraska–Lincoln, Lincoln, NE 68588, USA

Corresponding authors — Jing Lu, W. N. Mei, & Xiaocheng Zeng.
Address: Mesoscopic Physics Laboratory, Department of Physics, Peking University,
Number 209, Chengfu Road, Beijing 100871, China. Fax: 86 10 6275 1615 (Jing Lu).
Email: jinglu@pku.edu.cn (Jing Lu), wmei@mail.unomaha.edu (W. N. Mei), xczeng@phase1.unl.edu (Xiaocheng Zeng)

Abstract
Water soluble Gd-based metallofullerenes have potential application as magnetic resonance imaging contrast agent due to its higher proton relaxivities and lower toxicity. In this letter, we have investigated the structural and electronic properties of Gd@ C$_{60}$, which is the most abundantly produced Gd-based metallofullerene in carbon arc process, by using all-electron relativistic density functional theory. It is found that the Gd^{3+} ion is bonded to a hexagonal ring of C$_{60}$ by electrostatic interaction. The total spin multiplicity of Gd@C$_{60}$ is $S = 7$. The Gd atomic orbitals are hybridized with the C$_{60}$ molecular orbitals.

Water soluble Gd-based metallofullerenes (Gd@ C$_{82}$(OH)$_x$, Gd@C$_{60}$[C(COOH)$_{10}$], Gd@C$_{60}$(OH)$_x$) have attracted recent interest [1–3] as a possible new generation of magnetic resonance imaging (MRI) contrast agent because they not only can produce proton relaxivities greater than commercially available MRI contrast agent but also are safer than the latter because the toxic Gd ions are completely encaged inside the fullerenes and do not dissociate under physiological condition. Gd@C$_{60}$ is the most abundantly produced species of Gd-based metallofullerenes in carbon arc process. Unlike soluble Gd@C$_{82}$, which has been studied by extensive experiments and two theoretical works [4, 5], the structural and electronic properties of insoluble Gd@C$_{60}$ are overlooked largely. Only Lu et al. [6] have calculated the electronic structure of Gd@C$_{60}$ assuming that Gd is located on the center of C$_{60}$ and found that only two 6s electrons of Gd are ionized, leaving the 5d electron behind. Nevertheless, the electronic properties of metallofullerenes may change dramatically with different arrangements of the metal atom inside the fullerene cage.

In this Letter, we have presented for the first time the optimized structure of Gd@C$_{60}$ and the resulting electronic properties by using all-electron relativistic density functional theory. Double numerical atomic orbital basis set plus polarization function (DNP) [7] is used for C and Gd atoms. Generalized gradient corrected exchange-correlation functional proposed by Perdew and Wang (PW91) [8] is used. The electronic configuration of Gd is $4s^2 4p^6 4d^{10} 4f^7 5s^2 5p^6 5d^1 6s^2$. The calculated ground-state spin multiplicity of Gd$_2$ dimer is $S = 19$, which is in accordance with the previous all-electron relativistic density functional theory calculation [9]. The calculated bond length (3.00 Å) and bind energy (2.03 eV) of Gd$_2$ dimer are comparable with the previously calculated bond length (2.90 Å) [9] and experimental bind energy (1.784 ± 0.35 eV) [10].

Our computational procedures start from five initial positions for Gd inside C$_{60}$: (1) on the center of C$_{60}$, (2) on the top of the six-membered ring, (3) on the top of the five-membered ring, (4) on the top of the single bond and (5) on the top of the double bond. Full geometry optimization is performed without any symmetry constraint. The most stable structure of Gd@C$_{60}$ has the Gd ion situated on the center of the six-membered ring (Figure 1), whereas the previously assumed configuration with Gd on the cage center is 1.82 eV higher in energy. Addition of Gd slightly lengthens the proximal C–C double and single bonds by 0.04 and 0.02 Å, respectively. In Gd@C$_{82}$ [5] and La@C$_{60}$ [11], the Gd and La ions are positioned slightly away from the C–C double bond based on the density functional theory calculations with the effective core potential approximation. The calculated distances between the Gd ion and the proximal C atoms are 2.47 and 2.38–2.41 Å [5] in Gd@C$_{60}$ and Gd@C$_{82}$, respectively. The calculated distances between the La ion and the proximal C atoms are slightly larger with values of 2.55–2.64 Å [11] in La@C$_{60}$. The calculated binding energy of Gd inside C$_{60}$ (3.77 eV) is significantly smaller than that of Gd inside C$_{82}$ (5.64 eV [5]), but larger than that of La inside C$_{60}$ (2.65 eV) [11].

The total spin multiplicity of the ground state is $S = 7$. The spin densities on the Gd ion and C$_{60}$ are 6.74 and −1.26, respectively; therefore the seven spins on the Gd
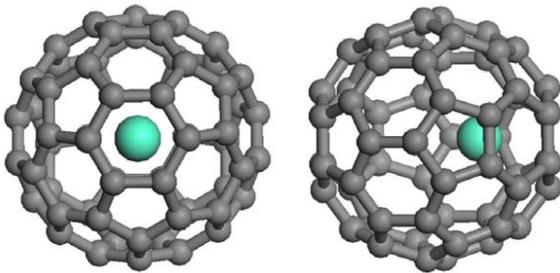

Figure 1. Optimized structure of Gd@C$_{60}$.

ion and one spin on C$_{60}$ are antiferromagnetically coupled, similar to the case of Gd@C$_{82}$ [5]. The spin multiplicities of $S = 5$, 7, and 9 are 0.08, 0.10 and 0.67 eV higher in energy, respectively, than that of $S = 7$. In the $S = 5$ spin multiplicity, the seven spins on the Gd ion and three spins on C$_{60}$ are antiferromagnetically coupled. In the $S = 9$ and 11 spin multiplicities, the seven spins on the Gd ion are ferromagnetically coupled with one and three spins on C$_{60}$, respectively. The molecular level diagram of the three lowest energy spin multiplicities is depicted in Figure 2. This energy difference between $S = 7$ and $S = 9$ spin multiplicity is greater by two orders of magnitude than the experimental value of 0.0023 eV [12] and the theoretical value of 0.0026 eV [5] in Gd@C$_{82}$, reflecting prompt enhancement in the spin coupling between Gd ion and fullerene with decreasing fullerene size.

From Figure 2, the Gd 6s and 5d-derived orbitals are empty and the C$_{60}$ t_{1u}-derived are half occupied, suggesting that the three valence electrons of Gd are completely transferred to C$_{60}$. The charge transfer from Gd to C$_{60}$ according to a commonly used Mulliken population analysis, however, is only 1.09 electrons. It was shown recently [13] that the natural population analysis is more suitable for determining charge transfer of a donor–acceptor system than Mulliken population analysis. The charge transfer from Gd to C$_{60}$ is 2.23 electrons according to the natural population analysis by using CEP–121G basis set for C and Gd atoms implemented in Gaussian 03 package [14]. The natural populations on the Gd 6s and 5d orbitals are 0.21 and 0.52 electrons, respectively. The charge transfer from Gd to C$_{82}$ according to the natural population analysis was 2.43 electrons with a population of 0.48 electrons on the Gd 5d orbitals. The population of about half electrons on the Gd 5d was ascribed to a back-donation of the occupied orbitals of the fullerene cage. The charge state of the encapsulated Gd ion therefore is approximately described as +3. The
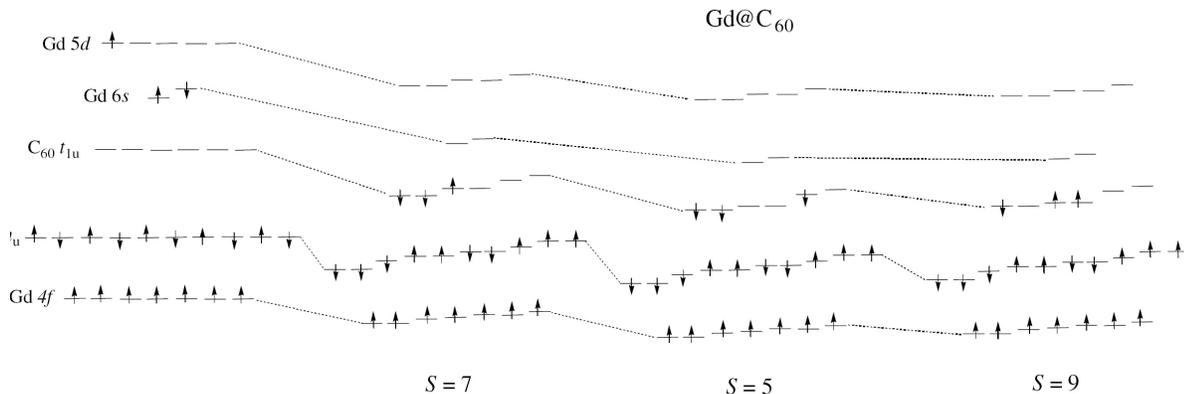

Figure 2. Electronic level diagram of Gd, C$_{60}$ and Gd@C$_{60}$ ($S = 5$, 7 and 9) near the Fermi level. The Gd two 6s and one 5d electrons are transferred to the C$_{60}$ t_{1u}-derived orbitals. The level degeneracy of Gd and C$_{60}$ is partially lifted upon complexation. In the $S = 7$ and 5 spin multiplicities of Gd@C$_{60}$, the net spins on the C$_{60}$ t_{1u}-derived orbitals are antiferromagnetically coupled with the seven spins on the Gd 4f orbitals. In the $S = 9$ spin multiplicity of Gd@C$_{60}$, the net spins on the C$_{60}$ t_{1u}-derived orbitals are ferromagnetically coupled with the seven spins on the Gd 4f orbitals.
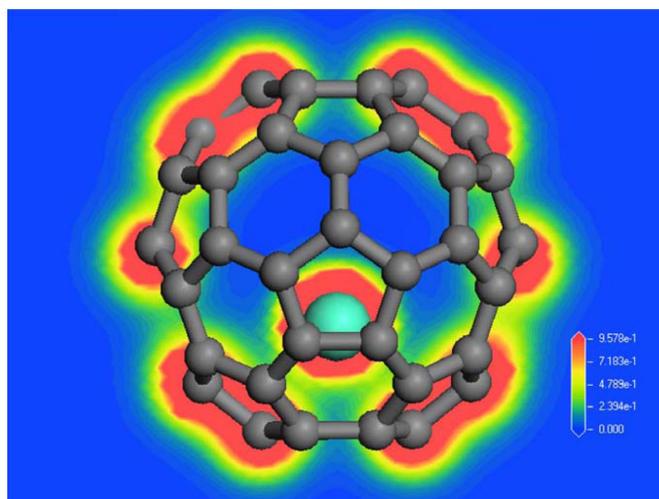
Figure 3. Electronic density in the plane passing through the Gd ion in Gd@C_{60}.
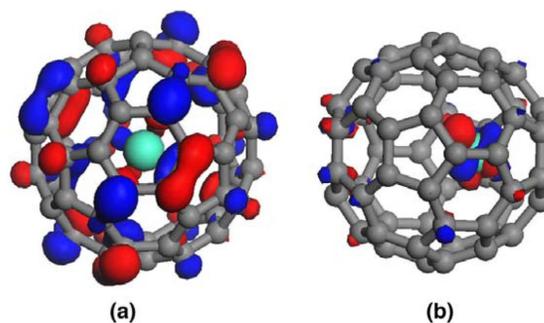

Figure 4. Isosurfaces (the isovalue is 0.03 a.u.) of: (a) the highest occupied molecular orbital Gd@C_{60} and (b) the lowest unoccupied Gd 5d derived molecular orbital in Gd@C_{60}. Red and blue are used to indicate the positive and negative sign of the wavefunction, respectively.

calculated dipole moment of Gd@C_{60} is about 1.83 Debyes as a result of off center arrangement of Gd inside C_{60}. Fig. 3 displays the electron density in a plane containing the Gd ion. There is no significant electron accumulation between Gd and proximal C atoms. Therefore the interaction between Gd and C_{60} is primarily ionic in character.

The highest occupied molecular orbital (HOMO) of Gd@C_{60} and the lowest unoccupied Gd 5d derived molecular orbital in Gd@C_{60} are showed in Fig. 4a,b, respectively. The HOMO of Gd@C_{60} is derived from one of the C_{60} t_{1u} orbitals but has some component on the Gd atom. On the other hand, the lowest unoccupied Gd 5d derived molecular orbital has some component on C_{60}. The orbital hybridization between the guest transition metal (and lanthanide) atoms and fullerene is another common character in metallofullerenes [15–18] in addition to the charge transfer, and accounts for the nonzero population on the Gd 6s-dominated orbital.

In conclusion, our all-electron relativistic density functional theory calculations show that the ground state of Gd@C_{60} has the Gd ion on the top of the hexagonal ring of C_{60}. The electronic structure of Gd@C_{60} is characterized by a nearly complete transfer of the three outmost valence electrons of Gd to C_{60} and the orbital hybridization between the Gd atomic orbitals and C_{60} molecular orbitals. The Gd 4f spins are nearly intact and antiferromagnetically coupled with that on C_{60}.

References

[1] K. Kato, Y. Kanazawa, M. Okumura, A. Taninaka, T. Yokawa, and H. Shinohara, *J. Am. Chem. Soc.* **125** (2003), p. 4391.

[2] E. Toth, R. Bolskar, A. Borel, G. Gonzalez, L. Helm, A.E. Merbach, B. Sitharaman, and L. J. Wilson, *J. Am. Chem. Soc.* **127** (2005), p. 799.

[3] B. Sitharaman, R. Bolskar, I. Rusakova, and L. J. Wilson, *Nano Lett.* **4** (2004), p. 2373.

[4] K. Kobayashi and S. Nagase, *Chem. Phys. Lett.* **282** (1998), p. 325.

[5] L. Senapati, J. Schrier, and K. B. Whaley, *Nano Lett.* **4** (2004), p. 2073.

[6] J. Lu, X. Zhang, and X. Zhao, *Appl. Phys. A* **70** (2000), p. 461.

[7] B. Delley, *J. Chem. Phys.* **113** (2000), p. 7756.

[8] J. P. Perdew and Y. Wand, *Phys. Rev. B* **45** (1992), p. 13244.

[9] M. Dolg, W. Liu, and S. Kalvoda, *Int. Quantum Chem.* **76** (2000), p. 359.

[10] A. Kant and S. S. Lin, *Monash. Chem.* **103** (1971), p. 757.

[11] W. Andreni and A. Curioni, *Appl. Phys. A* **66** (1998), p. 299.

[12] K. Furukawa, S. Okubo, H. Kato, H. Shinohara, and T. Kato, *J. Phys. Chem. A* **107** (2003), p. 10933.

[13] R. Yerushalmi, A. Scherz, and K. K. Baldridge, *J. Am. Chem. Soc.* **126** (2004), p. 5897.

[14] M. J. Frisch *et al.*, Gaussian 03, Gaussian, Inc., Pittsburg, PA (2003).

[15] J. Lu, X. Zhang, X. Zhao, S. Nagase, and K. Kobayashi, *Chem. Phys. Lett.* **332** (2000), p. 219.

[16] J. Lu, X. Zhang, and X. Zhao, *Chem. Phys. Lett.* **332** (2000), p. 51.

[17] K. Wang, J. Zhao, S. Yang, L. Chen, Q. Li, B. Wang, S. Yang, J. Yang, J. G. Hou, and Q. Zhu, *Phys. Rev. Lett.* **91** (2003), p. 185504.

[18] B. Kessler, A. Bringer, S. Cramn, C. Schlebusch, W. Eberhardt, S. Suzuki, Y. Achiba, F. Esch, M. Barnaba, and D. Cocco, *Phys. Rev. Lett.* **79** (1997), p. 2289.