Self-consistent Hartree-Fock approach to electronic structure of endohedral fullerenes

Verkhovtsev A.V.[1], Polozkov R.G.[1], Ivanov V.K.*[1], Korol A.V.[2], Solov'yov A.V.[2]

[1] *St. Petersburg State Polytechnic University, 195251, St. Petersburg, Russia*
[2] *Frankfurt Institute for Advanced Studies, 60438, Frankfurt am Main, Germany*
**e-mail: ivanov@tuexph.stu.neva.ru*

Since the first experimental observation of endohedral fullerenes [1], series of theoretical studies dedicated to the investigation of these compounds and their interaction with photons within different models (see [2] and references therein) have arisen. In this work we apply for the first time the self-consistent Hartree-Fock approximation to calculate the electronic structure of noble gas endohedral fullerenes by the example of compounds He@C_{60}, Ne@C_{60} and Ar@C_{60}.

The total electronic system consisted of all electrons of the encapsulated atom and 240 valence electrons of fullerene C_{60} is considered in the spherically symmetric field created by the ionic core of a fullerene and the nuclear charge of embedded atom placed in the center of the spherical layer. Thus the electronic configuration, for example for Ar@$C_{60,}$ consists of 258 electrons:

$$1s^2 2p^6 3d^{10} 4f^{14} 5g^{18} 6h^{22} 7i^{26} 8k^{30} 9l^{34} 10m^{34} 2s^2 3p^6 4d^{10} 5f^{14} 6g^{18} 7h^{10} 3s^2.$$

The valence electrons of the fullerene are distributed in a usual way with ratio of 3:1 over the σ (none-node) and π (one-node) orbitals, correspondingly. The fullerene ionic core is presented by a uniform distribution of positive charge ($Z=240$) over spherical layer of the finite thickness. Additional electrons from noble gas atom should be arranged either in a new shell which is absent in the configuration of the fullerene (for example, 3s in case of Ar@C_{60}) or in the partially filled fullerene orbitals by reason of minimal electronic energy principle.

Results of the calculations show that the inner-shell electrons (1s in He, 1s2s in Ne and 1s2s2p in Ar) remain to be the inner-shell electrons of the endohedral fullerene and they are located mostly near the embedded atom, while the behaviour of the outer atomic wave functions has revealed the strong hybridization of valence atomic and fullerene orbitals with the same values of angular momentum. It has been found that there is a significant redistribution of the electronic density of hybridized states within the HF approximation beside the Local Density Approximation. So it seems to be essential to take into account the non-local exchange interaction to calculate the electronic structure of endohedral complexes.

[1] J.R. Heath, S.C. O'Brien, Q. Zhang et al., *J. Am. Chem. Soc.* **107**, 7779 (1985).
[2] V.K. Dolmatov, in *Advances in Quantum Chemistry. Theory of Confined Quantum Systems*, eds. by J.R. Sabin and E. Brändas (Academic, New York, 2009), vol. 58, pp. 13-68.
[3] M.E. Madjet, H.S. Chakraborty and S.T. Manson, *Phys. Rev. Lett.* **99**, 243003 (2007).