Exchange and correlation in spherically confined atoms

Sergei F. Vyboishchikov

Institut de Química Computacional i Catàlisi, Universitat de Girona, 17071 Girona

In a spherically confined atom[1] electrons are exposed to the Coulomb nuclear attraction potential within a cavity of radius R_c, but outside of this cavity the potential is set to infinity:

$V(\mathbf{r}) = -Z/r$ for $r \le R_c$

$V(\mathbf{r}) = \infty$ for $r > R_c$

The electron density is confined to the cavity and vanishes outside. The electron correlation and exchange as well as orbital energies [2] and shapes [3] depend on the confinement radius R_c [4].

The confined atoms is a convenient model system for studying electron exchange and correlation. In the present work [5], local exchange potentials corresponding to the Hartree–Fock electron density have been obtained using the Zhao–Morrison–Parr method [6] for a number of closed-shell confined atoms and ions. The exchange potentials obtained and the resulting density were compared to those given by the Becke–Johnson model potential [7]. We demonstrate that introducing a scaling factor to the Becke–Johnson potential allows improving the quality of the resulting density. The optimum scaling factor increases with decreasing confinement radius. The performance of Karasiev and Ludeña's SCα-LDA method [8] for reproducing the Hartree–Fock electron densities in confined atoms has been also studied.

We also performed CISD calculations of confined atoms to evaluate the *correlated* electron density ρ^{CI} and the correlation density $\delta\rho = \rho^{\mathrm{CI}} - \rho^{\mathrm{HF}}$. Typically, $\delta\rho(r)$ is positive at large r and negative at intermediate r, while its behavior at short distances is more complicated. Moreover, $\delta\rho$ behaves differently at different confinement radii R_c.

References

1. Electronic Structure of Quantum Confined Atoms and Molecules; K.D. Sen (Ed.); Springer, **2014**.
2. V.K. Dolmatov, A.S. Baltenkov, J.-P. Connerade, S.T. Manson, *Radiation Physics and Chemistry*, **2004**, *70*, 417.
3. J. Garza, R. Varga, A. Vela, K.D. Sen, *J.Mol. Struct. (THEOCHEM)*, **2000**, *501–502*, 183.
4. A.L. Buchachenko, *J. Phys. Chem. B*, **2001**, *105*, 5839.
5. S.F. Vyboishchikov, *J. Comp. Chem.*, **2015**, *36*, 2037.
6. Q. Zhao, R.C. Morrison, R. G. Parr, *Phys. Rev. A*, **1994**, *50*, 2138.
7. A.D. Becke, E.R. Johnson, *J. Chem. Phys*. **2006**, *124*, 221101.
8. V.V. Karasiev, E.V. Ludeña, *Phys. Rev. A*, **2002**, *65*, 062510.