Comparison of the several correlated OEP methods in KS-DFT.

Szymon Śmiga[1)], Victor Lotrich[2)], Karol Jankowski[1)], Andrew Michael Teale[3)], Ireneusz Grabowski[1)]

[1]*Institute of Physics, Nicolaus Copernicus University, 87-100 Toruń, Poland*
[2]*Quantum Theory Project, Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA*
[3]*Department of Chemistry, Centre for Theoretical and Computational Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway*

Abstract

In recent years, a large emphasis is placed on the development of methods for the proper inclusion of the electron correlation effects [1–3] in the Optimized Effective Potential (OEP) methods. Based on the Kohn-Sham (KS) formalism of density functional theory (DFT) with the orbital-dependent exchange-correlation OEP functionals, *ab initio* DFT calculations has been performed for a few atoms (He, Be, Ne, Mg, Ar) and molecules (N2, H2O, CO). Correlated OEP results, has been compared with the results obtained with the standard density-dependent exchange-correlation DFT methods and several wave function theory (WFT) methods such as MP2 and CC. The results were compared in the terms of total ground state energies, correlation energies, correlation potentials and the differences between the orbital energies of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (HOMO-LUMO GAP). In addition to asses the impact of new exchange-correlation KS-OEP functionals on the electron density, the analysis of the electron radial density has been performed [4]. Analysis of the energies, potentials and the electron radial density clearly showed, that the results obtained in the correlated OEP and the WFT methods are significantly better than the results obtained from standard density-dependent exchange-correlation functionals. It has been shown that the best method of the second order OEP (OEP2-sc) leads in all cases to results qualitatively better then results obtained from MP2 method and comparable with results from CCSD. In addition it was shown, that the inclusion of the higher order correlations effects in the KS-OEP method (OEP-ccpt2 method) leads to further improvement of the results.

References

[1] I. Grabowski, S. Hirata, S. Ivanov, and R. J. Bartlett. *J. Chem. Phys.*, 116:4415, 2002.

[2] I. Grabowski and V. Lotrich. *Mol. Phys.*, 103:2087, 2005.

[3] I. Grabowski, V. Lotrich, and R. J. Bartlett. *J. Chem. Phys.*, 127:154111, 2007.

[4] I. Grabowski K. Jankowski, K. Nowakowski and J. Wasilewski. *J. Chem. Phys.*, 130:164102, 2009.