

MCPT-PNOF5: A useful method for dealing with strongly correlated systems

Mario Piris

Kimika Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU), P.K. 1072, 20080 Donostia,
Donostia International Physics Center (DIPC), 20018 Donostia,
IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Euskadi, Spain.

A series of natural orbital functionals, known in the literature as PNOFi ($i=1-5$), has been proposed recently [1] using a reconstruction of the two-particle reduced-density matrix (2-RDM) in terms of the one-particle RDM by ensuring necessary N-representability positivity conditions on the 2-RDM. PNOF5 [2] has proved to be the most successful. It yields a remarkable description of systems including substantial static correlation, like transition metal dimers [3], and good bond dissociation curves [4]. This functional affords a one-electron picture that agrees closely with the orbitals provided by the valence bond method and standard molecular orbital calculations [5].

It has been recently shown [6] that PNOF5 can be obtained as a particular case of the energy expression of an APSG wavefunction [7]. This result guarantees strictly the N-representability, size-extensivity and size-consistency of PNOF5. Accordingly, PNOF5 takes into account most of the non-dynamical effects, but also an important part of the dynamical electron correlation corresponding to the intrapair (intrageminal) interactions. However, no interpair (intergeminal) correlation is described by PNOF5. To correct this problem, perturbation corrections have been implemented to the generating PNOF5-wavefunction using a multiconfiguration perturbation theory size consistent at second order (SC2-MCPT) [8, 9].

In this presentation, the theory behind the MCPT-PNOF5 is outlined. Several examples ranging from van der Waals systems to covalent molecules are presented to illustrate the potential of the method. Our results are accurate values as compared to the available experimental data.

[1] Piris, M. *Adv. Chem. Phys.*, 134:387-427, 2007; *Int. J. Quantum Chem.*, 113:620-630, 2013.

[2] Piris, M., Lopez, X., Ruiperez, F., Matxain, J., Ugalde, J. *J. Chem. Phys.*, 134:164102, 2011.

[3] Ruiperez, F., Piris, M., Ugalde, J., Matxain, J. *Phys.Chem.Chem.Phys.*, 15:2055-2062, 2013.

[4] Matxain, J., Piris, M., Ruiperez, F., et. al. *Phys. Chem. Chem. Phys.*, 13:20129-20135, 2011.

[5] Piris, M., Matxain, J., Lopez, X., Ugalde, J. *Theor. Chem. Acc.*, 132:1298, 2013.

[6] Pernal, K. *Comput. Theor. Chem.*, 1003:127-129, 2013.

[7] Surjan, P. R. *in Topics in Current Chemistry, Springer-Verlag Berlin*, 203:63-88, 1999.

[8] Rolik, Z., Szabados, A., Surjan, P. R. *J. Chem. Phys.* 119:1922, 2003.

[9] Szabados, A., Rolik, Z., Toth, G., Surjan, P. R. *J. Chem. Phys.* 122:114104, 2005.