

Assessing orbital-based vs density-based methods: CBS extrapolation with minimal and subminimal basis sets

A.J.C. Varandas

*Departamento de Química, and Centro de Química,
Universidade de Coimbra 3004-535 Coimbra, Portugal
(e-mail: varandas@uc.pt)*

After a brief remark on the Born-Oppenheimer approximation,¹ the electronic problem is addressed by putting into perspective the methods used to study many- vs few-atom molecules. With the rule of thumb being Kohn-Sham density functional theory (DFT) for the former, orbital-based methods for the latter, such a dichotomy is mostly attributed to cost-effectiveness. This led us to compare the energetics and time performances of the two approaches for a vast number of molecules, reactions, and isomerizations.² Unexpectedly, second-order Møller-Plesset perturbation theory is found to perform at a cost similar to most parameterized DFT methods while maintaining its well known pattern of accuracy, frequently outperforming DFT. A key reason for this is recent progress on schemes for extrapolation to the complete basis set (CBS) limit of both Hartree-Fock and correlation energy components from the first steps of the hierarchy staircase,³ in particular from double- and triple-zeta basis sets: CBS(d,t). With massive MO calculations demanding even more cost-effective methods, we will show how minimal and subminimal basis sets can help on the endeavor. For this, we have developed a reliable analytic variant of the unified singlet- and triplet-pair extrapolation (USTE) scheme³, which is subsequently utilized to hierarchize any arbitrary basis set. With the entire procedure being simple and general, the method is illustrated for as small as the Huzinaga MINI basis sets and as enlarged bases as the sophisticated ansatz utilized in modern explicitly correlated MP2-F12 and CCSD(T)-F12 calculations. Extensively tested, the results show that CBS extrapolations from a subminimal and an extended basis set can yield correlation energies that outperform by far those obtained from Kohn-Sham density functional theory (KS DFT). If employing two subminimal basis sets, the results occasionally outperform KS-DFT but at a drastically smaller cost. To further test the method, we examine the isomerization energies of a set of 45 C₈H₈ isomers⁴, with the results showing good agreement with the best reported data. The present cost-effective, yet reliable, approach may therefore be expected to have a broad impact on chemistry and even materials science. Some prospective remarks conclude the talk.

¹A.J.C. Varandas, J. Providência, M. Brajczewska, and J.P. Providência, *Eur. Phys. J. D* **69**, 114 (2015).

²A.J.C. Varandas, M. M. González, L.A.M. Cabrera and J.M. G. Vega, *Chem. Eur. J.* **23**, 9122 (2017).

³A.J.C. Varandas, *Ann. Rev. Phys. Chem.*, in press.

⁴A. Karton and J.M.L. Martin, *Mol. Phys.* **110**, 2477 (2012).