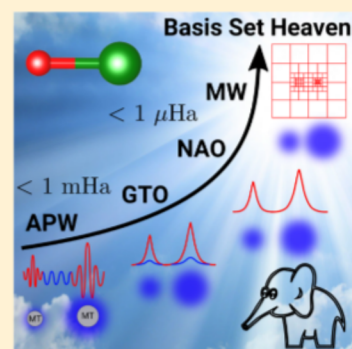


The Elephant in the Room of Density Functional Theory Calculations

Stig Rune Jensen,^{*,†} Santanu Saha,[‡] José A. Flores-Livas,[‡] William Huhn,[¶] Volker Blum,[¶] Stefan Goedecker,[‡] and Luca Frediani[†][†]Centre for Theoretical and Computational Chemistry, Department of Chemistry, UiT - The Arctic University of Norway, N-9037 Tromsø, Norway[‡]Department of Physics, Universität Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland[¶]Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708, United States

ABSTRACT: Using multiwavelets, we have obtained total energies and corresponding atomization energies for the GGA-PBE and hybrid-PBE0 density functionals for a test set of 211 molecules with an unprecedented and guaranteed μ Hartree accuracy. These quasi-exact references allow us to quantify the accuracy of standard all-electron basis sets that are believed to be highly accurate for molecules, such as Gaussian-type orbitals (GTOs), all-electron numeric atom-centered orbitals (NAOs), and full-potential augmented plane wave (APW) methods. We show that NAOs are able to achieve the so-called chemical accuracy (1 kcal/mol) for the typical basis set sizes used in applications, for both total and atomization energies. For GTOs, a triple- ζ quality basis has mean errors of ~ 10 kcal/mol in total energies, while chemical accuracy is almost reached for a quintuple- ζ basis. Due to systematic error cancellations, atomization energy errors are reduced by almost an order of magnitude, placing chemical accuracy within reach also for medium to large GTO bases, albeit with significant outliers. In order to check the accuracy of the computed densities, we have also investigated the dipole moments, where in general only the largest NAO and GTO bases are able to yield errors below 0.01 D. The observed errors are similar across the different functionals considered here.



Electronic structure calculations are nowadays employed by a large and steadily growing community, spanning condensed matter physics, physical chemistry, materials science, biochemistry and molecular biology, geophysics, and astrophysics. Such a popularity is in large part due to the development of Density Functional Theory (DFT) methods,¹ in their Kohn–Sham (KS) formulation.²

Although the exact energy functional of DFT is unknown, many approximate functionals offer an excellent compromise between accuracy and numerical cost, often rivaling the accuracy that can be obtained with correlated methods, such as coupled-cluster singles doubles (CCSD).^{3–5} During the last decades, extensive efforts have been undertaken to provide ever more accurate approximations to the exact exchange–correlation (XC) functional.⁶ This quest for higher accuracy is conceptually captured by John Perdew’s Jacob’s ladder analogy,⁷ leading to the heaven of chemical accuracy: errors of 1 kcal/mol or less in atomization energies and other energy differences that are of primary interest in chemistry and solid-state physics. Rungs on this ladder are the local density approximation (LDA), the generalized gradient approximation (GGA),⁸ meta-GGAs,⁹ and hybrid and double hybrid functionals.¹⁰ The best modern XC functionals come fairly close to this target, with errors of a few kcal/mol on a wide range of energetic properties relative to experiment, including atomic and molecular energies, bond energies, excitation and isomerization energies, and reaction barriers, for main-group elements as well as transition metals and solids.^{11,12}

The closer we get to chemical accuracy, the more important becomes the identification of errors due to various other algorithmic approximations (basis sets, integration grids and pseudopotentials,^{13–15} to cite a few), which can lead to comparable or even larger errors, but their influence is hard to quantify. The importance of this issue has recently been highlighted within the solid-state community, with a substantial effort to assess the influence of such approximations on the accuracy. Lejaeghere et al.¹⁶ compared the GGA-PBE⁶ calculated equations of state for 71 elemental crystals from 15 different widely used DFT codes, employing both all-electron methods as well as 40 different pseudopotential sets. For the equation of state, most DFT codes agree within error bars that are comparable to those of experiment, irrespective of the basis set choice: all-electron numeric atom-centered orbitals (NAOs), augmented plane wave (APW) methods, or plane waves with pseudopotentials. The basis set issue has also been highlighted by Mardirossian and Head-Gordon,^{17,18} in connection with the development of the B97M-V and ω B97M-V functionals. Although the functionals have been designed and optimized by making use of a large basis set (aug-cc-pVQZ for B97M-W and def2-QZVPD for ω B97M-V), the authors have extensively explored the effect of smaller bases on the functional performance.

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