Dr. Ganna (Anya) Gryn'ova | 15.11.2023

Reproducibility in DFT

Comparing solid state dft codes, basis sets and potentials

- Landmark community-wide study comparing 15 solid-state codes with 40 potentials or basis sets for PBE equations of state of 71 elemental crystals.
- Metric: Δ-value = the root-mean-square energy difference between the equations of state of the two codes (the energy-versus-volume curve), averaged over all crystals in a purely elemental benchmark set.
- Conclusion: "*most of the commonly used codes and methods are **now** found to predict essentially identical results*".

Science **2016**, *351*, aad3000.

How to verify the precision of density-functional-theory implementations *via* reproducible and universal workflows

- A dataset of 960 cubic crystal structures from elements with Z=1 to 96, including unaries and oxides across a range of coordination numbers and oxidation states.
- Comparing two all electron codes and a range of pseudopotential-based codes.
- Metric: Birch–Murnaghan parameters of the equations of state of the two codes.
- Conclusion: "*AiiDA common workflows perform automatic input parameter selection, provide identical input/output interfaces across codes, and ensure full reproducibility*".

Materials set: Z=1-56,72-83 (H to Ba, and Hf to Bi)
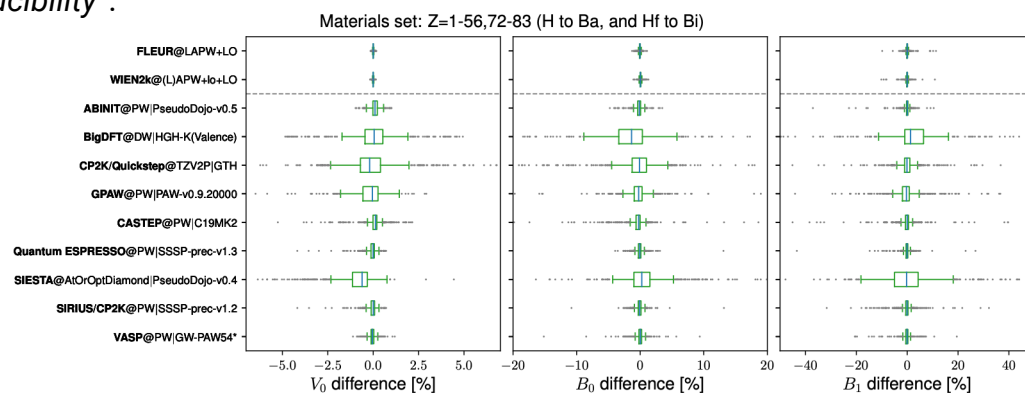
Discrepancy of each computational approach wrt the average all-electron reference dataset. Central blue – the median, outliers – grey points.

Nat. Rev. Phys. **2023**; image taken from preprint arXiv:2305.17274 under CC-BY license.

Mind the implementation!

- "Multiwavelets applied to metal–ligand interactions: Energies free from basis set errors" compares results with GTOs from ORCA to those with MWs from MRChem.
- Initially, the dataset was computed with BP86. Later, realised that the BP86 versions in ORCA and MRChem are not identical leading to several kcal/mol discrepancies in the CBS limit.
- Everything had to be recomputed with PBE.

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Reproducibility of density functional approximations: How new functionals should be reported

- The authors are developers of Libxc.
- Problem with DFT implementations – lack of reliable reference data resulting in non-equivalent implementations. Examples discussed: BP86, PW91, PBE, B3LYP, and others.
- Solution: proposed protocol ensuring reproducibility, *e.g.,* using a standard convergence criteria for quadrature grid, making the source code available, etc.

TABLE I. Exchange energies of the N and Ne atoms for variants of the PBE exchange functional, employing tabulated Hartree–Fock wave functions[89] evaluated with AtomicOrbitals[91] and a 2000 point radial quadrature with the default scheme of Ref. [40]. Libxc keywords are used to identify the functionals.

	Functional	$E_x(N)/E_h$	$E_x(Ne)/E_h$
Libxc	gga_x_pbe	−3.956 025 7	−4.448 308 7
XCFun	gga_x_pbe_mod	−3.956 028 1	−4.448 311 4
	gga_x_pbe_gaussian	−3.956 018 1	−4.448 300 3