How to add error bars to DFT data

J.Contreras-García[1]*, F. Peccati[1;2] and R. Laplaza[1;3]

[1]*Laboratoire de Chimie Théoorique, LCT, Sorbonne Université, CNRS, F 75005 Paris, France*
[2]*Institut des Sciences du Calcul et des Données, ISCD, Sorbonne Université, F-75005 Paris, France*
[3]*Departamento de Química Física and Instituto de Biocomputación yFísica de Sistemas Complejos (BIFI), Universidad de Zaragoza, 50009 Zaragoza, Spain*

Keywords: error bars, DFT, high pressure

*e-mail: contrera@lct.jussieu.fr

A close collaboration between simulation and experiment has become routine in the mutual validation of high pressure data. One of the main reasons behind this collaboration is the fact that with the increase in computing power, larger and more complex systems can be calculated at the quantum mechanical level. What often hinders this joint effort is the lack of a degree of uncertainty associated with DFT simulated data, which are usually presented as naked numbers without an associated precision, contrary to experimental values which are generally accompanied by an error bar that estimates the precision of the measurement.

This often leads, in the comparison of experimental and calculated results, to shady situations in which simulation parameters are tuned case by case, according to the so-called calibration, to match as closely as possible a given available experimental value, when there is no guarantee that the agreement is not the result of error cancellation and, consequently, that this same agreement will be preserved for a property outside the calibration set.

Instead of the common benchmarking approach, we propose a property-specific approach that provides an a priori assessment of the method dependence of a DFT calculation.

This is done by finding bracketing physical descriptions that apply to any calculation. Most solid state calculations are dominated by delocalization error [1], which is related to the over(under) electron localization provided by HF(DFT). Using these two opposite behaviors, we show that HF and LDA provide bracketing limits and we develop a simple and robust procedure to quickly provide error bars that help understanding the inherent error of a given calculation.

We first validate the robustness of the model on over 400 highly accurate vibrational frequencies, were we show the ability of the approach to i) provide error bars that enclose the reference data and ii) identify problematic simulations [2]. In a second step we focus in experimentally less precise data, i.e. transition pressure. Results are shown in Figure 1, where we can see that the HF-LDA error bar yields an error bar of the same order of magnitude as the experimental one. They also enable for example to identify the ZnS (B3-B1) transition as a more problematic simulation, whereas the choice of functional is less important for the KF (B1-B2) one. In some of these cases, the approach even enables to identify the wrong ordering of phases.

The general picture that emerges from this study is that a paradigm shift in the interaction between experimental and computational chemistry is needed. The different nature of the errors involved requires a different approach for error estimation. Experimental measures require several repetitions to assess their reproducibility and random errors. Since simulation errors are systematic, the estimation of the error must go through repetition under different conditions and a search of limiting physical behaviors.
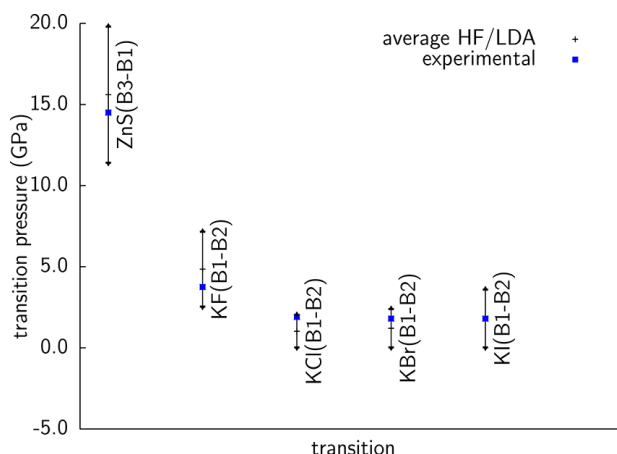

Figure 1. Error bars for simulated transition pressures. Experimental pressure are shown in blue.

Overall, this approach should help overcoming distrust in solid state simulations through a detour to the overwhelming questions: "which functional to choose?" and "How much can we trust the simulation?"

[1] A. J. Cohen, P. Mori-Sánchez, W. Yang, *Science* 2008, **321**, 792

[2] F. Peccati, R. Laplaza, J. Contreras-García, *J. Phys. Chem. C* 2019, **123**, 4767.