Estimating the error of a DFT calculation

V. Petzold, T. Bligaard, J. K. Nørskov, and K. W. Jacobsen

CAMD, Department of Physics, Technical University of Denmark

Kongens Lyngby, Denmark

During the past couple of decades, DFT has proven versatile not only in condensed-matter physics but also in quantum chemistry. DFT's increasing popularity combined with the quest for more and more accurate approximations to the unknown exact energy functional has resulted in a large number of functionals that all have strengths and weaknesses. Those strengths and weaknesses can be probed by comparing the functional's predictions to actual values, such as bond lengths and energies. In fact, extensive databases have been established to that purpose, so that statements such as: "Functional A predicts atomization energies wrong by x eV, on average" can be made.

We are investigating, if one can go one step further: Can the information of a functional's performance on a database be transformed into an error estimate on any quantity as complex as a reaction rate, that is calculated with the given functional? We approach the question by constructing an ensemble of DFT functionals (we stay in the framework of GGAs), which is used to generate a distribution of predictions[1,2]. The ensemble is defined using the maximum entropy principle under the constraint that the average squared estimated error equals the average squared actual error.

The actual investigations are done on a database of the 148 atomization energies from the G2 data set[3], and some 11 chemisorption energies. Overfitting issues are addressed with the leave-one-out cross validation as well as the bootstrap 632+ rule. As a by-product we find GGA functionals to be able to predict molecular atomization energies with an accuracy comparable to standard hybrid functionals - at a much lower computational cost.

[1] S. L. Frederiksen, K. W. Jacobsen, K. S. Brown, and J. P. Sethna, Phys. Rev. Lett. 93, 165501 (2004).

[2] J. J. Mortensen, K. Kaasbjerg, S. L. Frederiksen, J. K. Norskov, J. P. Sethna, and K. W. Jacobsen, Phys. Rev. Lett. 95, 216401 (2005).

[3] L. A. Curtiss, K. Raghavachari, P. C. Redfern, and J. A. Pople, J. Chem. Phys. Vol. 106, 1063 (1997).