How to estimate the prediction uncertainty of computational chemistry methods ?

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Prediction uncertainty is a very interesting performance estimator, filling the needs of the end user to choose an appropriate method [1]. Its estimation involves generally a statistical treatment of error samples on references databases, through error statistics or model calibration. Both approaches present difficulties because one is dealing mostly with systematic model errors rather than random errors.

• Standard error statistics, such as the mean unsigned errror, cannot be used to infer prediction uncertainty, notably because error distributions are not necessarily normal, even after linear scaling [2]. We propose to replace them by probabilistic indicators, such as Q_{95}, the 95 % percentile of the distribution of unsigned errors. If the errors distribution is normal, Q_{95} provides the enlarged uncertainty u_{95} recommended, for instance, in the thermochemistry literature [3].

• A major problem with error statistics is their non-transferability to other observables. The BEEF family of density functional approximations attempts to solve this problem by encoding the prediction uncertainty into its parameters posterior distribution via an *ad hoc* Bayesian calibration method [4]. We have shown that the BEEF approach is statistically unsatisfactory [5]. More elaborate calibration strategies, based on stochastic embedding models [6], might be worth to explore.

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