Development of a DFT functional for quantum radiochemistry

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Computational and, in particular, chemistry is an especially convenient tool in radiochemistry due to the possibility to reduce the number of required experiments and, thereby, reduce the dose absorbed by personnel. On the other hand, the usage of quantum chemical methods is limited in radiochemistry due to relativistic effects, the multiconfigurational character of the wavefunction of heavy elements or just limited computational resources. Density functional theory (DFT) seems to be an example of an efficient balance between accuracy and computational time. The problem of DFT approaches is their semiempirical and interpolation character, defined by data used for functional parameters fitting. Here we would like to propose an investigation aimed at developing new functional, designed especially for f-elements computations.

The design process is based on three main stages: collecting a reference database, developing a fitting algorithm and finally fitting the target functional. During the investigation, we collected a database with geometries and electron structures of actinide compounds calculated by a robust ab initio method. The database contains 104 compounds including single atoms from Ac to Cf and the most probable ionic forms. Each compound is presented in a single directory. The compound directory contains information about the structure in the struct.xyz file; energy (in kcal/mol), charge and multiplicity in the ecm.dat text file, and molecular orbitals in the Molden format.

The developed fitting approach is based on a Bayesian optimization with stochastic subsampling. The algorithm allows considering the “history” of fitting steps, reduces the computation time for each step, and avoids overfitting. While general testing the effectiveness of the approach, we showed an example of training specialized DFT functionals that are superior to the popular ones.

As a result, we used the database and the developed method to “retrain” popular PBE0 functional and increase its accuracy nearly twice relatively to the original one. The obtained accuracy (in terms of gas-phase geometry and thermodynamics of gas-phase reactions) appeared to be comparable with the experimental one.

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