Parametrization and Evaluation of Transferable Minimal Pseudo-Potentials to Avoid Electrons Spilling-Out in Polarizable Embedded QM/MM Calculations

Alireza Marefat Khah[a], Peter Reinholdt[b], Jógvan Magnus Haugaard Olsen[c], Jacob Kongsted[b] and Christof Hättig[a]

[a] *Quantum Chemistry Group, Ruhr University of Bochum, Bochum, Germany*
[b] *Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Odense, Denmark*
[c] *Department of Chemistry, The Arictic University of Norway, Trømso, Norway*
alireza.marefatkhah@rub.de

Recently, the polarizable embedded QM/MM PE-ADC(2) method has been implemented to calculate electronic excited state energies and molecular gradients in complex molecular environments [1]. Comparing to full-QM ADC(2) much more costly calculations, the PE-ADC(2) can deliver reasonable accuracy for excitation and fluorescent emission energies, excluding the cases with significant electron density leackage to the MM subsystem. A remedy for electrons spilling-out issue is to supplement MM sites with pseudo-potentials that approximate the effect of Pauli repulsion. In this study, we have parametrized a set of effective core potentials ECPs, comprised of only one pseudo-potential function for each angular momentum that are representing all electrons of the isolated atoms based on some energetics criteria. These optimized pseudo-potentials are used in the PE(ECP)-ADC(2) calculations to compute the excitation energies for a test set with different type of excitations and various embedding environments. It will be shown that the PE(ECP)-ADC(2), compared to full-QM PNO-ADC(2), improves the accuracy particularly for the cases that diffuse basis sets are used.

References

1. Alireza Marefat Khah, Sarah Karbalaei Khani and Christof Hättig *J. Chem. Theory Comp.* **14** (2018), 4640.