

EFFICIENT METHODS FOR THE ACCURATE DESCRIPTION OF ELECTRON CORRELATION IN LARGE MOLECULAR SYSTEMS WITHIN THE DIRECT AND BEYOND RANDOM PHASE APPROXIMATION

Daniel Graf, Matthias Beuerle, Henry F. Schurkus, Christian Ochsenfeld

*Chair of Theoretical Chemistry, Department of Chemistry,
University of Munich (LMU),
Butenandtstr. 7, D-81377 München*

An efficient method for calculating the (direct) random phase approximation (RPA) correlation energy is presented that is as accurate as the canonical molecular orbital resolution-of-the-identity RPA (RI-RPA) with the important advantage of an effective linear-scaling behavior (instead of quartic) for large systems due to a formulation in the local atomic orbital space [1]. The high accuracy is achieved by utilizing optimized minimax integration schemes and the local Coulomb metric attenuated by the complementary error function for the RI approximation. The memory bottleneck of former atomic orbital (AO)-RI-RPA implementations [2,3] is avoided by precontraction of the large 3-center integral matrix with the Cholesky factors of the ground state density reducing the memory requirements of that matrix by a factor of $N_{\text{basis}}/N_{\text{occ}}$. Furthermore, we present a parallel implementation of our method, which not only leads to faster RPA correlation energy calculations but also to a scalable decrease in memory requirements opening the way for investigating large molecules even on small- to medium-sized computing clusters. As an example, the interlayer distance of two covalent organic framework pore fragments (comprising 384 atoms in total) is analyzed.

While direct RPA greatly improves upon conventional density functional theory (DFT) in describing dispersion effects, it delivers unsatisfactory results for non-isogyric processes such as atomization energies due to its inherent self-interaction error. We further present a methodology which enables efficient calculations of beyond RPA correlation energies including exchange effects and therefore gives an opportunity to circumvent these problems also for molecules significantly larger than possible to date [4].

- [1] Graf, D.; Beuerle, M.; Schurkus, H. F.; Luenser, A.; Savasci, G.; Ochsenfeld, C. *J. Chem. Theory Comput.* **2018**, *14*, 2506–2515.
- [2] Schurkus, H. F.; Ochsenfeld, C. *J. Chem. Phys.* **2016**, *144*, 031101.
- [3] Luenser, A.; Schurkus, H. F.; Ochsenfeld, C. *J. Chem. Theory Comput.* **2017**, *13*, 1647–1655.
- [4] Beuerle, M.; Graf, D.; Schurkus, H. F.; Ochsenfeld, C. *J. Chem. Phys.* **2018**, *148*, 204104.