

## Author and title:

Dávid Mester; Efficient Excited-State Quantum Chemical Approaches for Large Molecules

## Publications related to the thesis:

1. D. Mester, P. R. Nagy, and M. Kállay, *Journal of Chemical Physics*, 2017, 146:194102.
2. D. Mester, P. R. Nagy, and M. Kállay, *Journal of Chemical Physics*, 2018, 148:094111.
3. D. Mester and M. Kállay, *Journal Chemical Theory and Computation*, 2019, 15:1690.
4. D. Mester and M. Kállay, *Journal Chemical Theory and Computation*, 2019, 15:4440.
5. D. Mester, P. R. Nagy, and M. Kállay, *Journal Chemical Theory and Computation*, 2019, 15:6111.

## Summary:

In this thesis numerous approaches have been presented for efficient quantum chemical calculations of excited-state properties of large molecules. In the first group of methods, we have successfully reduced the number of variables required for the calculations using and combining various approximations. In the remainder an effective fourth-power-scaling double hybrid TDDFT approach was developed, with which the errors can be significantly reduced compared to methods with similar cost.

A reduced-cost implementation of the CC2 and ADC(2) methods is presented. We introduce approximations by restricting virtual natural orbitals and natural auxiliary functions, which results, on the average, in more than an order of magnitude speedup compared to conventional algorithms. For the reduction of the size of the molecular orbital basis state-specific natural orbitals are constructed for each excited state using the average of the approximate MP2 and the corresponding CIS(D) density matrices. The various approximations are carefully benchmarked, and conservative truncation thresholds are selected which guarantee errors much smaller than the intrinsic error of the methods. Using the canonical values as reference, we find that the mean absolute error for excitation energies is 0.02 eV for both methods, while that for oscillator strengths is 0.001 in the case of ADC(2). The rigorous cutoff parameters together with the significantly reduced operation count and storage requirements allow us to obtain accurate excitation energies and transition properties using triple- $\zeta$  basis sets for systems of up to one hundred atoms.

A reduced-scaling algorithms for further computational savings are presented utilizing the locality of the molecular orbitals. First, an approximation is presented which can efficiently decrease the computational expenses of CIS and TDDFT methods, as well as of the related TDHF and TDA-TDDFT approaches. The approximation is the adaptation of the local density fitting scheme developed for Hartree–Fock calculations for excited states and reduces the quartic scaling of the methods to cubic. Our benchmark calculations show that, for molecules of 50 to 100 atoms, average speedups of 2 to 4 can be achieved for CIS and TDDFT calculations at the expense of negligible errors in the calculated excitation energies and oscillator strengths. Then a framework for the reduced-scaling implementation of excited-state correlation methods is presented. An algorithm is introduced to construct excitation-specific local domains, which include all the important molecular orbitals for the excitation as well as for the electron correlation. The sizes of the resulting compact domains are further decreased utilizing our reduced-cost techniques based on the natural auxiliary function and local natural orbital approaches. The results of benchmark calculations performed at the ADC(2) level are presented, and it is demonstrated that the speedups achieved are significant even for systems of fewer than 100 atoms, while the errors introduced by our approximation are highly acceptable. Our results show that the new reduced-scaling algorithm allows us to carry out correlated excited-state calculations using triple- $\zeta$  basis sets with diffuse functions for systems of up to 400 atoms or 13000 atomic orbitals.

Finally, a new type of combined double hybrid TDDFT-ADC(2) method is proposed for the calculation of spectral properties of molecular systems. The new ansatz is an extension of the previous double hybrid methods replacing the non-iterative doubles correction of CIS(D) by iteratively evaluated ADC(2)-like second-order terms, reminiscent of dressed TDDFT approaches. Our results show that, compared to the existing double hybrids, the ADC(2)-based methods improve the quality of the transition energies for valence states, especially for those of sizable double excitation character. For oscillator strengths, the performance of the new methods is significantly better. The proposed method with a mean absolute error of about 0.15 eV for excitation energies, outperforms other double hybrid approaches, ADC(2), its spin-scaled variants, and also the computationally more demanding CC2 model.