

Report TIER1, project 14-024

## *Quantum contributions to the polarizability*

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In this project, the ab initio quantum mechanical polarizability of first-row homonuclear dimers was calculated along their dissociation curve by means of finite-field extrapolations of density matrix renormalization group calculations. In order to find suitable finite-field values, the parameter range 0.0001 to 0.0300 atomic units was scanned for the smallest and largest dimers under consideration ( $\text{Li}_2$  and  $\text{F}_2$ ), both for the most compressed and most stretched geometries (0.9 and 2.0 times the equilibrium distance).

The calculation of the polarizability by means of finite fields is a delicate balance of accuracies. There are two ways to obtain the polarizability in this way: either as a difference of energies divided by the applied finite fields squared, or as a difference of dipole moments divided by the finite fields. By using both methods, a cross-check of the obtained values can be performed. Although smaller finite fields yield more accurate polarizabilities for exact calculations in exact arithmetic, the appearance of small finite fields in the denominator leads to increased errors for calculations which are imprecise or even for discrete arithmetic used on computers. As our obtainable accuracy decreased with increasing number of electrons in the system (because then there are more configuration state functions to expand the exact solution), we had to carefully assess the use of larger finite fields for the larger systems. This process required a few iterations, and by the beginning of October we had found a good set of fields for all systems and geometries.

The assessment of the finite-field values took more resources than foreseen, but nonetheless we were able to finish 80% of our production data within the granted computing time. The remaining calculations are now running on the tier-2 cluster at Ghent University, and we will soon be able to extract the ab initio polarizability reference data, which will then be used to assess existing (and design new) force-field parametrizations.