

From molecular properties to intermolecular interaction potentials

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Calculations of spectra of clusters, scattering cross-sections, properties of condensed phases and of biomolecular systems, as well as *in silico* material design have become mainstream methods in science and engineering and are expected to become even more important as computers pass the exaflop performance threshold. All such calculations require force fields, i.e., potential energy surfaces (PESs) which determine nuclear motions. We are now entering the era when physics-based PESs fitted to *ab initio* quantum mechanical calculations for dimers and trimers are becoming the potentials of choice in all these fields. Among *ab initio* methods, symmetry-adapted perturbation theory (SAPT) [1] is particularly well suited for such calculations due to its seamless connection to asymptotic interaction energies. Recently, generation of *ab initio* derived PESs became as simple as running standard electronic structure programs thanks to the automation of this process in the autoPES package [2].

An important part of the autoPES methodology is the use of asymptotic expansions of interaction energies derived from first principles. First, the molecular properties of monomers: multipole moments and static and dynamic polarizabilities are computed *ab initio*. The properties defined relative to the center of mass (COM) of each monomer are then expressed in terms of properties distributed among the atoms. This is necessary since the COM-based expansion (semi)converges only for very large separations R while the distributed expansion accurately reproduces the total SAPT interaction energies down to distances of about 1.5 times the radial van der Waals minimum separation. The use of the asymptotic expansion has several advantages: (a) one avoids expensive *ab initio* calculations in a large sector of the dimer configurations space; (b) the resulting PES is correct at all R ; (c) a physical interpretation of the components of interaction energy is directly related to monomer properties and, therefore, also to experimental observables; (d) the same methodology can be applied to develop empirical force fields, i.e., such force fields would use *ab initio* asymptotics and fit only the repulsive components.

[1] K. Szalewicz, Wiley Interdisc. Rev.–Comp. Mol. Sci. **2**, 254 (2012).

[2] M. P. Metz, K. Piszczatowski, and K. Szalewicz, J. Chem. Theory Comput. **12**, 5895 (2016).