

Overcoming Artificial Multipoles in Intramolecular Symmetry-Adapted Perturbation Theory

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Symmetry-adapted perturbation theory (SAPT) is a well-developed methodology to describe and analyze non-covalent interactions between molecules. For analogous weak interactions within a molecule, the first versions of intramolecular SAPT (ISAPT) lead to valuable insights into the relative contributions of the electrostatic, induction, dispersion, and exchange effects into the overall interaction. ISAPT aims to decompose the interaction of two nonbonded molecular fragments A and B covalently connected by a linker C. While some fragmentation patterns lead to meaningful ISAPT energy contributions, in other cases, unphysical results are observed, for example, repulsive electrostatic energies between hydrogen-bonded fragments. The reasons for this unphysical behavior relate to the treatment of interfragment link bond orbitals. In the original ISAPT formulation, link bond electrons with the balancing nuclear charges are assigned to the linker C. Unfortunately, this leads to artificial dipole moments at the interfragment boundaries, as the link A and B atoms are missing electrons on one of their hybrid orbitals. To tackle this problem, we propose a reassignment of the ISAPT link electrons so that each fragment, A/B or C, accounts for one electron from the link hybrid orbital. When this hybrid is constructed in the space of intrinsic atomic orbitals, the magnitude of spurious dipole moments is significantly reduced, leading to reasonable and basis-set stable values for all ISAPT corrections and all fragmentation patterns. We illustrate the performance of the new ISAPT variant on a number of systems exhibiting nonbonded intramolecular interactions, including pentanediols, linear and branched alkanes, and closed and open conformations of halogen- π bonded systems that were proposed as molecular balances.