

# Intramolecular symmetry-adapted perturbation theory

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Non-covalent interactions encompass a broad group of phenomena arising from e.g. van der Waals forces, hydrogen bonds, charge transfer. They are omnipresent in nature and increasingly exploited in materials design. Taking full advantage of these interactions requires elucidation of their underlying physics. Within this context, the quantum chemistry community made a large effort to extend the computational toolbox for delivering approaches that serve to visualize and interpret the nature of non-covalent interactions.[1] Symmetry-Adapted Perturbation Theory (SAPT)[2] can be considered as one of the most successful approaches, as it decomposes the interaction energy into physical and intuitive terms such as electrostatics, exchange, induction and dispersion.

Until recently, there was no equivalent energy decomposition scheme available for intramolecular interactions, which are as ubiquitous. Last year, to fill this gap, Parrish *et al.* have introduced ISAPT [3], while we have proposed a method based on the zeroth-order wavefunction previously introduced by Gonthier and Corminboeuf [4] and on the notion of Chemical Hamiltonian [5]. Within this “intra-SAPT” [6] approach, the interaction between the two weakly interacting fragments is first removed by projection operators and then brought back as a perturbation. The arising perturbation terms have a clear physical interpretation as Coulomb-exchange, induction and dispersion interactions.

We provide illustrative applications of Intra-SAPT that sheds the light on the energetic driving force bringing chains of unbranched hydrocarbons “hairpin alkanes” together, on the nature of intramolecular  $\pi - \pi$  stacking and hydrogen bond interactions in quasi-ring structures.

## References

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