

Recent Developments in the Efficient Calculation of Noncovalent Interactions

C. D. Sherrill and E. G. Hohenstein

School of Chemistry and Biochemistry, Georgia Institute of Technology,
Atlanta, GA 30332-0400, USA

Noncovalent Interactions govern phenomena as diverse as protein folding, drug docking, and crystal packing. They are difficult to describe theoretically because London dispersion forces often play a critical role, but these “instantaneous dipole / induced dipole” forces are inherently quantum mechanical and depend on the correlated motions of electrons. Hence, popular quantum mechanical methods like Hartree-Fock molecular orbital theory, or density functional theory, are not capable of describing them accurately because they lack a mathematical description of long-range correlated electron motions. Instead, one must use various post-Hartree-Fock electron correlation models, such as many-body perturbation theory or coupled-cluster theory. Unfortunately, even these methods do not give accurate results for typical noncovalent interactions unless very large basis sets are used and the highest practical levels of theory [e.g., coupled-cluster singles, doubles, and perturbative triples, or CCSD(T)] are used.

In addition to the strength of these interactions, their fundamental physical nature (in terms of electrostatic, exchange-repulsion, induction, and London dispersion forces) is of significant interest, especially when trying to understand how larger systems or substituents will affect them. Symmetry-adapted perturbation theory (SAPT) is very helpful in this regard because it provides a way to directly compute all of these energetic contributions to noncovalent interactions.

An overview of this field, and some recent advances making SAPT computations possible on much larger molecules, will be presented, along with some example applications.

[1] “Substituent Effects in Sandwich Configurations of Multiply Substituted Benzene Dimers are Not Solely Governed by Electrostatic Control,” A. L. Ringer and C. D. Sherrill, *J. Am. Chem. Soc.* **131**, 4574 (2009).

[1] “Density Fitting and Cholesky Decomposition Approximations in Symmetry-Adapted Perturbation Theory: Implementation and Application to Probe the Nature of pi-pi Interactions in Linear Acenes,” E. G. Hohenstein and C. D. Sherrill, *J. Chem. Phys.* **132**, 184111 (2010).

[3] “Efficient Evaluation of Triple Excitations in Symmetry-Adapted Perturbation Theory via Second-Order Moller-Plesset Perturbation Theory Natural Orbitals,” E. G. Hohenstein and C. D. Sherrill, *J. Chem. Phys.* **133**, 14107 (2010).