

# Intermolecular Force Field Parameterization from First Principles

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Understanding the forces acting between atoms and molecules is crucial for elucidation the organization and, as a consequence, the physicochemical properties of matter both in the gas and in the condensed phase. Equipped with the advanced intermolecular perturbation theory [1], it is now very timely to rethink a number of *ad hoc* concepts such as “ $\pi$ - $\pi$ ” or “ion- $\pi$ ” interactions invoked to describe the forces that drive association between molecules. Recent developments in the Symmetry Adapted Perturbation Theory (SAPT) [2] allow partitioning of the total intermolecular energy into different physically well-defined contributions (electrostatic, exchange-repulsion, dispersion and induction) against which the corresponding terms in the force field can be separately parametrized. An approach is described to include the missing *charge penetration* energy term *directly* into a force field using a sum over pairwise electrostatic energies between spherical atoms as originally suggested by Spackman [3]. This important contribution to the intermolecular potential can be further refined to reproduce the accurate electrostatic energy between monomers in a dimer by allowing for the radial contraction-expansion of atomic charge densities. This new short-range term is supplemented by a long-range electrostatic contribution described with atomic multipoles (up to quadrupoles) based on distributed multipole analysis [4, 5]. The other components of a force field (exchange-repulsion and dispersion) are parametrized to reproduce the corresponding contributions calculated within the SAPT framework. As a proof-of-concept, we have developed the force field parameters suitable for modeling intermolecular interactions between polycyclic aromatic hydrocarbons (PAH) [6]. We show that it is now possible to have a balanced force field suitable for molecular simulations of large molecules avoiding error cancellation to a large extent.

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