Intermolecular Force Field Parameterization from First Principles

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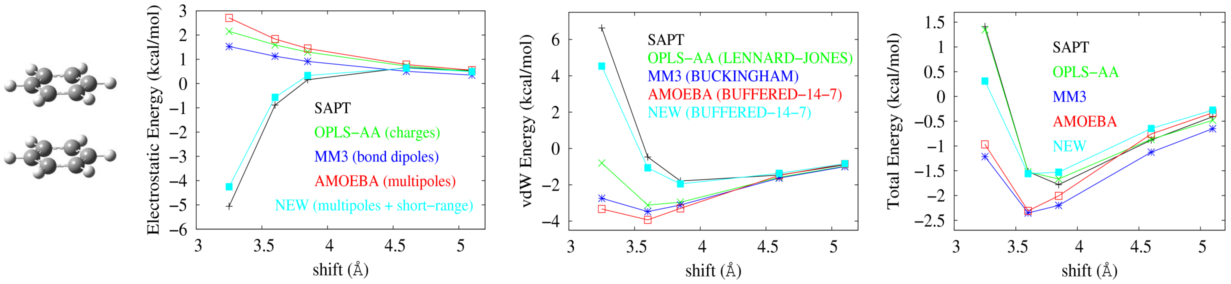
Accurate intermolecular forces are needed for simulations of aggregates of large organic chromophores, such as perylene bisimide [1], where a highly anisotropic charge distribution due to the extensive π-conjugation calls for a reliable force field since high quality fully ab initio calculations are computationally very demanding [2]. Recent developments in the symmetry adapted perturbation theory (SAPT) [3] 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 [4]. 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 [5, 6]. The other components of a force field (exchange-repulsion and dispersion) are parametrized to reproduce the accurate data calculated by SAPT(DFT) [7]. As a proof-of-concept, we have derived the force field parameters suitable for modeling intermolecular interactions between polycyclic aromatic hydrocarbons (PAH) [8]. It is shown that it is 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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