MS19 Experimental and theoretical advances in quantum crystallography

MS19-04
Toward a total interaction potential from experimental transferred electron density
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Abstract
The development of a fast, accurate and transferable model for the calculation of total interaction energy between two molecular charge densities has been a long-standing challenge in numerous research fields including quantum crystallography. For that, accurate but generally time-consuming quantum chemistry calculations have been performed and fast but often system specific empirical models have been developed. Here, we propose to base the interaction potential calculations on the knowledge of the charge density originated from X-ray diffraction data. In this purpose, the so-called Hansen and Coppens multipolar model [1] for the charge density has been used. In order to overcome the need of experimental diffraction data to refine the parameters of the density model, we transferred them from the ELMAM2 database [2]. This database provides atomic density parameters averaged over experimental molecular electron densities from high resolution X-Ray diffraction data, along with corresponding averaged atomic anisotropic polarizabilities. Thus, an accurate molecular charge density can be reconstructed, while accounting for the local environment thanks to the polarizabilities [3], in a very fast way. From this transferred charge density, we derived the total interaction energy divided into four terms, following the SAPT decomposition [4]. These terms include: an electrostatic (Coulombian) term, a dipolar induction (polarization) term, a dispersion term and a repulsion or exchange term. We designed each term with as few empirical parameters as possible to reproduce the SAPT reference data, using the benchmark database NENCI-2021 [5] for training and cross-validation. The electrostatic term, based on the unperturbed transferred charge density, needed no empirical parameter to reach a correlation coefficient $R = 97\%$ with the SAPT data. The dipolar induction term, based on the transferred atomic polarizabilities, reached with no fitted parameters a correlation up to $R = 90\%$. For the dispersion term, we started from the London dispersion energy, which depends also on atomic polarizabilities. By introducing parameters for chemical species, we obtained a correlation of $R = 98\%$ for this dispersion term. It is well-known that the exchange energy is correlated to the density overlap, namely the integral of the product of interacting charge densities. Comparing these integrals to the SAPT exchange energies we already obtained a correlation about $R = 92\%$. During this lecture, we will describe how we built these models based on the transferred electron density and show the details of the interaction energy results. Furthermore, this method would enable to compute accurately, in a fast and transferable way, the total intermolecular interaction energies in various systems such as organic dimers and crystals or protein-ligand complexes.

References
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SAPT vs our ELMAM Model dispersion energies

SAPT vs our "ELMAM Model" Dispersion Energies (kcal/mol)

$R^2 = 0.97$

$Edisp\_ELMAM = 1.02 * Edisp\_SAPT + 0.15$