

Modeling Electrostatic Penetration Effects with Atoms in Molecules

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Modeling electrostatic potentials is an essential aspect of the development of molecular mechanics force-field models. Over the past decades, least-squares fitting of partial atomic charges to the molecular electrostatic potential, known as ESP fitting, has been the most popular method to describe electrostatic interactions in force fields. Each atom is represented by a point charge bearing the fitted partial charge. Despite its popularity, this method has a few well-known drawbacks. The major issue is the statistical instability of the fitted charges, i.e. their sensitivity to seemingly irrelevant details such as minute geometry changes.¹ Another weakness is the inability of point charges to account for the so-called penetration effect. When two molecules in a dimer are well-separated, ESP charges can reproduce the electrostatic interaction. However, at shorter distances, the electron densities start to overlap, which leads to electrostatic interactions that can't be described by simple point charges.²

In this work, we propose a new method that allows a proper description of the penetration effect in force-field models. Instead of using bare point charges, every atom is represented by an electronic charge distribution, a sum of Slater density functions, and a point charge for the nucleus. The approach has some similarities with the density fitting in the Gaussian Electrostatic Model (GEM)³ but uses a simpler model for the electron density and a different method to obtain the parameters. A new Atoms-In-Molecules (AIM) method is proposed to derive the parameters: Minimal Basis Iterative Stockholder (MBIS), which is derived from the Iterative Stockholder Analysis.⁴ In MBIS, a promolecular density is constructed as a sum of atom-centered Slater density functions (one per atomic shell). All parameters in the promolecule are found by minimizing the Kullback-Leibler divergence of the pro-molecule w.r.t. an ab initio density. Using several molecular datasets, we will demonstrate the amenities of this method for modeling electrostatic potentials and electrostatic interactions, also nearby the molecular van der Waals surface.

References:

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