Constrained Dipole Moment Density Functional Theory for Charge Distributions in Force Fields for the Study of Molecular Fluids

Javier Carmona-Espíndola[1], Edgar Nuñez-Rojas[1], Valeria García-Melgarejo[2], José L. Gázquez[2], José Alejandre[2]

[1]Departamento de Química, CONACYT-Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, Ciudad de México, 09340, México.

[2]Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, México, Ciudad de México, 09340, México.

jcarmona_26@yahoo.com.mx

In this work, we present a new methodology to describe a system with a constrained dipole moment, CD-DFT. The self-consistent solution of this methodology leads to a unique density that minimizes the energy of the system for the pre-defined value of the dipole moment. With this methodology, we determined the atomic charges for the parametrization of force fields in clasical molecular dynamics [1]. To this end, we implemented the atomic dipole moment corrected Hirshfeld population method, ADCH [2]. This method modifies the Hirshfeld charges so as to obtain the same molecular dipole moment associated with a given electronic distribution. The pre-defined values for the dipole moment in the self-consistent calculations are the ones that reproduce the dielectric constant of the corresponding fluid. The force field parameters thus obtained give a reasonable description of several properties like heats of vaporization, self-diffusion coefficients, shear viscosities, isothermal compressibilities and volumetric expansion coefficients of pure substances.

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2. Lu, T.; Chen, F. W., Atomic dipole moment corrected Hirshfeld population method. *J. Theor. Comput. Chem.* **2012,** *11*, 163-183.