Development of a Fluctuating Charge Model for Transition Metal Complexes

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The concept of partial atomic charges is fundamental for the accurate description of molecules with Molecular Mechanics. This is because, a significant part of non-bonded interactions between polar species (atoms or atom groups) is electrostatic. Traditionally, force fields assign fixed partial charges to specific sites within a molecule and allow them to interact via a Coulomb-type interaction. This method fails for systems where polarization effects are important. One method of treating polarization that has found widespread applications in various chemical and biological systems is the geometry-dependent fluctuating charge model[1,2]. While variable charge schemes are available for organic and biological force fields, our aim is to develop a method that can be used with comparable accuracy for transition metals as well. Such a scheme for calculation of geometry-dependent charges is presented here. In this method the total electrostatic energy of a molecule is expressed as a function of partial charges as:

$$E(Q_1..Q_N) = \sum_{i=1}^{N}\left(E_i(0) + \left(\frac{\delta E}{\delta Q}\right)_{Q_i} Q_i + \frac{1}{2}\left(\frac{\delta^2 E}{\delta Q^2}\right)_{Q_i} Q_i^2 \right) + \sum_{i=1}^{N}\sum_{j<i} Q_i Q_j D_{ij}$$

Our model contains two parameters per atom type. To test the validity of the scheme we have developed a small reference set of organic molecules containing common elements and optimized the model parameters by fitting to DFT-based charges. This new fluctuating charge force field is then used to calculate observables, like dipole moments, of various organic molecules. Comparison with experimental and Quantum Chemical dipole moments show close correlation and similar trends. We are currently in the process of incorporating effects arising due to variable spin states of transition metal ions in this model. This fast yet accurate charge scheme will be part of the new version of our Molecular Mechanics program Momec3[3].

[1] Mortier, W. J., Ghosh, S. K., Shankar, S., *J. Am. Chem. Soc.* **1986**, *108*, 4315-4320
[2] Rappe, A. K., Goddard III, W. A., *J. Phys. Chem.,* **1991**, *95*, 3358-3363
[3] Comba, P., Martin B., The Momec homepage, *http://www.momec.uni-hd.de/*