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Valence Force Fields for Microporous Materials

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Empirical force-field (FF) models are widely used to simulate properties of microporous materials and the behavior of guest molecules in their pores and cavities. Provided that an FF gives a good approximation of the interatomic interactions, such simulations can be used to investigate, at a low computational cost, the diffusion of guest molecules, adsorption isotherms, breathing of metal-organic frameworks, vibrational spectra, and so on. Over the past decade, a vast amount of new porous materials were synthesized, and it becomes more and more challenging to derive suitable FF parameters that correctly describe the balance between various interactions (electrostatics, dispersion, polarization, Pauli repulsion, valence interactions, ...), which determine the properties of porous media and their interactions with guest molecules.

Recent improvements in the derivation of non-covalent interactions (mainly dispersion,[1] electrostatics and polarization[2]) do no longer exclude pairs of atoms that are already involved in valence terms (e.g. bond stretch, angle bending, etc.). However, this is one of the main assumptions used for the traditional derivation of valence FFs, where (i) rest parameters are equal to equilibrium internal coordinates and (ii) force constants are taken from the diagonal of the Hessian transformed to redundant internal coordinates.[3] In this work, we propose a new method to derive parameters for a valence FF, which can be superimposed with a non-covalent model (with or without exclusion rules), and which results in optimal predictions of ground state geometries and vibrational modes. The method will be illustrated with the derivation of an FF model for silica, which can be compared with several FF calibrations in the literature over the past two decades. [3,4,5]

Computational Methods

The proposed calibration scheme for valence parameters uses ab initio computations on a set of isolated representative clusters as training data. For each molecule in the training set, a geometry optimization is carried out and the Hessian is computed. Prior to the calibration of the valence parameters, all other components are derived: (i) the electrostatic model is based on bond-charge-increments fitted to the electrostatic potential, and (ii) the London dispersion and Pauli repulsion interactions are derived from an iterative Hirshfeld partitioning of the electronic density.

Our initial approach (I) is to derive the parameters from a non-linear least-squares fit of both the Hessian matrix elements and the Cartesian forces. This approach is not capable of fixing all parameters, and allows random fluctuations for certain linear combinations of parameters. This problem was already observed in the seminal papers of Van Santen [4] and Sauer. [5] The first improvement, approach II, introduces a set of additional equations that make the fitting procedure well-conditioned. In the extra equations, the derivatives of energy terms in internal coordinates that cancel out after the transformation to Cartesian forces, are set to zero. Despite this improvement, we still observe a poor reproduction of geometries and lower vibrational frequencies in the validation.

The main problem of approach II, is that the accuracy of the (zero) forces at the ground state is not the true objective of the FF model. It is the deviation of the FF geometry (after optimization) from the

DFT geometry that must be as small as possible. In approach III, the conventional force-matching equations are transformed into a new set of equations that compare FF with DFT geometries. In order to avoid a complete FF-optimization at each iteration of the parameter calibration, the optimal FF geometry is approximated by a single step from the Newton optimization procedure. Following this procedure, the implementation of the non-linear least squares procedure remains efficient, i.e. it is still feasible to compute the analytical derivatives of the FF predictions towards the parameters and one can still use the Levenberg-Marquardt algorithm to optimize the parameters.

Results and discussion

A training set of hydrogen-terminated silica clusters up to five Silicon atoms is constructed. Optimizations and frequency computations are carried out with Gaussian09 at the PBE0/6-311+G(d,p) level, and using a 6-311+G(2df,p) basis for oxygen. The latter is needed for a good description of the Si-O-Si bend. Parameters are derived with approaches I, II and III discussed above. A detailed analysis of each calibration reveals the weaknesses of approach I and II. Geometry optimizations and vibrational analysis of other clusters (not included in the training set) and periodic systems, shows that the parameters obtained with approach III are transferable to a wide range silica materials.

Conclusions

A new methodology is proposed to derive parameters for valence FFs that can be superimposed with non-covalent without any assumptions about exclusion rules. The method is applied to derive valence parameters for silica systems based on isolated cluster computations. Validation on larger clusters and periodic systems confirms the reliability of the new method

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