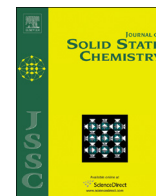




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Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Atomic charges for modeling metal–organic frameworks: Why and how



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ARTICLE INFO

Article history:

Received 7 May 2014

Received in revised form

6 August 2014

Accepted 11 August 2014

Available online 21 August 2014

Keywords:

MOF

Atomic charges

Monte Carlo

Molecular dynamics

DFT

Adsorption

ABSTRACT

Atomic partial charges are parameters of key importance in the simulation of Metal–Organic Frameworks (MOFs), since Coulombic interactions decrease with the distance more slowly than van der Waals interactions. But despite its relevance, there is no method to unambiguously assign charges to each atom, since atomic charges are not quantum observables. There are several methods that allow the calculation of atomic charges, most of them starting from the electronic wavefunction or the electronic density or the system, as obtained with quantum mechanics calculations. In this work, we describe the most common methods employed to calculate atomic charges in MOFs. In order to show the influence that even small variations of structure have on atomic charges, we present the results that we obtained for DMOF-1. We also discuss the effect that small variations of atomic charges have on the predicted structural properties of IRMOF-1.

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1. Introduction

Metal–Organic Frameworks have emerged as front-edge materials, due to their potential impact on several types of applications, mainly those based on adsorption and separation properties (such as hydrogen storage [1], methane and carbon dioxide capture [2,3], or hydrocarbon [4] and enantiomeric separation [4,5]). Unlike traditional nanoporous solids, i.e. zeolites, carbons, and clays, MOFs do not only exhibit enormous surface areas (beyond 5000 m²/g), but also a huge structural and compositional diversity, resulting from the large amount of research carried out, which has recently reached over 2000 scientific papers per year. Obviously, it is very expensive and time consuming to carry out experimental studies on several different materials. But computer modelling is a useful tool, which can help guiding the experimental search into new and potentially interesting materials. It is possible, for example, to use computer simulations to devise viable routes for materials selection, via large screenings [6,7]. Computer simulations can also provide a platform for understanding the material behavior at an atomic scale, which often leads to application-tailored materials design [8,9].

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Since the study of adsorption, separation and diffusion related phenomena involves the explicit consideration of hundreds, or even thousands of atoms (particularly in structures with large unit cells, such as MOFs), classical simulation methods are the first choice [10,11]. It is worth noting that recently, quantum mechanics-based calculations have emerged as valuable tools in this field [12,13], but in MOFs their computational cost still precludes its use for screenings of a larger number of materials, for the calculation of adsorption isotherms, diffusion of complex molecules, or the study of systems in which entropic effects are relevant, etc. In atomistic classical simulations the energy of the system can be written as:

$$E = E_{\text{bonding}} + E_{\text{non-bonding}} \quad (1)$$

where E_{bonding} involves contributions directly related to bonded atoms, and are described by the sum of bond, angles and dihedral terms, while $E_{\text{non-bonding}}$ includes the interactions between non-bonded atoms and has the form:

$$E_{\text{non-bonding}} = E_{\text{van der Waals}} + E_{\text{Coulombic}}. \quad (2)$$

The van der Waals interactions are usually described by the typical 12-6 Lennard–Jones potential:

$$E_{ij}^L = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3)$$

where r_{ij} is the distance between atoms i and j , ϵ is the energy at the minimum and σ is the distance at which the energy is zero. The Coulombic interactions are calculated as follows:

$$E_{ij}^{\text{Coulombic}} = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (4)$$

where q_i and q_j are the corresponding atomic partial charges.

The parameters used for the calculation of bonded and van der Waals interactions are usually taken from generic force fields, such as Dreiding [14], UFF [15] or specific force fields designed for families of molecules, like OPLS [16], TraPPE [17] or AMBER [18]. The Lennard–Jones parameters that describe the interactions between atoms of different type are computed using the Lorentz–Berthelot [19] or the Jorgensen mixing rules [20]. When specific molecules force fields are used for modeling adsorbates, the atomic charges are usually taken from the force field used. In a number of cases, however, using the generic or specific force fields the experimental adsorption data are not reproduced, and hence a transferable force field parameterization is required, via fitting of parameters to reproduce experimental data [21,22] or via fitting to reproduce ab initio surface energies [23–25]. The parameters that describe the van der Waals interactions and the interactions between bonded atoms are usually employed directly as taken from the generic force fields. But the atomic charges need to be calculated for each material. Since the atomic charges arise from the electron density of the solids, even small chemical differences between related MOFs lead to differences in the charges, as was recently shown for functionalized imidazolates [26].

For the computation of the intermolecular interactions (MOF–adsorbate and adsorbate–adsorbate interactions), which control adsorption, diffusion and separation processes, it is important to keep in mind that they are of non-bonded nature, and consequently their correct description depends on achieving a balance between van der Waals and Coulombic contributions [27]. This implies that, if a generic force field is used, it is necessary to use charges that would be not very different from those employed during the parameterization of the force field. For example, the parameters of the van der Waals interactions in the Dreiding and UFF force fields were fitted employing Gasteiger [28] and QEq charges [29], respectively. This seems to be one of the main reasons why calculated and experimental data do not agree, when generic force fields largely fail to model intermolecular interactions. As illustration, Babarao et al. [30] found that a good agreement with experimental CO₂ isotherms in ZIF-68 was obtained when ChelpG or Mulliken charges were used in conjunction with the Dreiding force field.

The effect of the choice of the atomic charges on computing adsorption and diffusion properties of MOFs has been a topic of increasing attention. A few years ago, Walton et al. showed that the inclusion of the electrostatic interactions between adsorbate molecules and the framework was crucial in reproducing the step-like adsorption of CO₂ in IRMOF-1 [31]. Watanabe et al. showed that even quadrupolar molecules, such as CO₂, can interact very distinctly with MOFs, being the electrostatic interaction more or less relevant than the van der Waals interactions, depending on the atomic charges employed [27]. They found that the influence of the charges on the adsorption properties is very material dependent, i.e. for some materials we observe the same adsorption behavior, for a wide range of atomic charges, but for other materials, slight changes in atomic charges generate large changes in the adsorption properties. They computed CO₂ adsorption isotherms up to 0.1 bar in IRMOF-1, ZIF-8, ZIF-90, and Zn(nicotinate)₂, employing charges calculated by the REPEAT, DDEC, Hirshfeld and CBAC methods, and also without considering charges. These methods exhibit significant differences in the values of the charges that they predict, e.g. Zn charges calculated with the

mentioned methods in IRMOF-1 are 1.2787, 1.2149, 0.4229 and 1.5955, respectively. However, the adsorption isotherms are very similar in Zn(nicotinate)₂, less similar in IRMOF-1 and ZIF-8 and very different in ZIF-90.

In a study with 20 different MOFs with different topologies, pore sizes, and chemical characteristics, it was found that the guest–framework electrostatic interaction can account for 10–40% of the CO₂ uptake at very low pressure, and these values decrease at least by factor of 4 at high pressures, where guest–guest interactions dominate [32]. Gutierrez-Sevillano et al. used three sets of framework charges, changing in a range of 30% of their values, to examine its effect on the adsorption of CO₂ in ten ZIFs of different functionalities, and found that, while adsorption heats are almost the same for ZIF-8 and small differences are observed for ZIF-96, the effect of varying framework charges on ZIF-3, -7, -93 and -97 is large [26]. The hydrophobic character of ZIF-8 seems to be responsible for the negligible effect that the choice of charges has on the values of CO₂ adsorption heats, which is supported by the results of Zhang et al., who found that simulated methanol adsorption in ZIF-8 is not affected by the framework charges [33].

When modelling water in MOFs, the choice of charges is much more relevant. Castillo et al. [34] studied water adsorption in HKUST-1, and found that, in order to reproduce the experimental adsorption isotherms in the low pressure range, the ab initio derived framework charges needed to be scaled up by 25%. And Salles et al. [35] studied the adsorption in the hydrophobic MIL-47, finding that the ab initio charges previously used for modeling CO₂ adsorption needed to be scaled down by 30%, in order to reproduce the correct water adsorption behavior.

The influence of the MOF framework charges on molecular diffusion has been a topic of less research. The calculated self-diffusion coefficients for CO₂ in ZIF-8 using charges obtained with the CBAC, REPEAT, and DDEC, and ESP methods show significant differences [36]. The latter set of charges provides results in good agreement with experimental values, but the other three sets overestimate the diffusion coefficient between 1.5 and 20 times. Wu et al. [37] used a different set of charges (as well as different Lennard–Jones potentials), and the calculated self-diffusion coefficient of CO₂ in ZIF-8 was two times larger than in the previously cited work.

Since in a number of MOFs the proper choice of the framework charges is of key importance to model correctly the adsorption and diffusion behavior, it is natural that the simulation of molecular separation would be also markedly influenced by the electrostatic interactions. For instance, the simulated CO₂/CH₄ selectivity in HKUST-1 shows reverse behaviors when charges are not considered at all than when there is a full account of both host–guest and guest–guest electrostatic interactions [38]. For quadrupolar molecules, such as CO₂ and N₂, it has been observed that the atomic charges produce an electric field inside the nanopores that largely enhances the selectivity due to the difference in quadrupole moments [39].

In the following section we will present a brief description of the most widely used methods for calculating atomic charges in MOFs, referring the reader to the relevant references for a more in-depth description. Then, we will present the results of the calculations we have carried out to illustrate the influence of the structure on the charge calculation of DMOF-1. We will also show how the different sets of framework charges predict different thermal behaviors of IRMOF-1.

2. Methods for calculating atomic charges in MOFs

There are several methods with which to calculate atomic charges. They are always developed with the aim of providing

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