

## **POINT CHARGE FITTING REDUX**

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### **ABSTRACT**

Point charges are a crude, but useful model of charge density on the molecular level. They are often used to infer other properties or as part of a force field for molecular simulation. Continuing the work presented at 6CSSSZ in Šibenik, I calculate effective point charges for the  $\text{AlPO}_4\text{-34}$  framework from ab-initio charge density using several methods and compare results. I demonstrate that for molecular simulations, charges obtained by fitting to electrostatic potential yield the best results.

Keywords: periodic electrostatics, point charge fitting.

### **INTRODUCTION**

Point charges assigned to each atom in a molecule are certainly a very limited model of molecular charge density. Simple ions may be described well, but molecules and periodic solids are most often too complex for such a simple model. Nevertheless, point charges are used a lot in practice. The reason is not hard to find: ab-initio charge density or more complex models (such as electrostatic multipoles) are not nearly as easy to reason about and infer from, or, in the case of molecular simulations, as computationally cheap.

The method of obtaining the values of the charges assigned to each atom depends on the definition of “effective charge”, which in turn depends on what we wish to learn from such a model. Examples are charge transfer, adsorbent-adsorbate interaction potential, phonon properties, etc. The methods commonly used to turn the charge density calculated by ab-initio methods into a point charge model can be roughly categorized into

- wavefunction projection,
- geometric partitioning,
- response to external electric field,
- electrostatic potential fitting.

Examples of wavefunction projection methods are the venerable Mulliken<sup>[1]</sup> and the related Löwdin<sup>[2]</sup> methods. They assign charge to each atom by projecting the wavefunction of the (delocalized) valence electrons onto atomic orbitals. Such a procedure is not unique; therefore, the charges obtained by projecting the wavefunction are, to some extent, arbitrary. Implementations of these methods are, however, widely available and these charges often yield useful information.

Geometric partitioning methods separate the space around atoms into subvolumes, each subvolume and the charge within it belonging to the nearest atom. The simplest is the Voronoy approach where each atom is assigned the charge that is closer to that atom than any other; the

space is partitioned into so-called Voronoy cells<sup>[3]</sup>. This approach is often inappropriate as the dividing surfaces between cells are always exactly halfway between two atoms, splitting any covalent bonds. A better approach is the Bader's method<sup>[4]</sup>, where each subvolume contains exactly one charge density maximum while its boundary is defined by the minimum of the charge density in the direction perpendicular to the said boundary. The charge density is thus assigned to each atom in a rather natural manner.

If we are interested in the response to an external electric field, it is appropriate to consider the Born effective charges. These are tensors defined by the change in crystal polarization when displacing a particular atom and are thus a property related to lattice vibrations. Since the polarization is a change of total energy with external electric field, the order of differentiation can be changed and a Born charge can be defined as a change in the force on a particular atom with the external field,

$$\mathbf{Z}_i^* = \frac{\partial \mathbf{P}}{\partial \mathbf{r}_i} = \frac{\partial^2 E}{\partial \mathbf{r}_i \partial \boldsymbol{\varepsilon}} = \frac{\partial \mathbf{F}_i}{\partial \boldsymbol{\varepsilon}}, \quad (1)$$

where  $E$  is the total energy,  $\mathbf{P}$  is the polarization,  $\mathbf{r}_i$  and  $\mathbf{F}_i$  are the position and force on the  $i$ -th atom and  $\boldsymbol{\varepsilon}$  is the electric field; bold letters denote vectors and tensors. Scalar values of the Born charges may be obtained with orientational averaging.

Electrostatic potential fitting attempts to reproduce the ab-initio electrostatic potential by adjusting the point charges. Charges obtained in this fashion are called Merz-Kollman charges when this approach is applied to isolated molecules<sup>[5]</sup>. As I have shown at 6CSSSZ, there are complications when applying this method to periodic materials. I have later learned that the complications are even more severe<sup>[6]</sup>. Nevertheless, I wrote a program for electrostatic potential fitting and successfully calculated the effective point charges for AlPO<sub>4</sub>-34. I proceeded to compare the performance of the charges obtained via different methods in molecular simulations of water sorption in AlPO<sub>4</sub>-34.

## COMPUTATIONAL

Ab-initio calculations were performed using the Quantum ESPRESSO package<sup>[7]</sup> at the same settings as were used in our previous work on AlPO<sub>4</sub>-34<sup>[8]</sup>. Monte-Carlo molecular simulations of water sorption were performed using the RASPA package<sup>[9]</sup>. Simulation runs of the Grand-Canonical ensemble were  $4 \cdot 10^5$  cycles long; one half of these were equilibration, the other half production. The framework was kept fixed in its triclinic conformation, which is the one AlPO<sub>4</sub>-34 assumes when hydrated. Also kept mostly fixed were those water molecules that are known to be coordinated to the framework and thus have practically no mobility<sup>[8]</sup>; they were only allowed to rotate. The rest of the water was free to move, rotate and exchange with the particle reservoir; all these Monte-Carlo moves were taken with equal probability. Water was modeled with the TIP4P/2005<sup>[10]</sup> force field while the framework used the Lennard-Jones interactions specified by either the UFF<sup>[11]</sup> or the CVFFaug<sup>[12]</sup> force fields together with point charges calculated with different methods. As CVFFaug was used to simulate water in aluminophosphates before, a set of simulations was performed with unaltered CVFFaug which comes with its own set of charges and is paired with the SPC/E<sup>[13]</sup> water model.

## RESULTS AND DISCUSSION

The charges obtained from ab-initio calculations are given in table 1. Löwdin and Born charges were computed with tools in the Quantum ESPRESSO package while the Voronoy and Bader charges were obtained with the program of Tang *et al.*<sup>[4]</sup> CFFaug charges are given by the force field. ESP stands for „electrostatic potential“ and is calculated with my own program. The DDEC6<sup>[14]</sup> method is more complex than other methods and aims to reproduce the electrostatic potential while keeping some semblance of chemists' intuition.

Table 1. Effective point charges in units of  $e_0$  for the  $\text{AlPO}_4\text{-34}$  framework obtained with different methods.

	CVFFaug	Löwdin	Voronoy	Bader	Born	DDEC6	ESP
Al	1.4	1.4	1.755	2.93	2.76	1.7550	0.87250
P	3.4	2.15	2.225	4.87	3.32	1.7350	0.87250
O	-1.2	-0.8875	-0.995	-1.95	-1.52	-0.8725	-0.43625

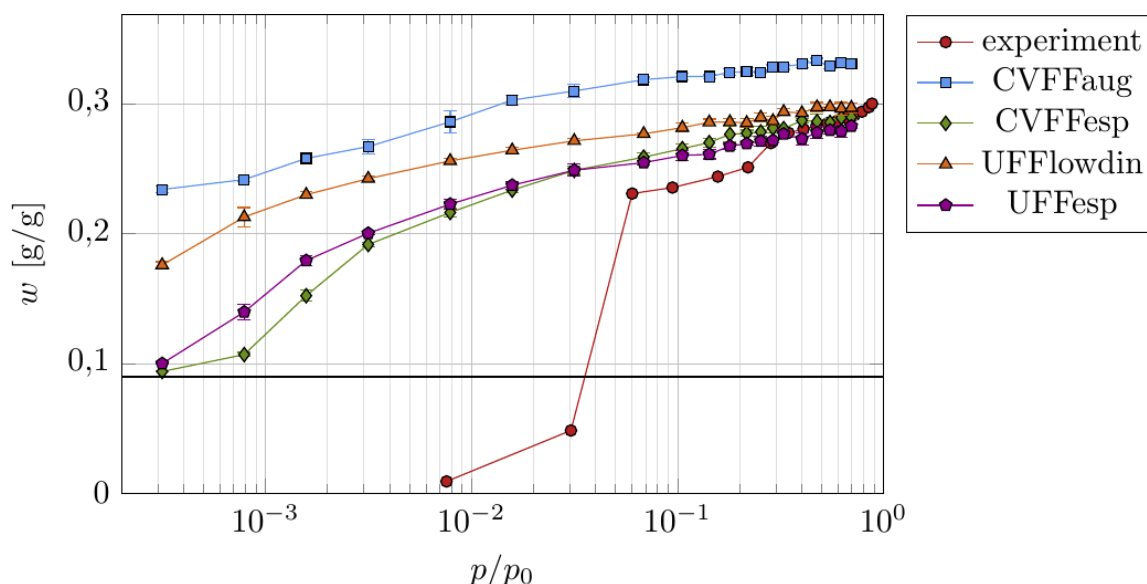


Figure 1. Water sorption isotherms in  $\text{AlPO}_4\text{-34}$ , simulated and experimental. The black line denotes the minimum loading attainable in a simulation because certain water molecules are kept fixed.

The CVFFaug force field results are taken as the baseline. Consistent with previous work<sup>[12]</sup>, this force field significantly overbinds water. We see that replacing the water model and using smaller charges improves the results. The ESP charges are the smallest by far, followed by Löwdin charges. Because of this, only these two sets of charges were considered for simulations. Results of the latter are shown in figure 1 and compared to experiment. Each isotherm is labelled with the name of the force field supplying the Lennard-Jones parameters (in capital letters) and the set of charges used. We see that even with the relatively small ESP charges, simulated adsorption is too strong; larger charges only make this worse. It can also be seen that the Lennard-Jones parameters do affect the results, but not as much as charges. For water sorption (unlike, for example, for  $\text{CO}_2$  sorption), charges are of paramount importance.

## CONCLUSION

I have described several methods of calculating effective point charges from ab-initio charge distribution and given their values for the AlPO<sub>4</sub>-34 framework. I have tested the performance of the most promising charges with Monte-Carlo molecular simulations. While the fixed framework approximation used in these simulations is too crude to give results comparable to experiment, it is evident that the charges used are very important and that, of all methods tested, electrostatic potential fitting yields charges that are the most appropriate for use in Grand-Canonical molecular simulations of adsorption. This makes sense since the point charges are supposed to model Coulombic interactions. However, it poses significant challenges for further development of aluminophosphate force fields: while it is clear that a force field describing aluminophosphate frameworks needs to include framework flexibility, the latter requires use of Born charges which are much larger than ESP charges. This may be addressed by a more complex model, e.g. a core-shell model, but such complexity has its costs and makes force field development much more difficult.

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