POINT CHARGE FITTING IN A TRICLINIC LATTICE

Jure Varlec
Kemijski inštitut, Hajdrihova 19, 1000 Ljubljana, Slovenia
E-mail: jure.varlec@ki.si

ABSTRACT

Point charges are often used in molecular simulations as part of the force field model of interatomic interactions and there are several ways of obtaining the values of such charges. Here, I present a method of calculating these charges from ab-initio calculations of charge density. Similar methods have been known for a long time and used on isolated molecules in vacuum. The approach presented here, instead, treats the material as fully periodic.

Keywords: Poisson equation, periodic electrostatics, point charge fitting

INTRODUCTION

Studying materials using molecular simulations requires a force field model for a particular material which describes forces between atoms. Usually, a force field consists of spring-like contributions to the total energy approximating covalent bonds, repulsive contributions approximating Pauli repulsion, contributions approximating dispersion, and contributions describing electrostatics. While functional forms of bonded and repulsive contributions vary a lot, dispersion and electrostatics most often use the energy terms of $-A/r^6$ and $q_1 q_2/r$, respectively, where r is interatomic distance, A is the dispersion parameter and q_1 and q_2 are effective point charges [1].

Obtaining force field parameters, such as A and q above, can be very difficult. A classical force field is a crude approximation of actual interatomic forces, and we must choose which properties of the material under study will be reproduced faithfully and which we care less about. Than we either obtain these properties experimentally or via ab-initio calculations and fit the force field parameters to these properties. Both the experimental and ab-initio route have their advantages and disadvantages and both are very time consuming. However, at least in the case of point charges, it seems at first that there should be a way to compute them from raw results of a single ab-initio calculation. After all, electron charge distribution is the very thing ab-initio calculations compute, everything else is derived from that.

There are two problems with this idea: there is no single way to assign a smooth charge distribution to some effective point charges, and there is in general no a-priori reason why such an assignment should be able to reproduce ab-initio molecular dynamics. The methods of assigning point charges can be divided into three classes: a) wave function methods which project the charge density on atomic orbitals (e.g. Mulliken or Löwdin charges [2]); b) geometric methods which partition the space into subvolumes for each atom (e.g. Voronoi or Bader charges [3]); c) methods which try to reproduce the electric field around molecules (e.g. Merz-Kollman charges [4]). The method described herein falls into the latter category, which offers the most hope of reproducing ab-initio molecular dynamics with a classical approximation.

METHODS

Fitting point charges to the electrostatic field calculated ab-initio is typically done for isolated systems in vacuum. When dealing with a crystal such as a zeolite, a representative part of the structure is extracted and analyzed in vacuum. In such a scenario, doing electrostatic calculations is easy, as the electrostatic potential at point $\vec{r}$ can be calculated simply as

$$\varphi(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \tag{1}$$

where ρ is the charge density. This is not true in a periodic system where it is well known that electrostatic sums are only conditionally convergent, requiring advanced methods of performing the summation. Moreover, if the unit cell is not cubic, we must account for a non-orthogonal coordinate system. One should also use different approaches for dealing with point charges or a smooth charge distribution. While all the methods are known, there is, to my knowledge, no existing software that would apply them to this problem.

Ab-initio calculations typically produce electronic charge density on a regular grid. To compute the resulting electrostatic potential, we solve the Poisson equation, defined as

$$\nabla^2\varphi(\vec{r}) = -\frac{\rho}{\varepsilon}, \tag{2}$$

on a three dimensional domain with periodic boundary conditions but a non-orthogonal coordinate system. Denoting the column-vector of Cartesian coordinates r and the column-vector of crystal coordinates f, the triclinic Laplacian operator is written as

$$\nabla^2\varphi(\boldsymbol{f}) = tr(\boldsymbol{M} \frac{\partial^2\varphi}{\partial f \partial f}), \tag{3}$$

where $\boldsymbol{M}$ is the metric tensor of the domain. We can now proceed with the well known Fast Fourier Transform based method of solving the Poisson equation, where we use the fact that the Fourier transform changes a linear differential equation into an algebraic equation.

This method, however, is ill-suited to computing the electrostatic potential of point charges, which means it can compute neither the ionic contribution to the electrostatic field nor the field of the point charge model. The closest thing to a point charge on a discrete grid is a parallelepiped-shaped charge distribution, which is not an adequate approximation, not least because the ions are rarely located exactly on grid points. If we really wanted to use a grid-based method, we could use one of several methods of charge smearing [5], which reduce aliasing artifacts but introduce other trade-offs, one of them being complexity of implementation. Instead, we chose to use a standard Ewald summation, which is routinely used for calculating the electrostatic energy of systems of point charges. Instead of calculating the energy, we adapt the method to compute the electrostatic potential, yielding

$$V\varphi(\vec{r}) = \sum_i \frac{q_i}{r} \text{erfc}(\alpha r) + \sum_{\vec{k}\neq 0} \sum_i \frac{4\pi q_i}{k^2} \exp[i\vec{k} \cdot (\vec{r} - \vec{r_j})] \exp(-k^2/4\,\alpha), \tag{4}$$

where Gaussian units are used, V is the volume of the unit cell and α is a parameter deciding how much of the sum is done in real space and how much in Fourier space [1].
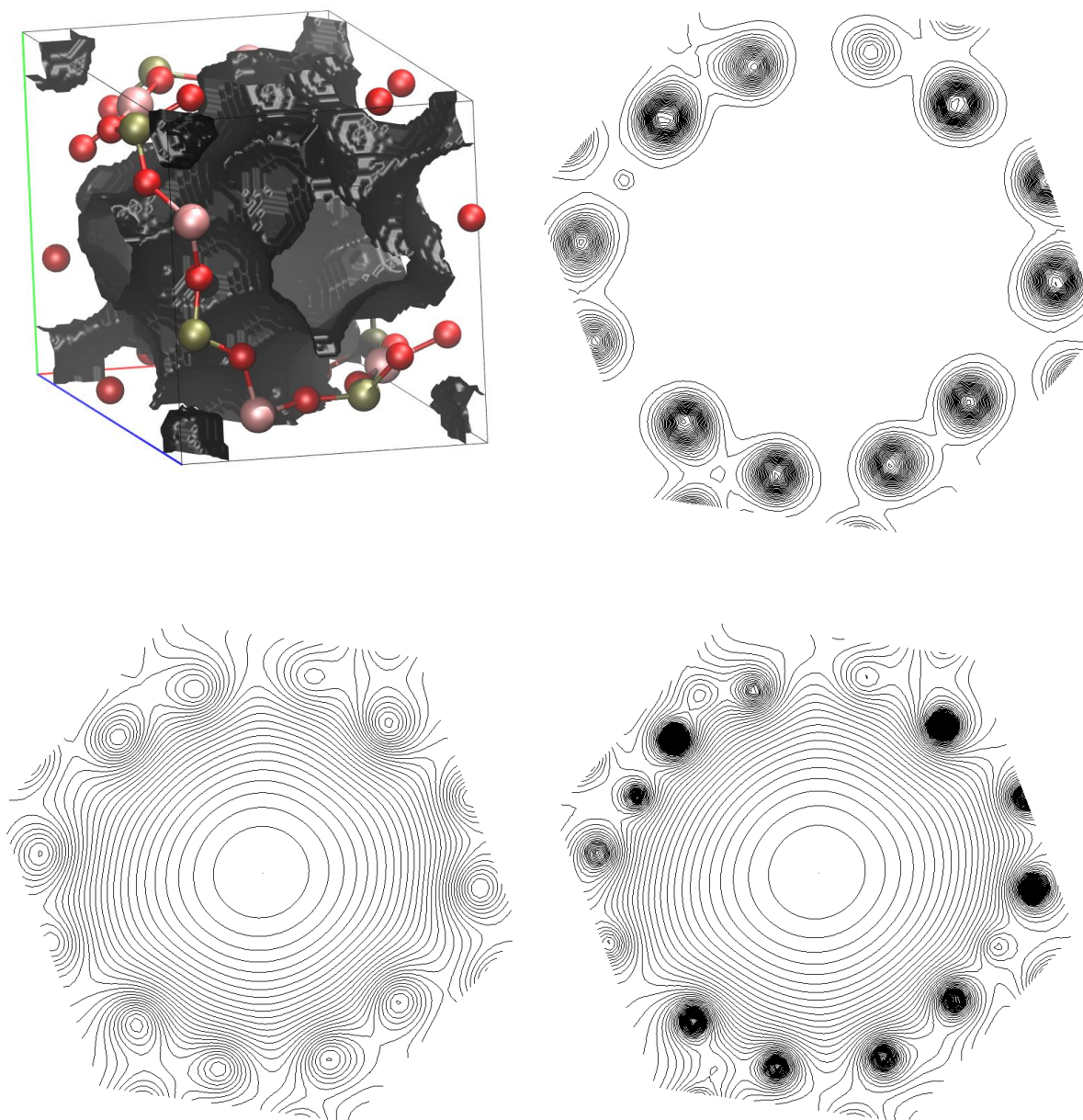

Figure 1. An example of AlPO$_4$-34. a) The unit cell of AlPO$_4$-34; the black volume represents the volume where test points can be inserted for the case of 2.0 Å exclusion zones around each atom. b) A slice through the AlPO$_4$-34 unit cell lying approximately in the plane of the ring. It shows the electronic charge density. c) The electrostatic potential produced by said charge density. d) The ionic potential. What we are trying to reproduce with a point charge model is the sum of (c) and (d).

Now that we are able to deal with both smooth and point charges, we may approach the problem of fitting a point charge model to the ab-initio potential. First, the electrons' potential is computed, to which we add the potential of the ions. The model's potential will be compared to this total potential in a fixed set of points in space, which we denote "test points". It is important that these points are not placed too close to the atoms: there is no way for the effective charge

model to reproduce the electrostatic field near a smooth charge cloud and trying to do so is meaningless. Kollman and Singh found [4] that the minimum reasonable distance from each atom is about 1.2 van der Walls radii. Next, we insert the point charge model. The locations of point charges need not coincide with locations of the ions; in fact, it may be beneficial to put more charges into the model than there are actual ions, as is the case with water [6]. The point charges of the model can then be fitted using the very effective Levenberg-Marquardt algorithm [7], noting that the number of degrees of freedom is one less than the number of charge species because we require that the total charge of the unit cell is zero.

CONCLUSION

I outlined a method of fitting effective point charges in a periodic lattice. The implementation is still under development, as there are many details to take care of, e.g. dealing with neutrality of the unit cell which is formally required and the fact that the electrostatic potential is only determined up to an additive constant. This method is expected to yield insights into suitability of point charges for modeling crystalline systems. It can also be extended to more complex models, such as point dipoles.

REFERENCES

[1] D. Frenkel, *Understanding molecular simulation: from algorithms to applications*, Academic Press, San Diego, 2nd ed., 2002.

[2] R. S. Mulliken, *The Journal of Chemical Physics*, 1955, **23**, 1833.

[3] W. Tang, E. Sanville and G. Henkelman, *Journal of Physics: Condensed Matter*, 2009, **21**, 084204.

[4] U. C. Singh and P. A. Kollman, *J. Comput. Chem.*, 1984, **5**, 129–145.

[5] T. Darden, D. York and L. Pedersen, *The Journal of Chemical Physics*, 1993, **98**, 10089–10092.

[6] B. Guillot, *Journal of Molecular Liquids*, 2002, **101**, 219–260.

[7] D. W. Marquardt, *Journal of the Society for Industrial & Applied Mathematics*, 1963, **11**, 431–441.