Semi-empirical atomic charges for use in computational chemistry of molecular sieves

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Abstract

Building on existing methods for the estimation of partial atomic charges by the use of semi-empirical density functional theory, we propose a method that is both reliable and computationally efficient when applied to solids. The modifications include the use of the s–p promotion energy for those elements where the range of charges found exceeds the boundaries of one particular valence subshell. In the case of Al, this is shown to work quite well. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Computational chemistry; Molecular sieve; Semi-empirical atomic charges

1. Introduction

Knowledge of the electronic properties of catalysts and reactants allows the catalytic scientist to develop an understanding of possible interactions between active surfaces and adsorbing and reacting molecules. Apart from the direct interactions of catalyst and substrates, understanding charge distributions can also assist in closely related fields like crystallization of inorganic solids, and the interpretation of spectroscopic analyses.

A large body of work has been devoted to describing the electronic properties of zeolites and catalysts after the initial steps in this direction by Mortier et al. [1]. These authors established a rigorous theoretical basis from electron density functional theory for the use of molecular electronegativity as a basis for charge calculations. They used their approach to derive charge distributions [2–4], the effect of atomic substitution [5], cation sitings [6–8], and reactivity estimates [9,10]. Mortier et al. built on the earlier work of Sanderson, Pauling, Parr, Mulliken and others. Rappé and Goddard [11] started from the same premise, and developed a very similar technique for charge equilibration.

Many others have designed empirical force fields for application in molecular mechanics or dynamics of zeolites and catalysts with or without substrates, that usually (but not always) involve

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electrostatic terms. Various approaches for estimation of charges have been applied. Some authors, e.g., Refs. [12,13,33], used fixed atomic charges based on the valences (i.e., $+3$ for aluminium, $+4$ for silicium, and -2 for oxygen). Others utilized fixed partial charges, e.g., Refs. [14–18]. Obviously, the most realistic way to use charges in molecular mechanics or dynamics calculations is to allow the electron distribution to vary according to geometric changes. This would imply the repeated calculation of charges during structure optimization, as is done for instance in the molecular mechanics codes developed at the Technical University of Delft [19–22].

The methods developed by Mortier, Rappé and Goddard provide the opportunity to do this in the context of parameterized molecular mechanics force field calculations. However, both methods have some drawbacks. In this work, we will present a refinement of the work of Mortier, Rappé and Goddard. The refined procedure is applicable to all elements in the periodic table, allows modeling of periodic structures and, above all, is designed for computational efficiency.

2. Atomic (point) charges

It is a common practice in molecular simulations to describe the interaction energy between two atoms A and B that are not connected through a chemical bond (non-bonded interaction) by an expression such as:

$$E_{AB}(R) = D_{AB}\, e^{-\frac{R_{AB}}{F_{AB}}} - \frac{C_{AB}}{R_{AB}^6} + \frac{Q_A Q_B}{4\pi\varepsilon_0\varepsilon R_{AB}} \tag{1}$$

in which the first term describes the short-range repulsion between two atoms when they are forced together (R_{AB} being the distance between A and B, D_{AB} and F_{AB} parameters) and the second term represents attraction (mutual polarization of electron clouds). The parameters in these first two terms can all be extracted from experiments on elements in their gaseous state (the first two terms constitute the Van der Waals interaction).

Unfortunately, the parameterization of the third term (the coulombic electrostatic interaction between the atoms in terms of a classical interaction between atomic charges) depends on the molecular structure and a method to reliably estimate or calculate these atomic charges given the molecular structure is a prerequisite for the computation of the electrostatic interaction between two atoms.

In view of their use in Eq. (1), the atomic charges are point charges assigned to the atomic positions in a molecule or solid and should be chosen such that the electrostatic potential around the molecule or within the solid is optimally reproduced.

Point charges could be taken from quantum mechanical calculations on the systems of interest. However, that would be self-defeating since the use of quantum mechanical calculations on large systems is precisely what is being avoided.

One way around this dilemma is to perform quantum mechanical calculations on small or medium-sized molecules that represent a part of the system that we are actually interested in, determine point charges on this molecule and use these in the actual system (assuming that they are transferable). Such procedures are indeed often followed in e.g., molecular modeling for drug design. However, for the particular applications that we are interested in, this method has some severe drawbacks.

For one thing, the transferability of the charges is somewhat questionable. There is no immediately apparent way to come up with a molecule that mimics, e.g., an infinite zeolite lattice. Any Si, Al and O containing cluster necessarily either has to be terminated (usually with a hydrogen), or has to be formally charged. Both approaches introduce effects that are not present in the zeolite which may lead to serious artifacts in the results. Although ingenious solutions have been proposed (e.g., the creation of a virtual type of hydrogen that mimics a silicate group), the problem has not yet been resolved.

Another disadvantage of charges determined from small molecular fragments is that, once assigned to the real system, they remain fixed throughout the simulation, thus introducing further uncertainties in the results of the simulation. In the real system, the electron density will follow changes in the geometry or the mutual location of molecules or a molecule and a lattice. The assignment of fixed charges, of course, prevents this real effect from happening in the simulation. Partly, it is recovered by using a dielectric constant (ε in Eq. (1)) larger than unity (the value for the vacuum), but the redemption is far from satisfactory.

3. Semi-empirical density functional theory

In recent years, many semi-empirical schemes, used to calculate atomic charges based on the empirical quantities of hardness and electronegativity, have been proposed. These quantities appear in the expansion of the energy of an isolated atom as a function of the charge on that atom:

$$E(Q) = E(0) + \chi Q + \eta Q^2 \tag{2}$$

It is usually tacitly assumed that Eq. (2) is approximately valid for moderate charges, Q. However, it can actually be demonstrated that Eq. (2) is the proper functional form.

Slater [23] has shown that the total energy of any system is a nearly quadratic function of the occupancy of an orbital or a subshell. Therefore, as long as the fractional charge corresponds to addition or removal of electronic charge from one particular valence subshell of the atom, we need not question the approximate validity of Eq. (2). However, whenever subshell boundaries are transgressed, it is expected to break down. This issue shall be discussed later.

The electronegativity χ and hardness η can be determined as follows. Consider the Ionization Energy and Electron Affinity (IE and EA) of an atom. According to Eq. (2) they are given by:

$$IE = E(+1) - E(0) = \chi + \eta \tag{3}$$

and

$$EA = E(0) - E(-1) = \chi - \eta, \tag{4}$$

respectively; hence,

$$\chi = \frac{(IE + EA)}{2}; \eta = \frac{(IE - EA)}{2} \tag{5}$$

With these relationships, the atomic electronegativity and hardness can be determined from the atomic spectra.

One could conceive of a scheme in which atomic charges in a molecule would be determined by minimizing the total energy defined as the sum of all atomic energies. In fact, such a scheme has been

published. However, it does not properly account for molecular topology. Any scheme which does, should at least include the coulombic interaction between charged atoms, i.e., the energy of a system of N atoms should be written in a series of mono- and diatomic terms:

$$E(Q_1, \ldots, Q_N) = \sum_A \left(E_A^0 + \chi_A Q_A + \eta_A Q_A^2 + \sum_{B < A} J_{AB} Q_A Q_B \right) \tag{6}$$

As yet unspecified, J_{AB} is the parameter that describes the interaction between a unit of charge on atom A and a unit of charge on atom B. This parameter will be dependent on the nature of A and B and their distance. Note that we only use the nuclear positions of the atom. The bond topology is not taken into account.

We now demand the energy to be minimal or, rather, to be stable to small variations in charge. As we require the total charge to be a constant, this implies that the energy is invariant to small charge transfer between atoms. We define the effective electronegativity of atom A (within the given system of N atoms) as:

$$\chi_A^{eff} = \frac{\partial E}{\partial Q_A}(Q_1, \ldots, Q_N) = \chi_A + 2\eta_A Q_A + \sum_{B < A} J_{AB} Q_B \tag{7}$$

and require the effective electronegativities of all atoms to be the same, under the constraint that the total charge is equal to some given value (usually 0, but not necessarily so); for a system of N atoms, this leads to a system of $(N + 1)$ equations given in matrix form by:

$$HQ = X \tag{8}$$

with

$$\forall i, j \leq N, i \neq j : H_{ii} = 2\eta_i \quad H_{ij} = J_{ij} \quad H_{i(N+1)} = 1 \quad H_{(N+1)i} = 1$$

$$H_{(N+1)(N+1)} = 0$$

$$\forall i \leq N: X_i = \chi_i \quad X_{N+1} = Q_{tot} \tag{9}$$

Q_{tot} being the total charge given to the system. After solving the equations, the solution vector Q will contain the computed charges (the first N elements) and the negative of the effective electronegativity of the molecule, to which all atomic effective energies are equal (the Lagrangian multiplier contained in element $N + 1$).

Often, instead of conserving only the total charge on the system, it is desirable to constrain the charge on several groups of atoms (i.e., several molecules, or a molecule and a crystal lattice), that are not expected to exchange charge. In that case we will need to solve $N + M$ equations (M being the number of groups of atoms for which to conserve the charge). The extension, however, is a straightforward one and will not be discussed.

This scheme has been implemented in several ways, most notably by Mortier, who called it the EEM (electronegativity equalization method) [1] and Rappé and Goddard, who dubbed their implementation the charge equilibration (QEq) method [11]. Since these methods served as a starting point for our investigations, we will briefly discuss them below.

4. The EEM method

Mortier set out to demonstrate that Eq. (6) can be derived from formal density functional theory, thereby providing a more rigorous theoretical justification than mere intuitive reasoning [1]. He did

not choose to determine χ and η from experimental data using Eq. (5), but instead treated χ and η as optimizable parameters by determining values that brought the calculated charges as close as possible to quantum mechanically calculated charges. For the electrostatic repulsion between atoms, he chose to use the inverse of the interatomic distance (eschewing conversion constants):

$$J_{AB} = \frac{1}{R_{AB}} \tag{10}$$

In order to obtain meaningful results, two types of hydrogen had to be defined—positive hydrogen (protons) and negative hydrogen (for hydrides).

The choice of quantum mechanical charges, to which fitting has been done, is, of course, arbitrary. In this case, these were Mulliken charges calculated by the STO-3G Hartree–Fock method. Mulliken charges are based on a partitioning of the Hartree–Fock density matrix and, as such, do not necessarily represent the electrostatic potential in the optimal way. Furthermore, STO-3G is the smallest possible basis set in a Hartree–Fock calculation that will give reasonable results. Fortunately, in this case, these two sources of error compensate to some degree, as the lack of freedom of expansion caused by the limitations of STO-3G generally yields Mulliken charges closer to partial charges found by fitting the electrostatic potential. Furthermore, although full electrostatic potentials are rarely published, it is noteworthy that STO-3G tends to yield dipole moments quite close to the experiment [24] (the dipole being the first term in the multipole expansion of the electrostatic potential).

However, the choice of quantum mechanical charges is not essential to the EEM method, and can easily be remedied by parameter estimation of χ and η with reference to a set of charges of better quality.

A more fundamental objection to the EEM scheme is the use of Eq. (10). Equating the interatomic repulsion to the inverse of the interatomic distance may appear to be consistent with Eq. (1), where the interaction of one atom with the electric field of the other also scales with the inverse of the interatomic distance. But, with non-bonded interactions, we are dealing with interatomic distances equal to, or exceeding, the sum of the Van der Waals radii of the two atoms involved. However, in employing the EEM scheme, we are also dealing with interactions between atoms at bonding distances. In expressing the interatomic interaction J_{AB}, we have to account for the fact that the charge of an atom actually has a diffuse character, and as R_{AB} approaches zero, J_{AB} will approach some finite value.

Hence, although we do not question the fundamental validity of the approach of Mortier, some modifications to the theory appear to be necessary.

5. The value of the dielectric constant

A criticism that is often addressed to the EEM method (and automatically reflects on similar methods) is the tacit assumption that the dielectric constant is equal to one, i.e., the value in vacuo. This assumption is particularly challenged when the method is used in condensed phases. We feel that this criticism is largely unfounded for the following reasons.

The dielectric constant describes the reaction of a molecular assembly or a solid to an electric field. It consists of two contributions:
· the polarization of electron clouds, which is instantaneous compared to typical time scales for nuclear movement; and

- nuclear rearrangement to accommodate the electric field (e.g., alignment of dipolar molecules in a liquid).

For the purposes of this discussion, the second contribution is not important. This type of polarization is expressed in molecular simulations. In as far as the computed charges are influenced by it, this can be taken care of in the proper manner by, e.g., doing a recalculation of the charges every so many steps in a molecular dynamics simulation.

The polarization of electron clouds is the contribution that we need to focus on. Since relocation of charge is what the semi-empirical density functional methods are all about, we may assume that the *molecular* contribution of charge polarization is well included in the method. However, since the atomic charge cloud is reduced to a point charge, typical atomic contributions are typically neglected. These atomic contributions can be thought of as distortions to the spherical nature of the charge distributions in free atoms. Neglect of the non-spherical deviations in the atomic charge clouds, however, is consistent with the neglect of chemical bonding in the current schemes.

Note that it is even possible to calculate the polarizability of a molecule or a solid by incorporating the interactions between the atomic charges and an externally applied electric field in Eq. (6) in a trivial manner.

In conclusion, there is no theoretical justification to include the dielectric constant in semi-empirical density functional methods. For practical reasons, one might choose to do so in calculations on solids, but the optimal value is expected to deviate only slightly from unity.

6. The QEq method

Rappé and Goddard also set out from Eq. (6) as their point of departure [11]. They recognized the invalidity of using Eq. (10) and proposed to calculate J_{AB} in the following manner: the charge is assumed to be due to electrons taken from, or put into valence atomic orbitals ϕ, with a charge distribution $\phi\phi*$, J_{AB} is then given by an integral:

$$J_{AB} = \iiiint\!\!\iint \frac{\phi_A(1)\phi_A^*(1)\phi_B(2)\phi_B^*(2)}{\sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}}\, dx_1 dy_1 dz_1 dx_2 dy_2 dz_2 \tag{11}$$

over all space ((1) and (2) refer to the coordinates of electrons 1 and 2, respectively). The integral looks rather unappealing, but can be evaluated analytically if we choose the so-called Slater functions as atomic orbitals:

$$\phi_A = N(n, \zeta_A) r_A^{n-1} e^{-\zeta_A r_A} \tag{12}$$

in which r_A is the distance of the electron from the nucleus of atom A, ζ_A is the orbital coefficient typical for atom A (see below), n is the main quantum number for the valence shell of atom A, and $N(n, \zeta_A)$ is the normalization factor.

The orbital coefficient ζ_A determines the spatial extension of charge and is therefore related to the average covalent radius R_A by

$$\zeta_A = \frac{\lambda(2n + 1)}{(2R_A)} \tag{13}$$

where λ was determined to be 0.4913 by fitting the charges calculated for alkali halides to the experimental ones (determined from the molecular dipole moments).

In the QEq scheme there is no fitting of χ and η—these are taken from atomic spectroscopy data. The only exception is hydrogen, where the authors, like Mortier, recognized the difficulty in

describing hydrogen as a negative and as a positive atom with the same set of parameters, but came up with a different answer. Rather than identify different types of H, they made both the orbital exponent ζ and the hardness parameter η for each separate hydrogen atom depend on the charge on that hydrogen:

$$\zeta_i(Q_i) = \zeta_H^0 + Q_i \tag{13a}$$

$$\eta_i(Q_i) = (1 + Q_i)\eta_H^0 \tag{14}$$

Obviously, Eqs. (13) and (14) require that we know the charges in order to calculate them. Hence, we have to solve the equations iteratively starting with an initial guess for all the charges to calculate η and ζ values, calculate new charges, etc., until the procedure becomes self-consistent.

With these modifications, charges obtained are, generally, in good agreement with charges fitted to good quantum mechanical calculations or to electric moments of small molecules. Nevertheless, application of the QEq method still poses some problems.

A practical problem is that although Eq. (11) is certainly an improvement from Eq. (10), it also represents a significant increase in computer time. In addition, if we want to apply periodic boundary conditions (which we need to do in modeling molecular sieves), the extension is far from trivial and will result in a scheme for which the computation time is out of proportion to its essential simplicity.

A further problem is that one finds that the scheme does not behave properly for some elements, including Aluminum. For these elements, charges found far exceed the number of valence electrons on the free atom. The originators of the QEq method recognized this, but their solution was to artificially constrain the charge to the values set by the number of valence electrons (i.e., for Al: $-5 \leq Q_{Al} \leq +3$). Although that excludes results that are physically meaningless, a consistent charge of $+3$ on Al is still an unacceptable answer, particularly in the area of molecular sieves. Here, the effects of Aluminum substitution into a zeolite framework, or the electrostatic potential within an aluminum phosphate, are precisely the kind of problems we will want to tackle with a scheme such as this. For these applications, it is essential to remedy the scheme in such a fashion that Al (and similar cases) are treated on equal footing with elements for which the method does appear to be successful.

Wishing to retain the rigorous basis and computational efficiency of the EEM method, as well as the use of fully experimental data (to avoid a major effort in parameter estimation) and general quality of the QEq scheme, we have devised, and will describe in the following paragraphs, solutions to the major objections given above to the QEq method:

· the expensive evaluation of molecular integrals: An empirical coulombic interaction function;
· the fact that the QEq method is not suited for extension to periodic boundary conditions: Periodic boundary conditions; and
· the fact that the QEq method utterly fails to predict reasonable charges for some elements, including the very important element Al: Involvement of lower subshells.

7. An empirical coulombic interaction function

In finding a proper functional for J_{AB} as a function of R_{AB}, we obviously want to retain as much of Eq. (11) as possible without the expenditure of computer time necessary for a full calculation between all pairs of atoms. There are two more or less obvious constraints to this functional form.

· At a very long distance, it should behave as Eq. (10) (as, indeed, does Eq. (11)), since at very long distances, the spatial extension of the charge clouds on A and B becomes negligible compared to the distance between them—to all practical purposes they do interact as point charges.

· As R_{AB} approaches zero, so should J_{AB} approach the value of Eq. (11) for $R_{AB} = 0$; we will denote this (finite) value by γ_{AB} (this value may not be very meaningful from a physical or chemical point of view as it requires atoms A and B to coincide, but the value makes perfect mathematical sense and there is no objection to using it as a parameter as we will do below). The value γ_{AB} is easier to calculate than values of Eq. (11) for $R_{AB} > 0$.

The problem of finding a proper functional form is, fortunately, not a completely new one. In fact, it has received attention in the area of semi-empirical molecular orbital methods which was so popular two decades ago. A prescription for an approximate J_{AB} that satisfies the two criteria set out above was given by Nishimoto and Mataga [25]:

$$J_{AB}^{NM} = \frac{1}{\dfrac{1}{\gamma_{AB}} + R_{AB}} \tag{15}$$

and another one by Ohno [26]:

$$J_{AB}^{Ohno} = \frac{1}{\sqrt{\dfrac{1}{\gamma_{AB}^2} + R_{AB}^2}} \tag{16}$$

We have plotted these functions, together with Eqs. (10) and (11), in Fig. 1 for a representative combination of elements, Al and O. It is obvious that the Ohno prescription is closer to Eq. (11) than
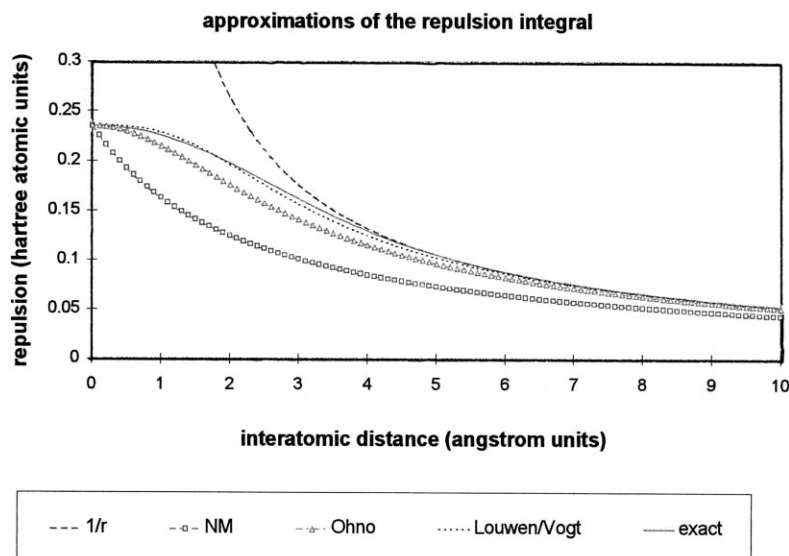

Fig. 1. Coulombic repulsion between electrons on an Al and an O atom as a function of interatomic distance (distance in Å, repulsion in Hartree units).

that of Nishimoto and Mataga, but still does not give a proper fit to the computed integral function. An analysis of why the Ohno prescription works better shows that the introduction of the second power (followed by taking the root) tends to make the curve more conservative, remaining closer to the value of γ_{AB} for small interatomic distance, and conforming more to point charge repulsion on the large R end. As the computed curve appears to be still more conservative, we have further increased the power to 3 with the striking result (see Fig. 1) that Eqs. (17) and (11) give almost similar results. This is true for a wide range of combinations of elements.

$$J_{AB}^{emp} = \frac{1}{3\sqrt{\dfrac{1}{\gamma_{AB}^3} + R_{AB}^3}} \tag{17}$$

The empirical repulsion between centers A and B given by Eq. (17) satisfies both our criteria and will further be used. To keep the scheme as computationally efficient as possible, the parameter γ_{AB} is calculated only once for each unique pair of elements (in this case, each H counting for one element because of Eqs. (13) and (14)).

Since Eqs. (15)–(17) are all really the same expression with a parameter power that takes on the values 1, 2 and 3, respectively, one might ask whether 3 is really the optimal value for power. It is not; the optimal value is about 2.7.

However, the improvement in the fit in going from 3 to 2.7 is marginal, and the expression would be much more expensive, in terms of computer time, to evaluate. The reason for this is that while raising to an integer power can be done by successive multiplications, non-integer powers require the calculation of a logarithm followed by calculation of the exponent function. We feel such expenditure of computer time to be unwarranted in view of the already excellent match between Eqs. (17) and (11).

8. Periodic boundary conditions

What remains is the question of how to extend the scheme to periodical boundary conditions. Here, we have chosen to use the so-called taper function method which allows us to fully exploit the empirical function for the coulomb interaction described above. The principle behind the taper function is the following.

In a fully periodic crystal we only need to treat the atoms in the unit cell. For a unit cell with N atoms we can rewrite Eq. (17) as:

$$\chi_A^{eff} = \frac{\partial E}{\partial Q_A}(Q_1, \ldots, Q_N) = \chi_A + 2\eta_A Q_A + \sum_{B < A} J_{AB} Q_B + \sum_{cells} \sum_{B' \in cell} J_{AB'} Q_{B'} \tag{18}$$

In which 'cells' denote all translated copies of the unit cell, the charges $Q_{B'}$ are copies of charges Q_B in the unit cell. Since all cells are uncharged, the total electrostatic potential due to all atoms in a cell will decrease with the distance of this cell to the unit (reference) cell (as the atoms in the cell become very close together relative to the cell–cell distance). This suggests neglecting interactions beyond a certain distance. The question is how to implement this. Rigorous cutoffs applied to atom–atom distances are to be avoided as they will introduce discontinuities (even though a cell is

uncharged, it does not mean that the charge is evenly distributed throughout the cell; a rigorous cutoff therefore could easily make an effectively charged cell from an uncharged one). We might conceive of neglecting all cells of which no atom falls within the cutoff radius, but there is still some discontinuity inherent in this. It has been demonstrated [22], that the following approach works well: determine two radii R_b and R_e ($R_b < R_e$). All interatomic interactions for $R < R_b$ (R being the distance between the two atoms) are fully taken into account. For $R > R_e$, all interactions are neglected. For intermediate R, the interaction is multiplied by a function $T(R)$ defined by:

$$T(R_b) = 1; T(R_e) = 0; \frac{dT(R_b)}{dR} = \frac{dT(R_e)}{dR} = \frac{d^2T(R_b)}{dR^2} = \frac{d^2T(R_e)}{dR^2} = 0 \tag{19}$$

If, in keeping with the above, we further define:

$$0 \le R < R_b \quad T(R) = 1; \ R > R_e \quad T(R) = 0 \tag{20}$$

we obtain a function that is continuous and has continuous first and second derivatives (a quality desirable for a number of applications) and satisfies the criteria outlined above. One such function is given in [22] and has been programmed in this form. Using this function T we can now rewrite Eq. (18) into:

$$\chi_A^{eff} = \frac{\partial E}{\partial Q_A}(Q_1, \ldots, Q_N) = \chi_A + 2\eta_A Q_A + \sum_{B < A} T(R_{AB}) J_{AB}^{emp} Q_B + \sum_{cells} \sum_{B' \in cell} T(R_{AB'}) J_{AB'}^{emp} Q_{B'} \tag{21}$$

and reduce the case of crystalline solids to one that can be treated in the same manner as a molecule, as only a finite number of atom pairs has to be dealt with.

We can demonstrate the general validity of the taper method by comparing charges calculated with the EEM scheme with quantum-mechanically derived charges. For this purpose, we will use two different implementations of Mortier's EEM scheme. We need to use the EEM scheme rather than the QEq scheme, because the QM charges available are Mulliken charges. We will compare the charges calculated for the zeolite chabazite. Quantum mechanical charges were calculated using the Crystal 88 program, which allows QM calculations in periodic systems. The charges were made available to us by E. Theunissen of the University of Eindhoven [27]. The chabazite structure as used by Theunissen has a silicon to aluminum ratio of 3. The structure as used is listed in Table 1.

The structure was not energy minimized, since Crystal 88 does not have that capability. However, for the transferability issue, that does not really matter. Charges were calculated using the EEM scheme using the implementation as present in the Delphi Molecular modeling program, as described by de Vos Burghart, which is a straightforward implementation of EEM. We have calculated the charges both using the standard dielectric constant used in Delphi, and with a dielectric constant of unity, which should render the normal EEM charges. As a third calculation, we implemented a taper function in our own version of EEM (Table 2).

It is obvious that there is an extremely good correlation between the EEM standard and the EEM technique applied with a taper function. This correlation demonstrates that there is no fundamental difference in accuracy between a taper function which we used and the Bertaut–Ewald summation used by Mortier for the description of long range effects. There is also a very good correlation

Table 1

Space group and unique atom coordinates of the chabazite structure used in Ref. [27] as well as in this paper for calculations of the atomic charges

Chabazite (CHA),
spacegroup $R3$ (146),
$a = b = c = 9.38871$ Å,
$\alpha = \beta = \gamma = 94.16275°$

Atom	X	Y	Z
O1	0.302	0.011	0.008
O2	0.898	0.240	0.249
O3	0.004	0.266	0.730
O4	0.688	0.976	0.985
O5	0.495	0.864	0.145
O6	0.492	0.161	0.865
O7	0.126	0.739	0.751
O8	0.276	0.016	0.735
H	0.017	0.654	0.340
Al	0.331	0.871	0.096
Si1	0.118	0.890	0.665
Si2	0.125	0.666	0.896
Si3	0.890	0.335	0.118

between the charges predicted by EEM in general and the charges calculated with Crystal 88. This indicates that the EEM-formalism can be transferred to periodic systems without any problem. The slight numerical difference between the values in the last two columns and the values derived by Crystal might be taken as an indication that a small correction such as assuming a dielectric constant of 1.15 would be required to get absolute matches. Such a small correction of the dielectric constant is more physically meaningful than the dielectric constant of 6.2 used by de Vos Burghart et al. However, we should remember that physical reality of the dielectric constant is not what these authors wanted to achieve. Rather, they used the dielectric constant as one of a set of adjustable parameters to reproduce zeolite structures.

Table 2

Chabazite atomic charges as reported in Ref. [27] (first column), in the EEM method with a dielectric constant suitable to the type of material (second column), with a dielectric constant of unity (third column) and with a dielectric constant of unity and employing the taper function method for convergence of the lattice sum (last column)

Atom	Crystal 88	EEM Delphi	EEM standard	EEM taper
O1	−0.738	−0.185	−0.870	−0.873
O2	−0.729	−0.183	−0.836	−0.836
O3	−0.721	−0.184	−0.828	−0.828
O4	−0.762	−0.192	−0.827	−0.829
O5	−0.724	−0.183	−0.821	−0.821
O6	−0.749	−0.190	−0.803	−0.802
O7	−0.745	−0.190	−0.788	−0.788
O8	−0.534	−0.187	−0.751	−0.752
H	+0.213	+0.022	+0.166	+0.168
Al	+1.213	+0.511	+1.372	+1.372
Si1	+1.388	+0.319	+1.639	+1.641
Si2	+1.443	+0.320	+1.664	+1.665
Si3	+1.444	+0.323	+1.683	+1.684

Thus, we have presented proof that the EEM formalism can be transferred to periodic systems, and we have presented evidence that a taper function is as useful as the Bertaut–Ewald formalism to describe long range effects.

Note that the taper method can also be used without modifications in less regular solids or at surfaces, this in contrast to the Ewald method.

9. Involvement of lower subshells

We now turn to the question of why some elements, most importantly Al, behave so poorly in the present scheme. The problem with Al is that the outermost valence subshell (3p) contains only one electron and has both a rather low electronegativity as well as a rather small hardness. The result is that the p electron is easily extracted (which is correct). However, electrons beyond the first valence subshell are assumed to be governed by the parameters valid for 3p. This is quite incorrect, as the 3s subshell will be far more electronegative than 3p. Thus, we are faced with the problem of how to remedy this defect without affecting the generality of the scheme. We have found the following approach to work rather well.

As explained above, the QEq method assumes all charges as having been taken from (or put into) the 3p subshell. That is not necessarily incorrect, even beyond a charge of $+1$ (for Al), if we account for the fact that the charge has to be taken from the 3s subshell and put into the 3p subshell first.

Assume two electronegativities χ_s and χ_p for the s and p subshells respectively. We further assume that for all positive charges, all electrons have been taken from the 3p subshell. A charge larger than $+1$ necessarily implies that additional (fractional) electrons have been taken from the 3s subshell. Per electron, we can now define the average electronegativity, dependent upon the charge:

$$\chi_{av}(Q) = \frac{\chi_p + (Q-1)\chi_s}{Q} = \chi_p + \left(1 - \frac{1}{Q}\right)(\chi_s - \chi_p) \ (1 \leq 3) \tag{22}$$

χ_p is of course the atomic electronegativity of the original scheme; the quantity $(\chi_s - \chi_p)$ is closely related to the difference in orbital energy between the 3s and 3p orbitals of Al at positive charges close to $1+$. We have, therefore, set this value to the transition energy for the Al$+$ ion: $3s^2 3p^0$ to $3s^1 3p^1$, basically the excitation energy of an electron from the 3s to a 3p orbital (or rather a multiplet of such orbitals). Henceforth, χ_{av} replaces χ_p as the parameter to be used in Eq. (21).

The introduction of a charge-dependent electronegativity hardly complicates the scheme, since Eqs. (13) and (14) already necessitated an iterative solution, in cases where H is present. Admittedly, no iterations were necessary in systems without hydrogen (e.g., zeolites with counterions other than protons), but note that while because of Eqs. (13) and (14) the matrix **H** has to be updated in Eq. (8) (by far the most time-consuming part in large molecules and particularly in crystals), Eq. (22) only requires an update of the X vector, at negligible computational cost.

Although for obvious reasons we have discussed the case of Al, a general implementation is straightforward. It requires us to know for each atom, the amount of electrons in its partially filled valence subshell (when applicable) and the energetic difference with the next lowest valence subshell (when present). The first parameter can be taken from the periodic table, the second from known experimental data.

10. Summary: a novel method for the semi-empirical determination of charges

We propose a novel method for the semi-empirical computation of atomic point charges. The method is defined as follows:
- Its basis is the QEq method;
- Instead of computed coulomb integrals, we use the empirical coulomb function;
- Periodic boundary conditions are introduced by the expedient of a Taper function that effectively reduces the solid to a large cluster;
- For elements like Al, where the computed positive charge is larger than the content or the negative charge is larger (in absolute sense) than the balance of the valence subshell, the promotion energy is introduced (as in Eq. (22)).

For an evaluation of the current method in comparison to the existing QEq scheme, we refer to Table 3.

In this table, we report atomic point charge calculations on some small molecules. Here, the Best available Value was either obtained from electrostatic potential fitting with very accurate quantum mechanical results (using procedures such as described above) or from experimental data (dipole and quadrupole moments). These values were used in the original evaluation of the QEq method [11].

As we can see, our modifications to the QEq method, while making it much more computationally efficient, have not detracted from the generally fair agreement with the Best Values.

Table 3

Atomic charges for some small molecules computed by the published QEq method [11] as well as by our modified method compared with values derived from fitting the electrostatic potential obtained by high-quality quantum mechanical calculations or derived from experiment (i.e., a dipole moment in the case of a diatomic molecule)

Water	This work	H(0.38) O(-0.76)
	Qeq [11]	H(0.36) O(-0.72)
	Best value [11]	H(0.33) O(-0.66)
Ammonia	This work	H(0.27) N(-0.81)
	Qeq [11]	H(0.25) N(-0.75)
	Best value [11]	H(0.27) N(-0.81)
CO_2	This work	C(0.96) O(-0.48)
	Qeq [11]	C(0.86) O(-0.43)
	Best value [11]	C(0.66) O(-0.33)
Formaldehyde	This work	C(0.06) H(0.18) O(-0.42)
	Qeq [11]	C(0.14) H(0.14) O(-0.42)
	Best value [11]	C(0.19) H(0.13) O(-0.45)
Formic acid	This work	C(0.64) H(0.13/0.40) O($-0.70/-0.47$)
	Qeq [11]	C(0.92) H(0.11/0.55) O($-1.08/-0.51$)
	Best value [11]	C(0.78) H(0.03/0.46) O($-0.67/-0.60$)
Formamide	This work	C(0.47) N(-0.73) O(-0.44)
	Qeq [11]	C(0.32) N(-0.63) O(-0.41)
	Best value [11]	C(0.48) N(-0.89) O(-0.28)
Methanol	This work	C(-0.12) O(-0.66) H(0.36/0.18/0.12)
	Qeq [11]	C(-0.18) O(-0.66) H(0.36/0.20/0.14)
	Best value [11]	C(0.21) O(-0.63) H(0.39/0.04/0.04)
Methyl cyanide	This work	H(0.16) C($-0.48/0.26$) N(-0.27)
	Qeq [11]	H(0.13) C($-0.35/0.18$) N(-0.23)
	Best value [11]	H(0.13) C($-0.43/0.43$) N(-0.39)
HCl	This work	H(0.32) Cl(-0.32)
	Qeq [11]	H(0.31) Cl(-0.31)
	Best value [11]	H(0.25) Cl(-0.25)

Table 4
Point charges on aluminum atoms in clusters calculated with density functional theory [28–32], the scheme proposed in this work, and QEq, as described in Ref. [11]

Cluster	DFT	Proposed scheme	Qeq
AlH_3	1.20	1.20	3.00
$(H_2O)Al(OH)_3$	1.52	1.50	3.00

To assess the validity of our approach for Al, we have performed ADF [28–30] calculations on AlH_3 and $(H_2O)Al(OH)_3$ employing the Vosko–Wilk–Nusair local density functional corrected for self-interaction [31,32] and performed a charge fitting to the electrostatic potential. The agreement turns out to be surprisingly good (Table 4).

We can therefore conclude that our method is certainly, at least, as successful as earlier schemes, but offers several additional advantages.

Since we have presented proofs on the general transferability of the formalism to periodic systems, we are convinced that the treatment of zeolites and zeolite-reactant interactions can be modeled successfully using the proposed scheme.

11. Limitations of the method

Despite the apparent success of the current method, there are limitations. The calculations are many orders of magnitude less demanding of computer time than even quite approximate quantum mechanical methods. One cannot realistically expect this to be achieved without some sacrifices. All schemes that are based upon Eq. (5) ultimately neglect chemical bonding. It is true that the interatomic distances are taken into account, but there is no information on the specifics of the interaction within any pair of atoms. As a rule of thumb, one, therefore, needs to be most careful when dealing with a system where the mode of chemical bonding deviates from that normally found for the elements involved. Thus, the scheme will predict quite reasonable charges for a molecule like carbon dioxide, where C has four and each O has two bonds, but fail to come up with proper charges for carbon monoxide (the charges on C and O being calculated as 0.47 and -0.47, respectively, in conflict with experiment where the values of -0.1 and 0.1, respectively are not only of different magnitudes but of different signs as well).

The recommended procedure for application of the QEq method, therefore, is to supplement it by occasional quantum mechanical calculations plus charge fitting on systems where the method has not yet been proven reliable by systems of similar composition. Thus, one avoids too much extrapolation but retains the possibility to calculate through many large systems in only a small amount of computer time.

Acknowledgements

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