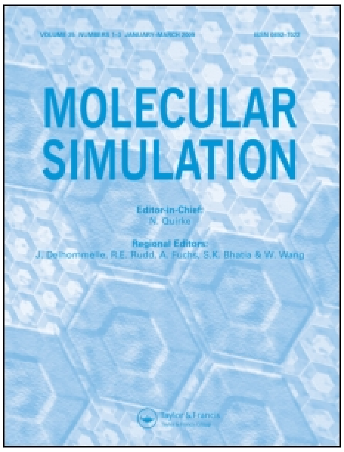
This article was downloaded by:
On: *14 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

New potential model for molecular dynamic simulation of liquid HF. I—Parameter optimization for charge equilibration method

E. Bourasseau[a]; J. -B. Maillet[a]; L. Mondelain[a]; P. -M. Anglade[a]
[a] Département de Physique Théorique et Appliquée, Commissariat à l'Enegie Atomique, bruyères-le-châ, France

To cite this Article Bourasseau, E. , Maillet, J. -B. , Mondelain, L. and Anglade, P. -M.(2005) 'New potential model for molecular dynamic simulation of liquid HF. I—Parameter optimization for charge equilibration method', Molecular Simulation, 31: 10, 705 — 713

To link to this Article: DOI: 10.1080/08927020500231817

URL: http://dx.doi.org/10.1080/08927020500231817

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular Simulation, Vol. 31, No. 10, August 2005, 705–713

New potential model for molecular dynamic simulation of liquid HF. I—Parameter optimization for charge equilibration method

E. BOURASSEAU*, J.-B. MAILLET, L. MONDELAIN and P.-M. ANGLADE

Département de Physique Théorique et Appliquée, Commissariat à l'Enegie Atomique, BP12, 91680 Bruyères-le-Châtel, France

(Received February 2005; in final form February 2005)

In order to build a complete potential model to perform classical molecular dynamic simulations of liquid HF, a new optimization method is proposed to obtain transferable parameters for charge equilibration method on the basis of *ab initio* reference data. The optimized parameters (the electronegativity χ and the Slater orbital exponent ζ for H and F atoms) appear to be able to reproduce the variations of the electrostatic potential calculated from an *ab initio* method in a liquid phase of HF molecules for different thermodynamic conditions. It is concluded that the proposed method is general, precise and efficient to obtain transferable and realistic parameters.

Keywords: Parameter optimization; Fluctuating charges; Charge equilibration method; Electrostatic potential

Downloaded At: 18:20 14 January 2011

1. Introduction

The main reason why molecular simulation is not yet a routine way to obtain thermodynamic properties of compounds used in industrial processes is the fact that potential parameters are not transferable enough to be used directly to a particular system without additional specific adjustment. Consequently, lots of efforts have been devoted to the extension of the thermodynamic regime of application of models outside their current envelope. As an example, Ungerer *et al.* have shown that their anisotropic united atoms potential model could be used to simulate liquid–vapor equilibria [1,2] as well as adsorption in zeolithes [3,4], short branched alkanes [5] and alkenes [6] as well as long linear and branched alkanes [5,7] and pure compounds [8] as well as mixtures [9,10]. To obtain such transferable potentials, they have developed a complete optimization method to ensure that the final parameters retain important physical meanings. The main idea is that the more realistic the potential model is, and the more representative the reference database is, the more transferable the optimized parameters will be.

In this work, we aim at obtaining a realistic and transferable model to simulate liquid HF. Following the ideas proposed in previously cited works, we developed in a first step a general method to obtain realistic parameters to take into account electrostatic interactions between HF molecules. Usually, a parameter optimization is performed by minimizing an error criterion representing the differences observed between some reference data and the same data calculated using the potential parameters to optimize. As discussed by Bourasseau *et al.* [6], three important points have to be considered to build such a method: the choice of a physically sound functional form representing the interatomic interactions, the elaboration of a suitable reference database, and the development of a proper and accurate minimization routine to reach one or several *minima* of the error criterion.

The first step was to choose an adequate potential form to model coulombic interactions between HF molecules. Indeed, charge transfer in this molecule leads to a permanent dipole moment of 1.8 D in the gas phase and the liquid is known to be strongly associated, with the existence of a 1-dimensional network of molecules linked by hydrogen bonds. Usually, the electrostatic part of the total potential is represented by the interaction energy between constant partial charges located on hydrogen and fluorine atoms (to reproduce the dipolar moment), and eventually between constant partial charges located on the two atoms plus one located between the two atoms

---

*Corresponding author. E-mail: emeric.bourasseau@cea.fr

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020500231817

(to reproduce the quadrupolar moment). For instance, the TIPS model proposed by Cournoyer *et al.* [11], allows to reproduce structural properties of HF liquid in standard conditions using this electrostatic representation. Nevertheless, this type of model appears unsuitable for the calculation of thermodynamic properties of HF at higher temperatures. To improve the TIPS model, Vallauri *et al.* introduced an additional parameter to take into account the molecule polarizability, including an induced dipole moment on each HF molecule [12]. This model reproduces correctly thermodynamic properties of liquid HF on a larger temperature range, but only under ambient pressure. In the same way, Della Valle *et al.* have recently proposed a new model where the polarizability of HF molecules is taken into account including a vibrational potential on the H—F bond [13]. Similar conclusions emerge from their results: temperature effects can be properly described, but pressure effects remain difficult to model. In fact, it appears necessary to take into account the evolution of the dipole moment from isolated molecules to dense fluid. Electrostatic models using constant charges, even including polarisability, are definitively not able to model this phenomenon. This type of conclusion has already been made about water system. Indeed, it is known that the water dipole moment varies from 1.85 D in the gas phase to more than 2.5 D in the liquid phase. In fact, it seems reasonable to consider that charge values should change with respect to their environment. As a consequence, to model dense systems of water, Rick *et al.* proposed to use the charge equilibration method to determine partial charges on atoms in regard with their particular environment during a molecular dynamic simulation [14]. This method, initially proposed by Mortier *et al.* [15], and then developed by Rappé *et al.* [16], seems to be well suited to describe HF system as well as water system; we thus chose to implement it to model properly electrostatic interactions in liquid HF.

Downloaded At: 18:20 14 January 2011

The second step of this work was to determine which data or property should be used as reference data for the subsequent fitting procedure of potential parameters. The key point is the selection of an ensemble of properties (experimental or *ab initio*) and representative of the properties we aimed at predicting. This set of reference data should be obviously sensitive to the values of parameters to optimize. In other words, we may include in the reference database some discriminant properties with respect to the parameters optimization. Moreover, this set of reference properties should depend only on the part of the potential we want to optimize — the selected properties for the optimization of electrostatic parameters in our case should not depend on the vibrational dynamic or intermolecular dispersion. This is made easier when a physical meaning is attributed to each parameter. We postulate that the optimization of those parameters on the basis of representative reference data that depend only on electrostatic properties leads to accurate and realistic parameters.

The third point is to develop a minimization procedure to obtain the optimized parameters. This is also a crucial point. Indeed, the shape of the surface produced by the error function in the parameter space is affected by the definition of this function. It could be flat, or presents some deep wells, so the routine procedure to explore this surface and minimize the error function has to be adapted accordingly.

This paper is organized as follows. First section describes more precisely the charge equilibration method. In the second section, we underline the difficulties of finding reference properties that depend only on electrostatic properties. The selected reference data are presented, as well as the chosen error criterion function. This section also describes the minimization routine. The following section presents the optimized parameters obtained after the minimization process, and some results concerning their evaluation. Finally the last section summarizes the conclusions.

2. Charge equilibration method

The central idea of charge equilibration method is based on the principle of electronegativity equalization of atoms within a molecule, first proposed by Sanderson [17]. He postulated that if some atoms, presenting different electronegativities, gather to form a molecule, their electronegativities will equalize. Later, Parr demonstrated this postulate using the Kohn–Sham theory, and he showed that the electronegativity depends on the local atomic environment [18] (In fact, he showed that electronegativity is the negative of the electron chemical potential). Consequently, if a given atom moves so that it feels a different electrostatic potential, its charge will take a different value in order to adjust the atomic electronegativity. This is a proof of the environment dependence of atomic charges.

The electrostatic energy of a system composed of N_{mol} molecules each with N_{at} atoms can be expressed as:

$$E(Q) = \sum_{i=1}^{N_{\mathrm{mol}}} \sum_{\alpha=1}^{N_{\mathrm{at}}} \left[E_\alpha(0) + \chi_\alpha^0 Q_{i\alpha} + \frac{1}{2} J_{\alpha\alpha}^0 Q_{i\alpha}^2 \right] + \sum_{i\alpha<j\beta} J_{\alpha\beta}(r_{i\alpha j\beta}) Q_{i\alpha} Q_{j\beta} \tag{1}$$

where $E_\alpha(0)$ is the ground state energy of atom α, χ_α^0 is the electronegativity of the isolated atom α, $Q_{i\alpha}$ is the partial charge on atom α of molecule i, $J_{\alpha\beta} Q_{i\alpha} Q_{j\beta}$ is the coulombic interaction between atoms α of molecule i and β of molecule j (separated by distance $r_{i\alpha j\beta}$), and $J_{\alpha\alpha}^0$ is the self-coulombic integral of atom α.

As a consequence, the electronegativity per unit charge of atom $i\alpha$ is given by:

$$\chi_{i\alpha} = \left(\frac{\partial E}{\partial Q_{i\alpha}} \right) = \chi_\alpha^0 + J_{\alpha\alpha}^0 Q_{i\alpha} + \sum_{j=1}^{N_{\mathrm{mol}}} \sum_{\beta=1,\, i\alpha \neq j\beta}^{N_{\mathrm{at}}} J_{\alpha\beta}(r_{i\alpha j\beta}) Q_{j\beta} \tag{2}$$

Applying the electronegativity equalization principle, the equilibrium charges are those for which

Downloaded At: 18:20 14 January 2011

electronegativities are equal:

$$\forall i = 1\ldots N_{\mathrm{mol}}, \quad \chi_{i1} = \chi_{i2} = \cdots = \chi_{iN_{\mathrm{at}}} \tag{3}$$

Moreover, charges are not independent variables since there is a charge conservation constraint. Each molecule is constrained to be neutral:

$$\forall i = 1\ldots N_{\mathrm{mol}}, \quad \sum_{\alpha=1}^{N_{\mathrm{at}}} Q_{i\alpha} = 0. \tag{4}$$

Consequently, the charge equilibration method consists on solving the following system composed of $N_{\mathrm{mol}}N_{\mathrm{at}}$ equations with $N_{\mathrm{mol}}N_{\mathrm{at}}$ unknown $\{Q_{i\alpha}\}$:

$$\forall i = 1\ldots N_{\mathrm{mol}}, \quad \begin{aligned} &\chi_{i1} = \chi_{i2} \\ &\chi_{i1} = \chi_{i3} \\ &\ldots \\ &\chi_{i1} = \chi_{iN_{\mathrm{at}}} \\ &\sum_{\alpha=1}^{N_{\mathrm{at}}} Q_{i\alpha} = 0. \end{aligned} \tag{5}$$

This method allows to determine, for a given atomic configuration, the partial charges respecting Sanderson's postulate. Knowing χ_α^0, $J_{\alpha\beta}$ and $J_{\alpha\alpha}^0$, it is possible to calculate accurately electrostatic interactions for each configuration in a molecular dynamic simulation.

χ_α^0 could be determined through *ab initio* calculations considering that it represents the first derivative of energy with respect to partial charge. In this work, we consider χ_α^0 (χ_{H} and χ_{F}) as parameters in the optimization process.

At long distances, the coulombic interaction $J_{\alpha\beta}$ between the two partial charges $Q_{i\alpha}$ and $Q_{j\beta}$ separated by a distance $r_{i\alpha j\beta}$ can be expressed as:

$$J_{\alpha\beta}(r_{i\alpha j\beta}) = \frac{e^2}{4\pi\epsilon_0 r_{i\alpha j\beta}} \tag{6}$$

Equation (6) is useful to model interatomic interactions when atoms of different molecules are involved. Nevertheless, if $r_{i\alpha j\beta} \to 0$, this expression diverges, whereas it should converge to $J_{\alpha\alpha}^0$. In fact, it appears necessary to add a screening correction term to model the coulombic interaction at small distances (in order to model the overlap of the electronic distributions). Several expressions have been proposed in the literature in order to evaluate this screening term. Following Rappé *et al.* [16] and Rick *et al.* [14], we chose to calculate the intramolecular interatomic coulombic interaction as the Coulomb overlap integral between Slater orbitals centered on each atomic sites:

$$J_{i\alpha j\beta}(r) = \frac{e^2}{4\pi\epsilon_0}\int \mathrm{d}\boldsymbol{r}_k\, \mathrm{d}\boldsymbol{r}_l |\Phi_{n_\alpha}(r_k)|^2 \frac{1}{|\boldsymbol{r}_k - \boldsymbol{r}_l - r|} |\Phi_{n_\beta}(r_l)|^2 \tag{7}$$

where the Slater orbitals are given by:

$$\Phi_{n_\alpha} = N_\alpha r^{n_\alpha - 1} e^{-\zeta_\alpha r} \tag{8}$$

and characterized by the principal quantum number n_α, the Slater exponent ζ_α, and a normalization factor N_α. Therefore, the self-coulombic interaction $J_{\alpha\alpha}^0$ ($= J_{\alpha\alpha}(r)$ when $r = 0$) is determined only by the value of ζ_α. For a hydrogen atom, $n_\alpha = 1$ and $J_{\mathrm{HH}}^0 = (5/8)(\zeta_H/4\pi\epsilon_0)e^2$, and for a fluorine atom, $n_\alpha = 2$ and $J_{\mathrm{FF}}^0 = (93/256)\times(\zeta_F/4\pi\epsilon_0)e^2$.

Finally, only two parameters per atom type (χ and ζ) are needed to evaluate the functions $J_{\alpha\beta}$, in order to determine partial charges and to calculate coulombic interactions. In the particular case of HF, this leads to the optimization of four parameters: χ_{H}, χ_{F}, ζ_{H} and ζ_{F}. Nevertheless, in order to resolve system (5), only the electronegativity difference $\Delta\chi = \chi_{i\alpha} - \chi_{i\beta}$ is required; the optimization process finally involves the following three parameters: $\Delta\chi_{\mathrm{HF}}$, ζ_{H} and ζ_{F}.

To complete the method description, it should be noted that periodic boundary conditions have been used in classical calculations in the three directions. To be consistent with our usual way to evaluate long range interactions in molecular dynamic simulations, we performed the classical calculations with a cutoff of 10 Å for coulombic interactions, and with a Taper function to make the interactions reach 0 at 10 Å.

3. Optimization method

3.1 Error function and reference data base

Usually, parameter optimizations are performed with respect to the minimization of an error function, representing the differences observed between some reference data (experimental measurements or *ab initio* results) and the same property calculated with the parameters to optimized in the given model. The more commonly used form for the error function is the following:

$$F = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{f_i^{\mathrm{calc}} - f_i^{\mathrm{ref}}}{\lambda_i}\right)^2 \tag{9}$$

where n is the number of reference data, f_i^{ref} is the i-th reference data value, f_i^{calc} is the value of the same property calculated with parameters to be optimized, and λ_i is the relative weight of the property i with respect to the error function.

The first reference data we introduced in the function F is the dipole moment of the molecule in the gas phase. Indeed, for a given interatomic distance, the dipole moment value depends only on partial atomic charges and as a consequence, depends only on the three parameters of the charge equilibration method $\Delta\chi_{\mathrm{HF}}$, ζ_{H} and ζ_{F}. Moreover, the equilibrium distance and dipole moment value of the isolated molecule are well known experimentally. The reference value entering the F function is equal to $\mu^0 = 1.826\,\mathrm{D}$ [19], for the equilibrium distance $d^0 = 0.9168\,\text{Å}$ [20]. As discussed above, electrostatic properties of an isolated molecule may differ notably from those of the condensed phase. Consequently, the dipole moment term should not be preponderant in the F function

Downloaded At: 18:20 14 January 2011

and its relative weight has to be chosen accordingly. Therefore, we decided to introduce the dipole moment in the F function using the following formulation:

$$\left(\frac{|\mu^{\text{calc}} - \mu^0|}{0.06}\right)^4 \tag{10}$$

The weighting coefficient $\lambda = 0.06$ has been chosen to give an adequate importance to the dipole moment in the F function regarding the other reference data. The exponent value of 4 has been chosen in order to obtain a flat function near the minimum, and abrupt parabolic branches.

The choice of reference data associated to the condensed phase is less obvious. Indeed, as discussed above, it is necessary to introduce data depending only on electrostatic interactions. As a consequence, averaged properties appear unsuitable for the optimization, as this would imply dynamic calculations including force evaluations with all potential contributions. This constraint prevents us from using statistically averaged data as well as experimental measurements. Only instantaneous data, calculated with *ab initio* methods on a set of configurations representative of a condensed fluid, can be included in the F function.

In a first attempt, we decided to use directly partial atomic charges obtained from *ab initio* simulations, to fit our parameters. The Bader analysis [21] allows to evaluate partial atomic charges from the electronic density calculated on a given configuration from an usual DFT code. The idea is to define a Bader volume around atoms following the electronic density minima. The integration of electronic density on each volume gives a partial charge on each atom. These partial charges could be compared with those obtained through charge equilibration method, and optimized parameters could be obtained by minimizing the following error function:

$$F^{\text{conf}}_{\text{charges}} = \sum_{i=1}^{N_{\text{mol}}} \sum_{\alpha=1}^{N_{\text{at}}} \left(\frac{Q^{\text{calc}}(i\alpha) - Q^{\text{Bader}}(i\alpha)}{Q^{\text{Bader}}(i\alpha)}\right)^2 \tag{11}$$

The above function defines the contribution of a single configuration to the global error function; in practice, several configurations could be used, taken from different *ab initio* simulations performed on a wide thermodynamic regime (high and low density and temperature). It is then assumed that parameters obtained in this way are transferable, i.e. able to reproduce *ab initio* atomic charges on a large range of temperatures and pressures in condensed phase configurations.

Unfortunately, Bader analysis did not succeed in the case of our dense systems of HF molecules. The H electron often appears too delocalized to allow a precise determination of electronic density minima around the corresponding H atom. Bader surfaces were not properly defined, leading to unrealistic values for atomic charges. As a consequence, *ab initio* charges were not used in optimization procedure for HF systems, but a work actually in progress aims at showing that the use of Bader charges to optimize charge equilibration method parameters can appear efficient and accurate for other systems.

Therefore, in a second attempt, we decided to introduce electrostatic potential data in the F function. *Ab initio* methods allow the calculation on a grid of the electrostatic potential created by the distribution of atoms in the simulation box. Due to the large number of grid points used in *ab initio* simulations (several millions), only a few of them (around 100) were randomly selected and the corresponding values of the electrostatic potential were introduced in the F function. Nevertheless, it is known that electrostatic potential calculated in a classical framework takes unrealistic values in the neighborhood of the atom cores (where quantum physic applies). An exclusion volume around the atoms was then used for the random selection of the data points. In this way, it appeared that classical values were not directly comparable to *ab initio* ones. In fact, the electrostatic potential is usually calculated with an undetermined constant in *ab initio* methods. This is due to the incapacity during the simulation of evaluating the potential at $\vec{g} = \vec{0}$ in the Fourrier space. Since this problem does not appear in classical calculations, it is necessary to introduce an additional constant in order to compare classical and *ab initio* results on the same basis. This constant was finally included in the optimization process as a supplementary parameter.

Finally, we used the VASP code [22] to perform *ab initio* simulations on a wide thermodynamic regime [23]. Trajectories under the dissociation were selected at a temperature of 500 K. Four configurations ($X \equiv A$–D), corresponding to four different densities, have been taken from those simulations. They are supposed to be representative of a condensed phase of HF fluid. On the basis of the electrostatic potential calculated on those four configurations, we define the following F function:

$$F_{\text{elec}} = \sum_{X=A}^{D} \sqrt{\sum_{i=1}^{N_{\text{points}}} \left(V^{\text{calc}}_{\text{elec}}(i_X) - V^{\text{ref}}_{\text{elec}}(i_X) + C_X\right)^2} \tag{12}$$

where $V^{\text{calc}}_{\text{ref}}(i_X)$ is the classically calculated value of electrostatic potential at the grid point i of configuration X, $V^{\text{ref}}_{\text{elec}}(i_X)$ is the corresponding *ab initio* calculated value, and C_X is the constant allowing the comparison of classical and *ab initio* results for configuration X.

The overall error function F employed in the optimization process of the parameters $\Delta\chi_{\text{HF}}$, ζ_{H} and ζ_{F}, is the following:

$$F = \sum_{X=A}^{D} \sqrt{\sum_{i=1}^{N_{\text{points}}} \left(V^{\text{calc}}_{\text{elec}}(i_X) - V^{\text{ref}}_{\text{elec}}(i_X) + C_X\right)^2} + \left(\frac{|\mu^{\text{calc}} - \mu^0|}{0.06}\right)^4 \tag{13}$$

Therefore, if a realistic and satisfying minimum is obtained, the form of this function ensures that optimized

Downloaded At: 18:20 14 January 2011

parameters allow to reproduce the isolated molecule dipole moment together with the electrostatic potential of the liquid phase in different thermodynamic conditions.

3.2 Minimization routine

To realize the optimization, we developed an original code, allowing the calculation of the F function with successive parameter sets, and the minimization of this function in regard with the parameters. The calculation of the error function includes the determination of partial charges on a given atomic configuration using the charge equilibration method, and the evaluation of electrostatic potential through the coulombic formulation at each selected grid point included in the F function. It also includes the calculation of the dipole moment on the basis of calculated partial charges on the isolated molecule with an intramolecular distance set to 0.9168 Å.

The minimization routine we chose uses the Powell method. For each parameter to optimize, it proceeds to surround a minimum, and minimizes the function using parabolic interpolations. Then, it determines directions through which minimization appears efficient, and repeat this procedure in those directions. The routine stops the minimization when a satisfactory convergence is reached. This method is purely analytic and allows to obtain minima on flat surfaces.

4. Results

4.1 Optimization details

The exploration of the error function in the parameter space was confined to a physically sound zone, i.e. a space in which the values of potential parameters retain their physical meaning. We imposed Δ_χ to be optimized between 3.0 and 6.0 J, ζ_H between 0.5 and 2.5 × $10^{10}\,\mathrm{m}^{-1}$ and ζ_F between 3.0 and 5.5 × $10^{10}\,\mathrm{m}^{-1}$. For parameter values outside this envelope, the F function is set to infinity.

The reference database has been set as the following:

- Data set A: Evaluation of electrostatic potential on an instantaneous configuration taken from a VASP simulation of HF at $T = 500\,\mathrm{K}$ and $\rho = 2.567\,\mathrm{g\,cm}^{-1}$. $N_A = 62$ points have been randomly selected outside an atomic exclusion volume of radius 1.42 Å.
- Data set B: Evaluation of electrostatic potential on an instantaneous configuration taken from a VASP simulation of HF at $T = 500\,\mathrm{K}$ and $\rho = 2.193\,\mathrm{g\,cm}^{-1}$. $N_B = 72$ points have been randomly selected outside an atomic exclusion volume of radius 1.5 Å.
- Data set C: Evaluation of electrostatic potential on an instantaneous configuration taken from a VASP simulation of HF at $T = 500\,\mathrm{K}$ and $\rho = 1.861\,\mathrm{g\,cm}^{-1}$. $N_C = 80$ points have been randomly selected outside an atomic exclusion volume of radius 1.6 Å.
- Data set D: Evaluations of electrostatic potential on an instantaneous configuration taken from a VASP simulation of HF at $T = 500\,\mathrm{K}$ and $\rho = 1.300\,\mathrm{g\,cm}^{-1}$. $N_D = 80$ points have been randomly selected outside an atomic exclusion volume of radius 1.9 Å.

Details of the *ab initio* simulations are given in [23]. The optimization process has been done to obtain 50 successive minimizations from random initial conditions.

4.2 Minimization results

As it has been described above, the value of the F function was automatically set to infinity if one of the parameters left the physically sound zone previously defined during the minimization process. In fact, 12 of the 50 successive minimizations have been concerned and led to infinite values of the F function. As shown in figure 1, the successful minimizations have converged to finite values for the error function, distributed around 16.5. Nevertheless, this distribution is not significant, and all minima can be considered as equivalent: indeed, due to the analytical expression of the F function, a small error on the dipole moment would imply large deviations in F (for example, a relative error of 10% on the dipole moment implies $F = 100$). These minima can be distinguished by the corresponding value of the optimized parameters, as shown in the same figure. Optimized values for ζ_H are comprised of values between 1.22 and 2.24 × $10^{10}\,\mathrm{m}^{-1}$. These values can be compared to the value proposed by Rick *et al.* [14] used to simulate fluctuating charge of hydrogen atom in water: 1.89 × $10^{10}\,\mathrm{m}^{-1}$. Optimized values for ζ_F are included in the range [3.59–4.56] × $10^{10}\,\mathrm{m}^{-1}$. These values can be compared to the value used by Rappé *et al.* [16] to simulate fluctuating

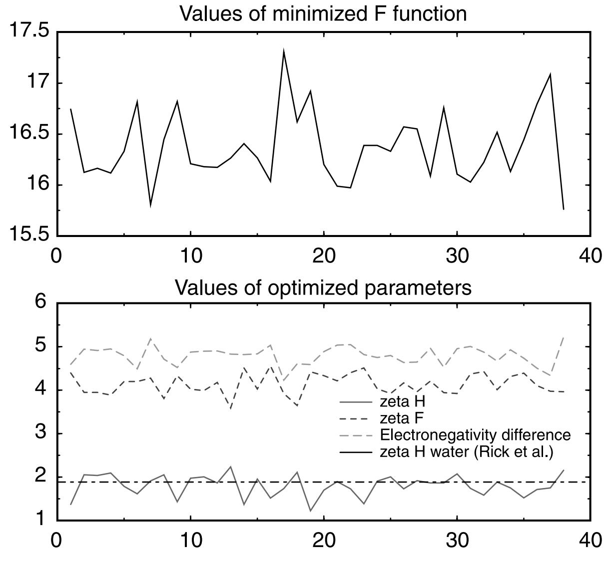


Figure 1. Upper graph: Minimized values of the F function for the 38 successful minimizations. Lower graph: Values of optimized fluctuating charge parameters for corresponding minimizations (ζ_H and ζ_F in $10^{10}\,\mathrm{m}^{-1}$, $\Delta\chi_{HF}$ in J).

Downloaded At: 18:20 14 January 2011

charge of fluorine atom in hydrofluorocarbon molecules: $3.54 \times 10^{10}\,\mathrm{m}^{-1}$. Both the ranges of values for ζ_H and ζ_F are in accordance with previously published parameters. Rick *et al.* used a value of $3.04 \times 10^{10}\,\mathrm{m}^{-1}$ for ζ_O in water. This value is coherent with our results, considering the expansion of the Slater orbital $2s$ with the number of valence electron. Finally, the optimized value of $\Delta\chi_{HF}$ stands between 4.23 and 5.23 J. The usual value admitted in chemistry to compare electronegativities of hydrogen and fluorine atoms is about 4.0 J, regarding Pauling or Mulliken electronegativity tables. Rappé *et al.* have proposed and used $\Delta\chi_{HF} = 6.34\,\mathrm{J}$, whereas Rick *et al.* used $\Delta\chi_{HO} = 3.19\,\mathrm{J}$ for water system. The values of fluctuating charge parameters after optimization are then consistent with those used in the literature. Nevertheless, the existence of many minima associated with very different values of parameters but leading to the same accuracy in terms of the error function is amazing.

At this point, it appears judicious to visualize the shape of the error function in the parameter space. The function F has then been calculated on the selected range of variation of potential parameters i.e. [4.0–5.5] for $\Delta\chi$ with a increment of 0.03 J, $[1.0\text{–}2.5] \times e^{10}$ for ζ_H with an increment of $0.03 \times e^{10}\,\mathrm{m}^{-1}$ and $[3.0\text{–}5.0] \times e^{10}$ for ζ_F with an increment of $0.03 \times e^{10}\,\mathrm{m}^{-1}$. An hypersurface is obtained in the three dimensional parameter space, where the function F is colored accordingly to its local value. All minima described previously belong to the same zone, which appears as a canyon more than a single well. A slice of this function perpendicular to the $\Delta\chi$ direction is shown in figure 2. The valley is clearly seen, and explains the existence of many distant minima. This valley is the result of the use of equation (10) to reproduce dipole moment. The other part of the function F, i.e. the electrostatic potential, is responsible of the rugosity inside the valley, leading to the formation of many minima.

Figure 3 shows the values taken by parameters C_X for the four considered configurations for each successful minimization. In each case, the variation of C_X is very small among the different minima; its standard deviation is about 0.2% for A and B configurations, and under 0.13% for C and D configurations. These parameters are then considered as constants which account for the methodological difference between classical and *ab initio* calculations. This difference is related to the treatment of long-range interactions, and thus depends on the density of the system: it is seen to increase with density while vanishing in the case of an isolated molecule.

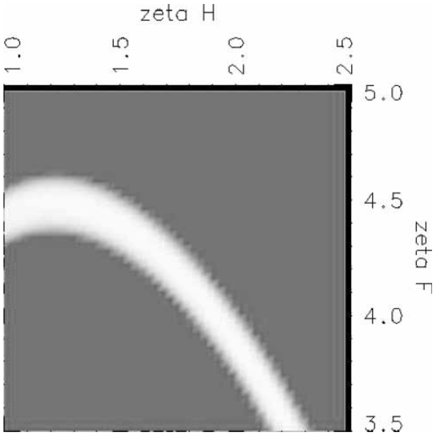


Figure 2. Slice of the F function in a plan defined by $\Delta\chi_{HF} = 4.75\,\mathrm{J}$. The F function is colored accordingly to its value, white for low values and black for high values.

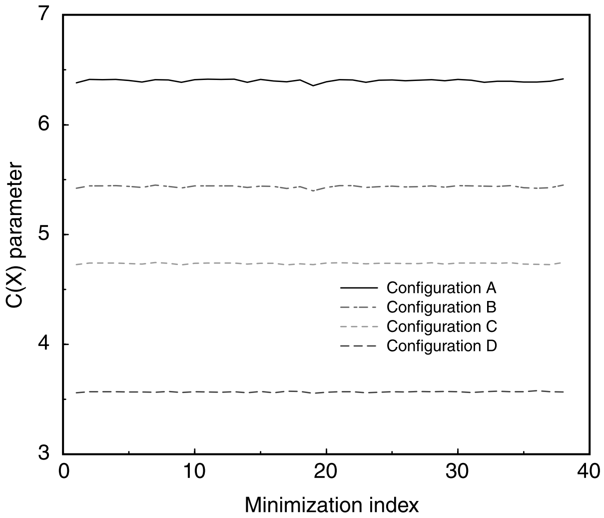


Figure 3. Optimized values of parameters C_{conf} representing the shift needed to compare the two methods: classical calculations and *ab initio* simulations. Results were obtained for the 38 successful minimizations and for each configuration, from the higher density (A) to the lower (D).

Finally, all minima are located at the bottom of a valley drawn by equation (10), which goes through the range of validity of parameters to optimize. The choice of the analytical expression of the F function is justified a posteriori by the existence of many minima on this domain. Nevertheless, questions concerning the discrimination between these minima remain: is the difference between them (lower than 2) large enough to be relevant ? To answer this question, we attempted to analyze the two lowest minima (cases 7 and 38) for which F equals to 15.81 and 15.76, respectively. We also decided to analyze the case corresponding to the highest minima (case 17) for which F takes the value 17.31.

4.3 Analysis of the three parameter sets

The three parameter sets are presented in table 1. Regarding the three cases, a variation of about 25% can be observed for the parameter $\Delta\chi_{HF}$ between cases 7 and 38

Table 1. Values taken by the minimized F function, and by the optimized parameters in the three evaluated minimization cases: 7, 17 and 18.

	Case 7	*Case 17*	*Case 38*
F	15.81	17.31	15.76
$\Delta\chi_{HF}$ (J)	5.182	4.234	5.228
ζ_H ($10^{10}\,\mathrm{m}^{-1}$)	1.916	1.739	2.159
ζ_F ($10^{10}\,\mathrm{m}^{-1}$)	4.277	3.922	3.964

Downloaded At: 18:20 14 January 2011

(the best ones) and case 17 (the less successful one). Moreover, it seems that a direct correlation between $\Delta\chi_{\mathrm{HF}}$ and F in the minima exists, as can be seen in figure 1. Lower variations are seen concerning ζ_{H} and ζ_{F}, and no correlation with the error function is detected. However, they exhibit an opposite variation in figure 1, the effect of one parameter balancing the other in the minimum.

Table 2 presents the corresponding values of the dipole moment on the isolated molecule, with an intermolecular distance set to 0.9168 Å. The three calculated values are equivalent and slightly underestimate the experimental data. The relative error is between 1.65 and 1.86%.

To verify that the optimized parameters allow the calculation of electrostatic potential of a condensed phase of HF, we performed the calculation of this potential at each point of the *ab initio* grid, for each studied configuration and in each of the three cases. Figures 4 and 5 respectively, present the electrostatic potential calculated from the electronic density in the *ab initio* simulations and from partial atomic charges in a classical framework with the parameters of case 7 for the configuration D. These figures show a slice of the 3-dimensional grid on the (x, y) plan. The lower the potential values are, the more dark the area appears, and the color tends to black when potential is negative, and tends to white when it is positive. In figure 4, white zones represent high absolute values (it corresponds to atom cores in the *ab initio* vision), and in figure 5, white zones represent values located under 1.2 Å from any atom core (it corresponds to unrealistic values in the classical vision). It is important to note that *ab initio* values in figure 4 have been shifted of $C_{\mathrm{conf}} = C_D = 3.5658$ eV in order to make the comparison on the same basis.

It appears that the classical description is in accordance with the *ab initio* one. Dark and clear areas are localized in the same regions, which is very satisfactory from the point of view of the parameter optimization but also on the physical relevance of these parameters. Nevertheless, some differences can be observed. First it appears in figure 4 that the potential is systematically positive (color tends to white) near atom cores (around white areas). This is due to the fact that the *ab initio* description takes into account the presence of electron clouds near atom cores. As a consequence, electrostatic potential is always positive near an atom, regardless of its nature (hydrogen or fluorine). On the other hand, we note in figure 5 that in the classical framework, the potential is positive near hydrogen atoms (color tends to white), and negative near fluorine atoms (color tends to black). This is due to the fact that charges have systematically opposite values for two atoms in the same molecule (molecular electroneutrality). This difference may not have a major impact in classical simulations because atoms belonging to different molecules are not expected to probe this conflicting area, near the atom core. Moreover, we took care to select points distant for at least 1.5 Å from any atom when defining the F function, so this difference did not bias the parameter optimization. Secondly, another difference is observed in the maximum and minimum values of the potential. In the *ab initio* case, values are included in the range [−1.09; 2.03] eV whereas they are included in the range [−2.63; 2.81] eV in the classical case. This underlines the limit of our model: the optimized parameters allow the description

Table 2. Calculated dipole moment of isolated molecule with the three evaluated parameter sets, compared with experimental value taken from [19].

	Case 7	*Case 17*	*Case 38*	*Exp. [19]*
$\mu(D)$	1.792	1.795	1.796	1.826

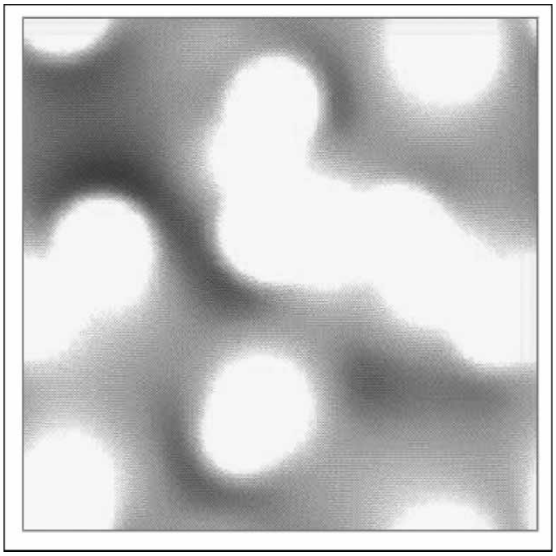


Figure 4. Electrostatic potential taken from *ab initio* calculation for configuration D. Here is a slice on the (x, y) plan. *Ab initio* data have been shifted of $C_D = 3.5658$ eV. The white areas correspond to atom cores where potential values are very high. The lower the potential values are, the more dark the area appears.

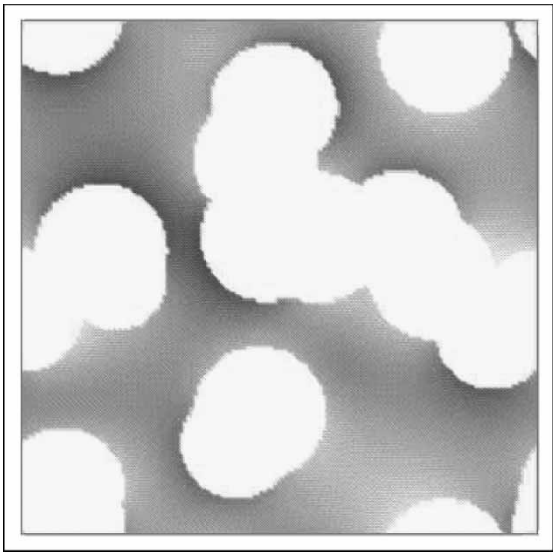


Figure 5. Electrostatic potential taken from classical calculation for configuration D with parameters set number 7. Here is a slice on the (x, y) plan. The white areas correspond to unrealistic values under 1.2 Å from any atom. The lower the potential values are, the more dark the area appears.

Downloaded At: 18:20 14 January 2011

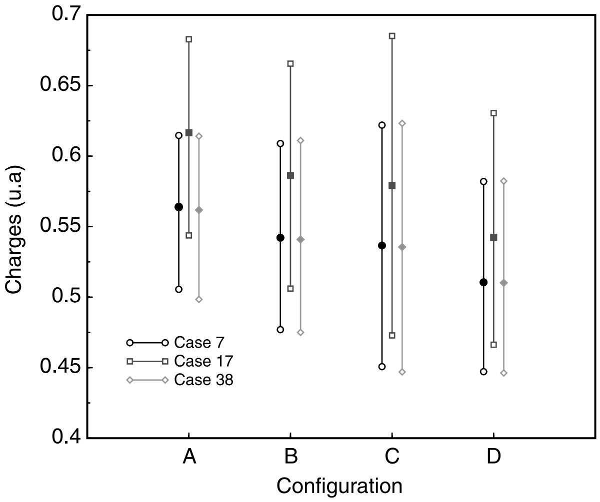


Figure 6. Hydrogen charge distributions for each configuration and for the three parameter sets. Open symbols represent maximal and minimal charge values, and dark symbols represent the average charge values for all configurations.

of the variations of the electrostatic potential, but not of its absolute values. Nevertheless, this is not a crucial point in the case of molecular dynamic simulations where forces drive the dynamics, depending only on the derivative of the potential and not on absolute values. In the same way, this is not a problem in case of Monte Carlo simulations, where only potential differences are calculated.

Similar conclusions emerge from the analysis of the results obtained from the other configurations and for the other parameter sets.

Figure 6 shows the charge distribution on the 32 hydrogen atoms in each configuration calculated with the three parameter sets. The same tendency is observed concerning the evolution of the averaged charge with density. Indeed, in the three cases, the more dense configuration (*A*) implies the highest charge average, and the average value decreases with density. This is consistent with results obtained concerning water system: in the dense phase, the intermolecular distance decreases, and charge transfer increases, leading to higher charge values [14]. This observation justifies the use of fluctuating charges, even in homogeneous systems. With a model using constant charges, it would have been impossible to reproduce this dependance with density. As an illustration, a constant charge model fitting charges on the basis of the isolated molecule dipole moment would have lead to charges equal to 0.414 u.a. in all cases, which are very different from those presented in figure 6.

In figure 6, an important difference is observed between the two favorable cases (7 and 38) and the worse case (17). In the first two cases, the charge distributions are very similar, and centered on 0.55 u.a. On the other hand, the charge distribution in case 17 is centered on 0.58 u.a. For all four studied configurations, there is a shift of about 0.04 u.a. between charge distributions. It is interesting to link this difference observed on charge distributions with the difference observed on minimized value of the F function in the three cases. This underlines a conjunction which has already been made before that charge values are more discriminant properties to perform the optimization on.

To conclude with the evaluation of the three studied minimization cases, the F function appears sufficiently well defined to obtain realistic and accurate parameter sets. Nevertheless, it is important to note that an additional analysis is necessary to discriminate all local minima. In our case, the minimization led to two almost equivalent parameter sets: cases 7 and 38. Nevertheless, ζ_{H} in the parameter set number 7 presents a value very close to the ζ_{H} parameter proposed by Rick *et al.* to simulate water system [14]. At this stage, it could be useful to consider parameter transferability as an additional discriminating argument.

5. Conclusions

This work has allowed the development of a general and efficient optimization method to obtain accurate and transferable charge equilibration method parameters (transferable over different thermodynamic conditions). This method involves three steps: the choice of a physically sound model for the potential, the definition of the error function to minimize, and the development of a minimization routine taking into account the specificities of the system. The second step is usually the most important. It includes the elaboration of a relevant reference database on which the minimization is performed. The choice of reference data is linked to the expected capabilities of the potential as well as to model specificities.

This method has been tested to optimize fluctuating charge parameters for hydrogen and fluorine atoms to simulate liquid HF systems. Data concerning isolated molecule and condensed phase fluid have been included in the reference database. In particular, electrostatic potential data taken from *ab initio* simulations have been used. The optimization, performed using a Powell minimization routine, led to realistic and consistent parameters. It appeared that electrostatic potential data can be used to optimize parameters, but charge values determined by Bader analysis would be a more discriminant criteria. As the charge analysis was not successful with HF system, work is actually in progress to validate the method on another fluid. Another way to shape the error function in a nicer fashion would be to include data from other systems. A leading advantage of that would be the natural transferability of the related parameters.

A closer perspective of this work will be the use of optimized parameters to perform molecular dynamic simulations. This implies the optimization of dispersion–repulsion parameters, actually in progress.

To conclude, it is important to note that the method presented here is general and could be applied to any molecular system, with as many parameters and reference data as it is needed.

References

[1] E. Bourasseau, P. Ungerer, A. Boutin. Prediction of equilibrium properties of cyclic alkanes by Monte Carlo simulation—new anisotropic united atoms intermolecular potential—new transfer bias. *J. Phys. Chem. B*, **106**, 5483 (2002).

[2] P. Ungerer, C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau, A.H. Fuchs. Optimisation of the anisotropic united atoms intermolecular potential for n-alkanes. *J. Chem. Phys.*, **112**, 5499 (2000).

[3] P. Pascual, A. Boutin, P. Ungerer, B. Tavitian, A.H. Fuchs. Adsorption of linear alkanes in zeolites ferrierite from molecular simulations. *Mol. Simulat.*, **30**, 593 (2004).

[4] P. Pascual, P. Ungerer, B. Tavitian, A. Boutin. Development of a transferable guest–host force field for adsorption of hydrocarbons in zeolites II. Prediction of alkenes adsorption and alkanes/alkenes selectivity in silicalite. *J. Phys. Chem. B*, **108**, 393 (2004).

[5] E. Bourasseau, P. Ungerer, A. Boutin, A.H. Fuchs. Monte Carlo simulations of branched alkanes and long chain n-alkanes with anisotropic united atoms intermolecular potential. *Mol. Simulat.*, **28**, 317 (2002).

[6] E. Bourasseau, M. Haboudou, A. Boutin, A.H. Fuchs, P. Ungerer. New optimization method for intermolecular potentials: Optimisation of a new anisotropic united atoms potential for olefines: Prediction of equilibrium properties. *J. Chem. Phys.*, **118**, 3020 (2003).

[7] E. Bourasseau, I. Mokbel, J. Jose, P. Ungerer. Measurement and prediction of vapour pressures of 2,6,10,14-tetramethylpentadecane (pristane). Experimental and Monte Carlo simulation results. *Fluid Phase Eq.*, **225**, 49 (2004).

[8] M.G. Ahunbay, S. Kranias, V. Lachet, P. Ungerer. Prediction of thermodynamic properties of heavy hydrocarbons by Monte Carlo simulations. *Fluid Phase Eq.*, **224**, 73 (2004).

[9] M.H. Lagache, P. Ungerer, A. Boutin. Prediction of thermodynamic derivative properties of natural condensate gases at high pressure by Monte Carlo simulation. *Fluid Phase Eq.*, **220**, 211 (2004).

[10] P. Ungerer, A. Wender, G. Demoulin, E. Bourasseau, P. Mougin. Application of Gibbs ensemble and NPT Monte Carlo simulations to the development of improved processes for H_2S-rich gases. *Mol. Simulat.*, **30**, 631 (2004).

[11] M.E. Cournoyer, W.L. Jorgensen. An improved intermolcular potential function for simulations of liquid hydrogen fluoride. *Mol. Phys.*, **51**, 119 (1984).

[12] P. Jedlovszky, R. Vallauri. Computer simulation study of liquid HF with a new effective pair potential model. *J. Chem. Phys.*, **107**, 10166 (1997).

[13] R.G. Della Valle, D. Gazzillo. Towards an effective potential for the monomer, dimer, hexamer, solid and liquid forms of hydrogen fluoride. *Phys. Rev. B*, **59**, 13699 (1999).

[14] S.W. Rick, S.J. Stuart, B.J. Berne. Dynamical fluctuating charge force fields: Application to liquid water. *J. Chem. Phys.*, **101**, 6141 (1994).

[15] W.J. Mortier, S.K. Gosh, S. Shankar. Electronegativity equalization method for the calculation of atomic charges in molecules. *J. Am. Chem. Soc.*, **108**, 4315 (1986).

[16] A.K. Rappé, W.A. Goddard. Charge equilibration for molecular dynamic simulations. *J. Phys. Chem.*, **95**, 3358 (1991).

[17] R.T. Sanderson. An interpretation of bond lengths and classification of bonds. *Science*, **114**, 670 (1951).

[18] R.G. Parr, W. Yang. *Density-Functional Theory of Atoms and Molecules*, Oxford University, Oxford (1989).

[19] C.G. Gray, K.H. Gubbins. *Theory of Molecular Fluids*, Clarendon Press, Oxford (1984).

[20] K.P. Huber, G. Herzberg. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold (1979).

[21] R.F.W. Bader. *Atoms in Molecules—A Quantum Theory*, Oxford University Press, Oxford (1990).

[22] G. Kresse, J. Furthmüller. Efficiency of *ab initio* total energy calculations for metals and semiconductors using a plane—wave basis set. *Comput. Mat. Sci.*, **6**, 15 (1996).

[23] J.-B. Maillet, E. Bourasseau, V. Recoules. *Ab Initio* molecular dynamic study of liquid hydrogen fluorine under pressure, accepted to *Phys. Rev. B*.

Downloaded At: 18:20 14 January 2011