

Ionic Charge Reduction and Atomic Partial Charges from First-Principles Calculations of 1,3-Dimethylimidazolium Chloride

Jochen Schmidt,^{†,‡} Christian Krekeler,^{†,‡} Florian Dommert,^{†,§} Yuanyuan Zhao,[†]
Robert Berger,^{†,||} Luigi Delle Site,[‡] and Christian Holm^{*,§}

Frankfurt Institute for Advanced Studies (FIAS), Johann Wolfgang Goethe-Universität, Ruth-Moufang-Str. 1, D-60438 Frankfurt am Main, Germany, Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany, Institute for Computational Physics, Universität Stuttgart, Pfaffenwaldring 27, D-70569 Stuttgart, Germany, and Clemens-Schöpf Institute for Organic Chemistry and Biochemistry, TU Darmstadt, Petersenstr. 22, D-64287 Darmstadt, Germany

Received: November 12, 2009; Revised Manuscript Received: March 12, 2010

We present a detailed calculation of partial charges for the 1,3-dimethylimidazolium chloride ionic liquid. We first analyze MP2 electronic structure calculations and DFT results on isolated ion pairs with various methods of assigning partial charges to the atomic centers. In a second run we analyze the trajectory of a 25 ps long Car–Parrinello MD run of 30 ion pairs under bulk conditions using a charge fitting procedure due to Blöchl. Both, the single ion pair and the bulk system, provide us with a similar total ionic charge considerably less than unity. Especially the liquid state DFT results give convincing evidence for a reduced ionic charge on the ions. The similarity of both results suggest that the delocalization of the Cl charge is due only to local interactions. The relevance of our results is 2-fold; on the one hand they shed light on the basic property of the liquid and its reduced ionic character, and on the other hand, the ab initio derived partial charges provide a fundamental theoretical basis for the recent attempts to use the total ionic charge as an adjustable parameter. Furthermore, all our partial charges are subject to large fluctuations, hinting to the importance of polarization effects.

I. Introduction

In recent years room temperature ionic liquids (IL) have enjoyed an enormous increase in attention. This is due to the fact that ILs are considered as green solvents with an almost vanishing vapor pressure, and they are potential designer solvents for many applications such as catalysis, battery solvents, and fuel cells, just to name a few. From a physical point of view, ILs are molten salts with a melting point below 373 K, that often consist of bulky organic cations and anions. A commonly used compound for an IL is a combination of an imidazolium-based cation containing a methyl group at one of the nitrogens and a long alkyl side chain at the other nitrogen. The properties of such ILs can be changed just by varying the alkyl chain length, therefore this allows for the first possibility to “tune” the solvent. Another way to influence the properties of the solvent is the choice of the anion. Mostly they are heteroatomic, such as BF_4^- , Tf_2N , or SCN , to give just a few examples. Several reviews have appeared recently.^{1–10} Although experiments are conducted for a large variety of such substances and properties, theoretical work is so far restricted to a modest amount of computer simulations. Most of the models available do not provide a complete satisfying description of both, the static and the dynamic properties of the system. Therefore, the development of better force fields is up to now a major open problem. However, ionic liquids have been studied theoretically from an ab initio point of view,^{11–19} and via many classical

molecular dynamics (MD) simulations in the past years (see e.g., refs 20–27). The classical MD approaches employed various kinds of force fields,^{22,28,29} including polarizable ones,³⁰ and multiscale coarse-graining models.³¹ A common conclusion from these studies is that the dynamics of the ILs are consistently too slow in the simulations.^{32,33} It has been argued^{22,20,34,35} that nonequilibrium molecular dynamics methods are better suited to obtain the diffusive motion and that they reach the true diffusive behavior faster than equilibrium simulations. Also, some arguments favor polarizable force fields, that is, Voth et al.³² found a much faster diffusive behavior by a factor of 3 compared with the nonpolarizable model, because of the additional screening mechanism in the former model that reduces the cage effect responsible for trapping ions in a local cage.

A possible solution for standard nonpolarizable force fields consists of an overall charge scaling of the atomistic partial charges, resulting in an ionic charge deviating from ± 1 e. This speeds up the dynamical behavior of the liquid because of the lower electrostatic binding. Such a practical solution has been used already in the study of polymer electrolytes³⁶ and has been implemented for ionic liquid force fields by several groups.^{20,26,37–39} Still, there has been so far no clear motivation for reducing the charges, except the attitude to treat the overall ionic charge as another degree of freedom for the force-field.

Kossmann et al.¹⁹ calculated [DMIM][Cl] clusters with second-order Møller–Plesset perturbation theory (MP2) and density functional theory (DFT) techniques, and obtained from an extrapolation to infinite clusters also a reduced charge of the chloride of about -0.823 e. Bühl et al.¹⁶ have presented an ab initio MD simulation of [DMIM][Cl] followed by a Mulliken population analysis. They found a charge between -0.7 and -0.8 e for the chloride. However, the shortcomings of methods

* To whom correspondence should be addressed. E-mail: holm@icp.uni-stuttgart.de.

[†] Johann Wolfgang Goethe-Universität.

[‡] Max Planck Institute for Polymer Research.

[§] Universität Stuttgart.

^{||} Clemens-Schöpf Institute for Organic Chemistry and Biochemistry.

such as Mulliken or natural population analysis (NPA) are known and have been investigated extensively.⁴⁰ Their dependence on the basis set was the main reason for the development of other methods, which are based on the fitting of the electrostatic potential (ESP) in the vicinity of a molecule. Typically, methods such as CHELPG⁴¹ or RESP⁴² are employed when assigning partial atomic charges for a classical force field. In such a procedure, the potential at some points around the molecule are chosen and atomic charges are adjusted such as to reproduce the ESP. Of course, points that are too close to the molecule have to be excluded, because a simple point charge cannot replace a charge density when approaching the respective atom. Therefore, these methods become insufficient when switching from isolated molecules to the bulk. The question then of what points to exclude cannot be answered straightforwardly. Another possibility is to use a Bader analysis,⁴³ which uses zero-flux surfaces to divide atoms. This is also straightforward for ion pairs but becomes increasingly more tedious when one wants to apply it to a bulk system. We will present in the forthcoming an analysis of the atomic partial charges in the bulk for [DMIM][Cl] using a method that has been proposed by Blöchl.⁴⁴ It is based on an analysis of the reciprocal space charge density and thus does not require the exclusion of any real space points. Therefore, it is perfectly suitable for a calculation under periodic boundary conditions.

The article is structured as follows. First we describe in some detail the Blöchl method of fitting partial charges. Then we apply it to the case of a single ion pair where the electron density was obtained with various methods like MP2 and DFT functionals and then compare the various methods for fitting partial charges. Subsequently, we analyze 100 snapshots obtained from a 25 ps long CPMD run on 30 ion pairs and discuss the implications of the obtained partial charges and the observed fluctuations for possible force fields. We conclude our paper with a summary of the most important findings and give an outlook for further studies.

II. Theoretical Background and Technical Details

The basic idea of the derivation of atomic point charges following the method introduced by Blöchl⁴⁴ is that the interaction between separated charge densities can be expressed entirely through their multipole moments. The complete procedure, which originally was invented for electrostatic decoupling of periodic images within a plane-wave based density functional theory (DFT) code, is described in the above-cited paper. We will only summarize the fundamental ideas here.

In a plane-wave-based calculation the charge density $n(\mathbf{r})$ is always present in both real and inverse space, because the electrostatic interactions under periodic boundary conditions can efficiently be treated in the reciprocal representation. It can easily be shown that all multipole moments of a charge density can be expressed in reciprocal space by the value and all derivatives of the charge density at the reciprocal lattice vector $\mathbf{G} = 0$. The difficulties when evaluating atomic partial charges usually arise from the fact that the basis functions cannot easily be assigned to a certain atom. Therefore, we introduce a model charge density \tilde{n} , which is composed of Gaussian functions $g_i(\mathbf{r})$, centered at each atomic site

$$\tilde{n}(\mathbf{r}) = \sum_i q_i g_i(\mathbf{r}) \quad (1)$$

To describe the interactions of the original density $n(\mathbf{r})$ with surrounding charges correctly, its multipole moments have to

be reproduced by \tilde{n} . This can be achieved by fitting the reciprocal density in the vicinity of $\mathbf{G} = 0$. The respective parameters of the model density, the q_i values, are obtained from the extremal condition of

$$F(q_i, \lambda) = \frac{V}{2} \sum_{\mathbf{G} \neq 0} w(\mathbf{G}) |n(\mathbf{G}) - \sum_i q_i g_i(\mathbf{G})|^2 - \lambda [n(\mathbf{G} = 0)V - \sum_i q_i g_i(\mathbf{G} = 0)V] \quad (2)$$

where $w(\mathbf{G})$ is a weighting function that rapidly decays for increasing \mathbf{G} , V is the volume of the simulation cell, and λ is a Lagrangian multiplier. The $\mathbf{G} = 0$ term is treated separately in order to avoid convergence problems of the weighting function. The degree of freedom for fitting the model density is introduced by using several Gaussians with different decay length r_c at each atomic site. After optimizing the model density, the desired atomic partial charges can be obtained by summing all respective q_i values for the considered atom. Because the actual fitting is carried out in the reciprocal space, this method is well suited for bulk systems, which are usually simulated under periodic boundary conditions. The arbitrary exclusion of real space points, necessary in other methods, is obsolete here, leading to a much more controllable procedure.

It has been shown by Blöchl that 3–4 Gaussians per site lead to very accurate results for the charges. The minimum decay length should be $0.5a_0 - 1a_0$, the decay length of the other Gaussians are obtained by multiplying the previous length with a progression factor of 1.5. That means that if the smallest length is r_0 , the second one is $1.5r_0$, etc. We have checked explicitly that for H₂O the atomic charges from the Blöchl method agree with standard approaches, such as RESP or CHELPG, within 1%.

Wherever in this work we report results from a fit of the atomic charges with the Blöchl method, we use 4 Gaussians per atomic site. The smallest one has a decay length of $0.5a_0$, the progression factor for the other decay lengths is 1.5. The weighting function is $w(\mathbf{G}) = 4\pi(\mathbf{G}^2 - G_c^2)^2/(\mathbf{G}^2 G_c^2)$ for $|\mathbf{G}| < G_c$ and zero elsewhere. The cutoff $G_c^2/2$ is $3.5E_h$ (7 Ry). It has been shown that the atomic charges are not very sensitive to the cutoff, if set to a value higher than $1.5E_h$ (3 Ry).⁴⁴

For testing purposes, we have used one isolated ion pair of [DMIM][Cl] in the four equilibrium structures shown in Figure 1. These are the same as presented in our previous publication.⁴⁵ The partial charges have been evaluated using the MP2 density (with the core electrons frozen) obtained with an aug-cc-pVTZ basis set (for details see ref 45), employing RESP and CHELPG (for details see refs 41, 42). Furthermore, the density from DFT approaches obtained with the same basis set using the BP86 functional^{46,47} and the PBE functional⁴⁸ was employed within the CHELPG, RESP, and the Bader method. Coupled cluster singles and doubles densities (with core electrons kept frozen) were also employed (using the aug-cc-pVDZ basis set). For these purposes we have used the programs Gaussian⁴⁹ and Bader.^{50–52}

Throughout this work the following parameters have been used for all DFT calculations in combination with the Blöchl method. We have used the quantum chemical program package CP2K,⁵³ especially its DFT module, called QUICKSTEP. We employed the GPW method⁵⁴ with periodic boundary conditions. The Blöchl approach is applicable only for periodic boundary conditions, and hence cannot simulate a truly isolated pair, in contrast to the MP2 methods presented in the result section.

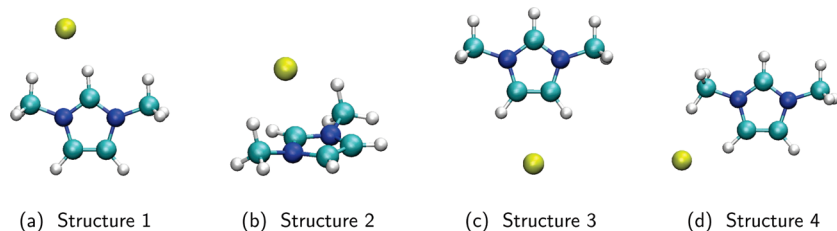


Figure 1. Four structures of an isolated [DMIM][Cl] ion pair, taken from 45.

TABLE 1: Partial Charges (in e) of the Cl in the Four Structures Shown in Figure 1 Derived from MP2, BP86, and PBE with aug-cc-pVTZ Basis Set Using CHELPG (C) and RESP (R), Bader Analysis (Ba), and from the Plane-Wave Blöchl (Bl) Method Presented Here with the PBE Functional

structure	MP2 - C	MP2 - R	MP2 - Ba	BP86 - C	BP86 - R	BP86 - Ba	PBE - C	PBE - R	PBE - Ba	PBE - Bl
1	-0.74	-0.74	-0.85	-0.70	-0.70	-0.80	-0.70	-0.70	-0.80	-0.68
2	-0.71	-0.72	-0.81	-0.64	-0.65	-0.73	-0.64	-0.65	-0.72	-0.63
3	-0.85	-0.85	-0.91	-0.80	-0.80	-0.86	-0.80	-0.80	-0.86	-0.80
4	-0.78	-0.79	-0.86	-0.74	-0.74	-0.82	-0.73	-0.74	-0.81	-0.73

However, the cell has been chosen sufficiently large to avoid interactions with the next images, which has been tested by monitoring the energy. For these calculations the cell size was 12 Å in all directions. We employed the PBE exchange-correlation functional⁴⁸ in combination with the norm-conserving pseudopotentials of Goedecker and co-workers.⁵⁵ The Gaussian basis set was a triple- ζ valence basis set augmented with two sets of d-type or p-type polarization functions (TZV2P); the density cutoff was $140E_h$.

The partial charges for bulk [DMIM][Cl] have been obtained from Blöchl calculations performed for 100 snapshots, which have been randomly chosen from a long MD trajectory of 30 ion pairs under periodic boundary conditions. Although the number of ion pairs might still appear to be too small to call this system bulk, the observed radial distribution functions have decayed already sufficiently fast, and the electrostatic interactions are screened after essentially the first shell,⁵⁶ so that this wording is justified. The dynamical and static properties that can be extracted from this simulation will be presented elsewhere.⁵⁷ In this work we will concentrate only on the atomic partial charges and discuss the resulting ionic charge. The MD simulations have been carried out using the following settings. A configuration, provided by classical MD, was taken as an input configuration for a Car–Parrinello MD simulation, using the CPMD software package.⁵⁸ We employed the plane-wave pseudopotential approach, with an energy cutoff of $35E_h$ (70 Ry) and the PBE exchange-correlation functional.⁴⁸ The simulation of 30 [DMIM]Cl in a cubic box with the box length of 18.05 Å, was carried out at 425 K with a fictitious electron mass of $600m_e$, and a time step of $4\hbar E_h^{-1/2}$ has been applied. After 5 ps of equilibration, data was collected for 25 ps for the analysis.

III. Results and Discussion

A known issue of many commonly used exchange-correlation functionals in DFT is that they tend to overestimate delocalization of electrons under certain circumstances.^{59–61} This has been attributed to the self-interaction error (SIC) present in common DFT calculations. Correction schemes are available, but most of them are computationally very expensive and their accuracy can hardly be estimated for generic systems.^{62–64} Therefore, we tested our approach on a system containing only one isolated ion pair in order to assess the quality of the DFT representation of the density.

The test systems were the four geometries of a [DMIM][Cl] ion pair as taken from ref 45 and depicted in Figure 1. We calculated the atomic partial charges for all structures with an MP2 approach, as well as with DFT using the BP86 and the PBE functional. No periodic boundaries are used when we applied the CHELPG, the RESP, and the Bader method. Only for the case of the Blöchl approach we were forced to use periodic boundary conditions, see previous section. Force field approaches have recently used ionic charges of about $\pm 0.8 e$, therefore we explicitly look at the Cl charge. The results are shown in Table 1. RESP and CHELPG give almost identical results for all investigated cases, which is simply a consequence of their conceptual similarity. The two DFT results, again, do not differ too much from each other, meaning that both functionals lead to a similar density and they demonstrate that the charges derived from the Blöchl method agree with those from CHELPG and RESP. It is noteworthy that the Bader method consistently yields about 15% larger partial charges when compared to RESP or CHELPG. We are left, however, with the remarkable fact that even MP2 leads to a partial charge on the Cl which is significantly larger than $-1 e$. This means, that a single ion interacts with its surroundings as if the ionic charges are scaled to about 70–80% of their “physical” values. Thus, the idea of a reduced ionic charge for the classical MD simulation of such a liquid seems to be justified. The deviation between partial charges from MP2 and nonhybrid (pure) density functionals is for the structures **1**, **3**, and **4** about 6%, for the π -complexed structure **2** we find about 12%. We assume this to be the typical error due to the overestimation of the delocalization in nonhybrid functionals. Indeed, coupled cluster singles and doubles (CCSD) partial charges, obtained with the smaller aug-cc-pVDZ basis set, deviate by less than 2% from the MP2 data (e.g., CCSD-CHELPG for structures **1–4**: $-0.75 e$, $-0.72 e$, $-0.86 e$, $-0.79 e$) and hybrid density functionals with significant Fock exchange contribution (such as BHandHLYP) give rise to partial charges similar to MP2 and CCSD (e.g., BHandHLYP-CHELPG for structures **1–4**: $-0.74 e$, $-0.71 e$, $-0.86 e$, $-0.78 e$).

Still, one ion pair cannot be considered representative for the bulk. We have recently published results on quantum chemical calculations that investigate clusters of up to eight ion pairs, showing that there is a significant effect on the electrostatic properties, where the dipole and quadrupole moments were investigated.⁴⁵ We therefore investigated a much larger system size in a periodic environment to obtain reliable information

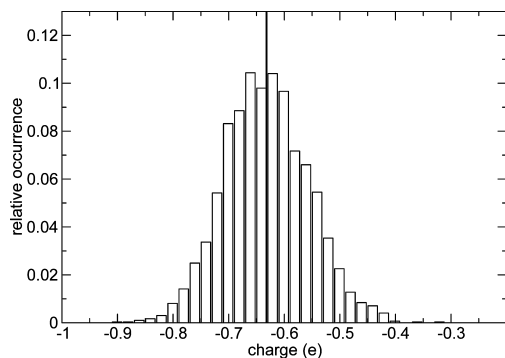


Figure 2. Partial charges for Cl, obtained from a sampling over 100 snapshots. The black line indicates the average.

about the bulk behavior. As mentioned before, the Blöchl method naturally qualifies for such a task, because it is based on the reciprocal space density, which is naturally available in a simulation with periodic boundary conditions. We have conducted a long MD simulation of 30 ion pairs for about 25 ps and extracted 100 snapshots from the production part of the CPMD trajectory. For these snapshots we calculated the partial charges with the Blöchl method.

First, the atomic partial charges of the Cl ion will be presented, because they directly allow an assessment of the overall charge scaling. Figure 2 presents the charges obtained from the snapshots. We find a rather broad distribution that is centered around $-0.63 e$ with a rmsd of $0.08 e$. The bulk simulations indeed yield a similar picture as suggested by the isolated ion pair. The effective charge located on the cation and anion is only about $\pm 0.63 e$. For completeness, we also performed another Bader analysis on 10 snapshots produced by the CPMD runs, where we took the atomic coordinates of the unit cell and discarded the periodic images (thereby considering a cluster in the gas phase). The electron density was produced using the PBE functional with a smaller triple- ζ basis set augmented by polarization functions (TZVP). The average Cl charge we obtained from this analysis was about $-0.82 e$. With nonhybrid functionals such as PBE the HOMO–LUMO gap for these clusters becomes extremely small, rendering the SCF calculation difficult to converge. Thus, chlorine atoms at the surface with charges deviating significantly from $-1 e$ were excluded from the analysis. We find the same feature as before namely that the Bader analysis gives a larger value for the partial charge. However, this value is very close to the value we obtained for the isolated pair, and also the ratio of the Blöchl charge to the Bader charge is roughly the same.

Our results suggest the following scenario. First, there is an apparent charge redistribution between the electronic orbitals, due to electron delocalization. So there is a sound physical reason why one should not take integer electronic charges for the ions. This is seen in high level electronic structure calculations, but also comes out of our employed DFT studies, although nonhybrid functionals overemphasize the trend by about 10%. Whereas the CHELPG, RESP, and Blöchl method give all very similar values, the Bader analysis consistently gives a somewhat smaller delocalized charge.

Our second finding is even more interesting, since we observed only small differences between an isolated ion pair and a bulk-like system. This suggests that charge delocalization is a very local effect, and, surprisingly for the partial charges, do not depend very much on the ionic environment of other ions. What we observe, however, is a significant spread of the calculated partial charge, it depends very much on the environ-

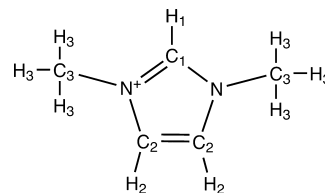


Figure 3. The dimethylimidazolium cation with the numbering scheme used in this work.

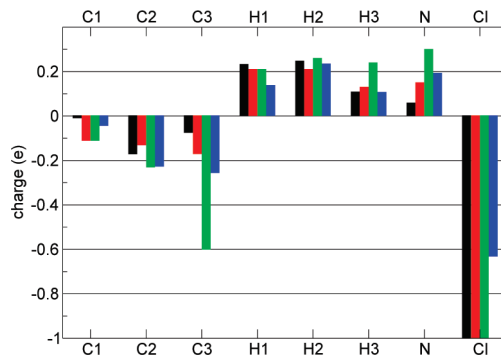


Figure 4. Partial charges for [DMIM][Cl] obtained via different ways. Charges from Wang et al. are black, those from Lopes et al. are red, this work with a static calculation of the single cation is green, and the dynamic Blöchl calculation is drawn in blue. The numbering scheme is introduced in Figure 3.

ment for each single snapshot, but yields a similar average value as for the ground state structure. This feature has also been observed when analyzing the dipole moments obtained from our long CPMD run.⁵⁷

One should keep in mind here that our Blöchl fitting procedure is designed to find atomic partial charges in order to reproduce the interaction with another, separated, charge density. Similar to the methods using the electrostatic potential at some points in space, we can only report the partial charges “as seen from outside”. Still, this can give valuable information for a model of these liquids with classical force fields. Obviously, the cation and anion—from other cations’ and anions’ point of view—interact as if they only had a reduced net charge.

Of course, the charge fitting procedure not only yields results for the Cl ion, but also for all other atoms. We present the optimized partial charges from the bulk calculation in Figure 4. The respective numbering scheme is shown in Figure 3. For comparison, we also provide the partial charges from two commonly employed force fields, namely the one from Lopes et al.²⁸ and the force field of Wang et al.²⁹ as well as a static calculation of an isolated cation, optimized on the DFT level, with the Blöchl approach. Obviously, even the three static methods yield very different results. This can most likely be attributed to the different quantum chemical methods that have been used. Still, Lopes and Wang force fields have been shown to result in comparable properties of the simulated bulk,³³ while the partial charges exhibit significant differences (Table 2). The dynamical scheme is the only one that provides a total ionic charge smaller than $\pm 1 e$, resulting in a charge distribution that can hardly be compared to the other models. Still, the proton charges are comparable to the static calculations (only H₁ shows a significant reduction), whereas the carbon charges show large deviations. Compared to the force field of Lopes et al., we find a much smaller charge for C₁. This could lead to an increased affinity for hydrogen bonds at the H₁ site, which has actually been shown to be too low for Lopes.¹¹ In the Wang force field this respective charge is even smaller. The methyl carbon C₃

TABLE 2: Partial Charges (in e) for [DMIM][Cl]^a from the Lopes et al.²⁸ and the Wang et al.²⁹ Force Fields, along with Our Results Obtained from a Static Calculation on a Single Cation, and the Blöchl Analysis of the CPMD Run^a

atom	q^{Lopes}	q^{Wang}	q^{static}	q^{MD}	Δq^{MD}
H ₁	0.21	0.2329	0.21	0.138	0.103
H ₂	0.21	0.2476	0.26	0.235	0.107
H ₃	0.13	0.1085	0.24	0.107	0.111
C ₁	-0.11	-0.0083	-0.11	-0.043	0.164
C ₂	-0.13	-0.1705	-0.23	-0.226	0.171
C ₃	-0.17	-0.074	-0.60	-0.255	0.274
N	0.15	0.0591	0.30	0.193	0.166
Cl	-1.0	-1.0	-1.0	-0.631	0.075

^a The numbering scheme is introduced in Figure 3. ^a Δq^{MD} is the RMSD over the 100 snapshots.

exhibits the broadest distribution of the partial charges, possibly due to its dynamics and the mobility of the attached H₃ protons. In general, the cationic atoms' charge rmsd is much larger than in the case of the anion, which can be explained by the more flexible electron structure, that is, there are simply more electrons that are less strongly bonded than in Cl.

In principle, our procedure, using a Blöchl fit on a bulk like system can provide atomic partial charges for classical force fields that are consistent with the electrostatic potentials as seen by a test charge at some distance. Consistent for us also means, that the parameters used for a bulk simulation have also been obtained from an ab initio calculation (here DFT) at this level and not only from an isolated molecule. Our results clarify why a scaling down of the partial charges in classical force fields to noninteger values might improve the comparison to experiments. In general, such results underline once more the peculiar character of ionic liquids and the connections between the various scales entering into the problem. The local redistribution of the charges with a delocalization away from the Cl ion due to the immediate surrounding by other ions is characterized by high fluctuations that do occur on the long time scale of all the possible local structural realizations. These in turn do depend on the overall structure of the liquid. There appears no convenient, immediate remedy available for a consistent description of such systems, what is needed is a model that includes these electron-based features but at the same time allows for large and long simulations.

IV. Conclusions

We have presented an analysis of the partial atomic charges of [DMIM][Cl] based on an ab initio MD simulation of ground-state structures of one isolated ion pair and, more importantly, on 30 ion pairs under bulk-like conditions. Using the Blöchl method, that is a reciprocal space approach for the evaluation of the charges, we can directly assess the behavior of the ions in the liquid state, unlike other methods. We show on the one ion pair level that this method yields results that agree well with the standard procedures, such as RESP or CHELPG. An additionally performed Bader analysis gives consistently larger partial charges when compared to the previous methods, largely independent of the quantum chemical method used to determine the electron density and of the case of an isolated pair or the bulk-like structure.

Additionally, we have investigated the influence of DFT on the partial charges and find that, compared to MP2, standard nonhybrid (pure) exchange-correlation functionals tend to overestimate the delocalization of the charge. We find ionic charges that are 6–12% smaller than in MP2 (and CCSD)

calculations. Our analysis of the bulk reveals an average partial ionic charge of $\pm 0.63 e$ in the bulk when using the Blöchl method. Our analysis supports the idea of using the overall charge as another fitting parameter in classical force fields describing ionic liquids, since a reduction of the ionic charge will accelerate the dynamics. The unique feature of our approach is that the Blöchl fitting can provide partial charges for all atoms of the compound from a DFT bulk simulation, and therefore allows to evaluate the respective parameters for a force field from first principles without being restricted to isolated molecules. Another important finding of our study is the large fluctuations observed in basically all partial atomic charges. This is something a standard classical force field cannot reproduce, and would suggest that polarizability might be an important feature for describing accurately ILs. However, it is a priori not clear which observables would benefit first from the polarizability, since a reduction in ionic charge might already be sufficient to accelerate the dynamics, and give a better agreement between classical force field simulations and experimental results. As a word of care we stress that to construct a usable new force field based on Blöchl charges requires a reparametrization of the short-range forces, which is beyond the scope of the present article. This and the question if our Blöchl partial charges lead to an improved description of [DMIM][Cl] will be studied in future investigations, see ref 65 for a first step into that direction. Beyond the strictly methodological indications for theory, these results also suggest a possible way to tune macroscopic liquid properties. For example, by varying the electronegativity one may tune the amount of charge delocalization, while changing the ionic shape gives control on the possible local structural realization and thus possible control over the fluctuations that in turn are responsible for the dielectric properties. In this sense this study may open up a possible route to an in silico design of material properties. Here we provide the first step into this direction.

Acknowledgment. We would like to thank the Deutsche Forschungsgemeinschaft (DFG) for the funding of our project within the SPP 1191. Computer time was obtained through the Frankfurt Center for Scientific Computing (CSC) and the computer center of the MPG in Garching.

References and Notes

- (1) Popolo, M. G. D.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108* (5), 1744–1752.
- (2) Weingärtner, H. *Angew. Chem., Int. Ed.* **2007**, *47* (4), 654–670.
- (3) Hunt, P. A. *Mol. Simul.* **2006**, *32*, 1–10.
- (4) Earle, M. J.; Seddon, K. R.; Abraham, M. A.; Moens, L. *Clean Solvents, ACS Symp. Ser.* **2002**, *819*, 10–25.
- (5) Böwing, A. G.; Jess, A.; Wasserscheid, P. *Chem. Ing. Tech.* **2005**, *77* (9), 1430.
- (6) Sheldon, R. A.; Lau, R. M.; Sorgedragar, M. J.; van Rantwijk, F.; Seddon, K. R. *Green Chem.* **2002**, *4*, 147–151.
- (7) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772–3789.
- (8) Wasserscheid, P.; Welton, T. Eds. *Ionic Liquids in Synthesis*; Wiley-VCH: 2002.
- (9) Baudequin, C.; Brégon, D.; Levillain, J.; Guillen, F.; Plaquevent, J.-C.; Gaumont, A.-C. *Tetrahedron: Asymmetry* **2005**, *16*, 3921–3945.
- (10) Ding, J.; Armstrong, D. W. *Chirality* **2005**, *17*, 281–292.
- (11) Bhargava, B. L.; Balasubramanian, S. *Chem. Phys. Lett.* **2006**, *417*, 486–491.
- (12) Popolo, M. G. D.; Lynden-Bell, R. M.; Kohanoff, J. *J. Phys. Chem. B* **2005**, *109* (12), 5895–5902.
- (13) Hunt, P. A.; Kirchner, B.; Welton, T. *Chem.—Eur. J.* **2006**, *12* (26), 6762–6775.
- (14) Zahn, S.; Bruns, G.; Thar, J.; Kirchner, B. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6921–6924.
- (15) Zahn, S.; Uhlig, F.; Thar, J.; Spickermann, C.; Kirchner, B. *Angew. Chem., Int. Ed.* **2008**, *41*, 3639–3641.

- (16) Bühl, M.; Chaumont, A.; Schurhammer, R.; Wipff, G. *J. Phys. Chem. B* **2005**, *109* (39), 18591–18599.
- (17) Hanke, C. G.; Price, S.; Lynden-Bell, R. M. *Mol. Phys.* **2001**, *99* (10), 801.
- (18) Ludwig, R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4333–4339.
- (19) Koßmann, S.; Thar, J.; Kirchner, B.; Hunt, P. A.; Welton, T. *J. Chem. Phys.* **2006**, *124*, 174506.
- (20) Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B* **2002**, *106*, 12807–12813.
- (21) Urahata, S. M.; Ribeiro, M. C. C. *J. Chem. Phys.* **2005**, *122* (2), 024511.
- (22) Micaelo, N. M.; Baptista, A. M.; Soares, C. M. *J. Phys. Chem. B* **2006**, *110*, 14444–14451.
- (23) Liu, X.; Zhou, G.; Zhang, S.; Wu, G.; Yu, G. *J. Phys. Chem. B* **2007**, *111* (20), 5658–5668.
- (24) Zhou, G.; Liu, X.; Zhang, S.; Yu, G.; He, H. *J. Phys. Chem. B* **2007**, *111* (25), 7078–7084.
- (25) Sieffert, N.; Wipff, G. *J. Phys. Chem. B* **2007**, *111* (25), 7253–7266.
- (26) Zhao, W.; Eslami, H.; Cavalcanti, W. L.; Müller-Plathe, F. Z. *Phys. Chem.* **2007**, *221*, 1647–1662.
- (27) Köddermann, T.; Paschek, D.; Ludwig, R. *ChemPhysChem* **2007**, *8* (17), 2464–2470.
- (28) Canongia Lopes, J. N.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110* (39), 19586–19592.
- (29) Liu, Z. P.; Huang, S. P.; Wang, W. C. *J. Phys. Chem. B* **2004**, *108* (34), 12978–12989.
- (30) Yan, T.; Li, S.; Jiang, W.; Gao, X.; Xiang, B.; Voth, G. A. *J. Phys. Chem. B* **2006**, *110* (4), 1800–1806.
- (31) Wang, Y.; Voth, G. A. *J. Phys. Chem. B* **2006**, *110* (37), 18601–18608.
- (32) Yan, T.; Burnham, C. J.; DelPopolo, M. G.; Voth, G. A. *J. Phys. Chem. B* **2004**, *108* (32), 11877–11881.
- (33) Dommert, F.; Schmidt, J.; Qiao, B.; Zhao, Y.; Krekeler, C.; Delle Site, L.; Berger, R.; Holm, C. *J. Chem. Phys.* **2008**, *129* (22), 224501.
- (34) Cadena, C.; Zhao, Q.; Snurr, R. Q.; Maginn, E. J. *J. Phys. Chem. B* **2006**, *110* (6), 2821–2832.
- (35) Kelkar, M. S.; Maginn, E. J. *J. Phys. Chem. B* **2007**, *111* (18), 4867–4876.
- (36) Müller-Plathe, F.; van Gunsteren, W. *J. Chem. Phys.* **1995**, *103*, 4745.
- (37) Bhargava, B. L.; Balasubramanian, S. *J. Chem. Phys.* **2007**, *127* (11), 114510.
- (38) Youngs, T. G. A.; Hardacre, C. *ChemPhysChem* **2008**, *9* (11), 1548–1558.
- (39) Sieffert, N.; Wipff, G. *J. Phys. Chem. B* **2006**, *110*, 13076.
- (40) Martin, F.; Zipse, H. *J. Comput. Chem.* **2004**, *26* (1), 97–105.
- (41) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11* (3), 361–373.
- (42) Bayly, C. I.; Cieplak, P.; Cornell, W. D.; Kollman, P. A. *J. Phys. Chem.* **1993**, *97*, 10269–10280.
- (43) Bader, R. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: 1990.
- (44) Blöchl, P. E. *J. Chem. Phys.* **1995**, *103*, 7422–7428.
- (45) Krekeler, C.; Schmidt, J.; Zhao, Y. Y.; Qiao, B.; Berger, R.; Holm, C.; Delle Site, L. *J. Chem. Phys.* **2008**, *129* (17), 174503.
- (46) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (47) Perdew, J. P. *Phys. Rev. B* **1986**, *33* (12), 8822–8824.
- (48) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (49) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P.; Morokuma, Y. K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, version 02*; Gaussian, Inc.: Wallingford, CT, 2004.
- (50) Henkelman, G.; Arnaldsson, A.; Jónsson, H. *Comput. Mater. Sci.* **2006**, *36*, 254–360.
- (51) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. *J. Comput. Chem.* **2007**, *28*, 899–908.
- (52) Tang, W.; Sanville, E.; Henkelman, G. *J. Phys.: Condens. Matter* **2009**, *21*, 084204.
- (53) Hutter J. Computer code CP2K, 2000–2008. <http://cp2k.berlios.de>.
- (54) Lippert, G.; Hutter, J.; Parrinello, M. *Mol. Phys.* **1997**, *92* (3), 477–487.
- (55) Goedecker, S.; Teter, M.; Hutter, J. *Phys. Rev. B* **1996**, *54*, 1703.
- (56) Lynden-Bell, R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1733–1740.
- (57) Krekeler, C.; Schmidt, J.; Dommert, F.; Zhao, Y. Y.; Berger, R.; Holm, C.; Delle Site, L. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1817–1821.
- (58) CPMD, <http://www.cpmid.org/>, Copyright IBM Corp. 1990–2008; Copyright MPI für Festkörperforschung Stuttgart, 1997–2001.
- (59) Lægsgaard, J.; Stokbro, K. *Phys. Rev. Lett.* **2001**, *86* (13), 2834–2837.
- (60) Mallia, G.; Orlando, R.; Roetti, C.; Ugliengo, P.; Dovesi, R. *Phys. Rev. B* **2001**, *63* (23), 235102.
- (61) Pacchioni, G.; Frigoli, F.; Ricci, D.; Weil, J. A. *Phys. Rev. B* **2000**, *63* (5), 054102.
- (62) Perdew, J. P.; Zunger, A. *Phys. Rev. B* **1981**, *23* (10), 5048–5079.
- (63) VandeVondele, J.; Sprik, M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1363–1367.
- (64) d’Avezac, M.; Calandra, M.; Mauri, F. *Phys. Rev. B* **2005**, *71*, 205210.
- (65) Dommert, F.; Schmidt, J.; Krekeler, C.; Zhao, Y. Y.; Berger, R.; Delle Site, L.; Holm, C. *J. Mol. Liq.* **2010**, *152*, 2–8.

JP910771Q