**Point-by-Point Reply**

*Our responses are given in red below, whereas changes made to the manuscript are given in blue in the revised version.*

Reviewer 1 Comments:   
  
This manuscript evaluates the performance of the effective fragment potential for the intermolecular interactions in ionic liquids by comparing the results term by term to results from symmetry adapted perturbation theory (SAPT). The authors employ two model IL families based on imidazolium and pyrrolidinium based cations with eight different anions. Overall, this is a paper that presents interesting insights and should be suitable for publication after the issues below have been addressed:   
  
The most important issue to be addressed is the term-by-term comparison. As stated by the authors in pp. 10 "Polarization in EFP is analogous to induction in SAPT with one exception. The SAPT induction term also contains the charge-transfer energy ..."   
Thus, SAPT does not separate the charge transfer, e.g. JCP, 140, 094106, 2014. Therefore, the one-to-one comparison for each of the second order terms is slightly misleading. Especially since there is not one single way to decompose the energy and EFP is based on a variational decomposition (not perturbational). Therefore, it is recommended that the authors also compare the sum of the polarization and charge transfer from EFP to induction from SAPT, as well as provide a more thorough explanation of the errors in the total intermolecular interaction energy 

# This is an important point raised. The reason for why the sum of the polarization and charge transfer terms from EFP were not directly compared to the SAPT induction comes from the fundamental difference in definitions of the charge-transfer energy. In SAPT, charge transfer is included as part of induction and is basis set dependent, vanishing in the complete basis set limit. In contrast, induction does not depend on basis set.

In the few cases (mainly halides) that we managed to run SAPT2+3 with the aug-cc-pVTZ basis set, it was established that the SAPT Induction interaction changed only marginally going from AVDZ to AVTZ (< 1 kJ mol-1 on average). In the same series of calculations, the CT decreased by 8 kJ mol-1 on average. It has to be noted that the CT energy is -7 kJ mol-1 on average for other typical ionic liquid anions as calculated with the aug-cc-pVDZ, suggesting that it would fall below chemical accuracy with increasing basis set. In contrast, the trend in the CT energy from EFP goes in the opposite direction increasing from 2 kJ mol-1 with AVDZ to 7 kJ mol-1 with AVTZ. We believe that the difference in behaviour of the CT energy with increasing basis set warrants for exclusion of the CT energy from the induction term.

To further clarify this point we have modified the text on page 13 (shown in blue in the revised manuscript):

“It has to be pointed out that due to the difference in the definitions of charge transfer in the EFP and SAPT approaches the EFP polarization term was directly compared to the SAPT induction without inclusion of the CT energy.”

-The authors neglect to cite several potentials for ionic liquids that are based on energy decomposition analysis such as those developed by the group of J.R. Schmidt (JPCL, 5, 2670, 2014) or the AMOEBA potential for ILs (JPCB, 118, 7156, 2014) or other polarizable IL potentials such as APPLE&P from the Borodin group. 

#We thank the reviewer for this comment. On page 2 we have now amended the text to incorporate recent publications on the development of polarizable force fields for ionic liquids (shown in blue in the revised manuscript):

“This challenge of predicting properties for ionic liquids has been taken upon by several groups previously using classical force fields.6,7 The advantage of classical methods is that simulations can be run on large systems with relatively little computational effort. Some notable examples of molecular dynamics that have found success in the realm of ionic liquids include the polarisable potentials developed by Borodin et al.2,8 Induction was shown to be very important in the prediction of physical properties of ionic liquids, with polarisable force fields that explicitly include induction effects performing better for these complex systems.9,10 Furthermore, methods which offer an energy decomposition of the intermolecular interaction, have been constructed, such as an AMOEBA (a multipolar force field) force field for imidazolium-based ionic liquids,11 and the 1-butyl-3-methylimidazolium tetrafluoroborate force field developed by Choi et al.12 The latter parametrised intermolecular interaction terms to reproduce SAPT energies. This resulted in a better force field that performed well in the prediction of thermodynamic and transport properties of the ionic liquid when compared to experiment. The authors expect their force field to be transferable due to the parametrisation being based on first principles.”

-subsection 2.2, pp. 10: There is no mention of the overlap damping employed in EFP to account for penetration effects in the Coulomb and Polarization terms. 

#We thank the reviewer for pointing out this oversight. We have modified the text on page 11 to address this point:

“To prevent ‘polarisation collapse’ at short intermolecular distances, EFP employs Gaussian-type damping, due to its mathematical simplicity and independence of the choice of Coulomb damping.76”

-pp. 14, subsection 3.0.3: The authors could cite the work by Sherrill et al (JCP, 140, 094106, 2014) to justify the SAPT level employed for the reference.

# On page 17 (former page 14) we have mentioned the work by Parker et al. to justify our choice of basis set for SAPT2+3 calculations:

“This is in line with the results presented by Parker et al., where for SAPT2+3, the basis set with the lowest mean absolute error was aug-cc-pVDZ. This holds true across all the different subsets, which are categorisations of the systems based on the dominating interactions, such as hydrogen-bonding, dispersion, and mixed. (Tables III and IV, pp. 094106-7,8)15 ”

-pp. 16 top, it is unclear what is being compared for the differences between the basis sets. What do the authors mean by Coulomb being underestimated by 2.7 kJ/mol in triple zeta? what is the reference?

# On pages 17 and 18 we have modified the text to clarify this point:

The differences between these two basis sets are reported in the ESI. The consistency between the two basis sets (E(aug-cc-pVTZ) - E(aug-cc-pVDZ)) is immediately apparent: with the triple-ζ basis set, electrostatics is always weaker compared to the double-ζ basis set, by 2.7 kJ·mol−1 on average (3.0 kJ·mol−1 for imidazolium systems and 1.9 kJ·mol−1 for pyrrolidinium systems). Exchange follows the same trend, with the larger basis set giving a larger exchange energy of 4.9 kJ·mol−1 on average. It is not surprising that the larger aug-cc-pVTZ basis set leads to greater recovery of the dispersion energy by 5.6 kJ·mol−1  on average. There is no such pattern observed in the induction energy, with both basis sets giving excellent agreement to each other below 1 kJ·mol−1. Note that the difference between the two basis sets for charge-transfer 8.6 kJ·mol−1 on average with a standard deviation of 1.7 kJ·mol−1. Charge-transfer is expected to decrease with increasing basis set size in SAPT, as observed. And therefore, agreement between basis sets cannot be based on the comparison of charge-transfer energies. In the total interaction energy, the largest difference of 9 kJ·mol−1  comes from [C1mim][Cl] , specifically for the in-plane configuration p2. The average difference for the total interaction energy is 7.3 kJ·mol−1 with a standard deviation of 1.2 kJ·mol−1.

-Table 3: define acronyms 

#Table 3 now includes the definition of the TILAs and Hal acronyms in the table caption for readers’ convenience.

-Table 4: define units (e.g. in caption)

# In Table 4 the table caption has been modified to contain units.

-Figure 4: It is unclear which data corresponds to the raw results, and which to the scaled. This figure needs to be re-worked.

# The figure caption for Figure 4 has been changed to:

“Distribution of the raw and scaled differences (kJ mol-1) between SAPT and EFP, by energetic component and anion type, coloured by cation. Raw differences between SAPT and EFP are solid line unfilled densities, whereas the filled distribution represent differences after scaling.”

Reviewer 2 Comments:   
  
The authors present a very thorough comparison of the effective fragment potential method (EFP) for its use to describe the interaction in isolated ionic liquid ion pairs in the gas phase. As benchmark, SAPT2 and SAPT2+3 were used, which can be regarded as state-of-the-art. It was found that the performance of EFP depends much on the choice of the basis set and it is hard to predict only from the zeta-level and choice of augmented and polarization functions whether a certain basis set will work well. Overall, the performance of EFPs for ionic liquid ion pairs was worse than anticipated. A detailed analysis of the individual interaction components will enable the future development of improved EFP potentials for ionic liquids. The paper is well-organized and will enable the further improvement of methodology for the efficient simulation of ionic liquids, which is a very important subject and therefore the MS can be recommended for publication in JCTC after the following minor corrections are performed.   
  
1. Please upload the ESI. It was missing in this submission. 

# The ESI file was originally uploaded in the “tex” directory, as esi.pdf. It is generated from the .tex file named esi.tex.

2. Figures 1 and 2: It is hard to see the geometry. Perhaps two views (top and side, or similar) would be more helpful. In Figure 1: Is p1 a stereoisomer of p4? Also, it does not make sense to indicate double bonds in the imidazolium ring. Perhaps a schematic figure might serve better overall.

# Figures 1 & 2 have been reworked to make the representation of the studied ion pair configurations clearer.

3. Only optimized geometries were used, but it is questionable whether optimized geometrical parameters for ion pairs are useful as they come in all ranges in the real liquid. This reviewer wonders if non-optimized geometries would show different trends in the performance than optimized geometries. 

#The reviewer raises an excellent point. For ionic liquids ion pairs represent an extreme case of the intermolecular distances that are usually shorter by at least 0.5 Å compared to those observed in MD simulations. As a result of these shorter distances the intermolecular interaction in ion pairs is also stronger. It is common for the interaction to reduce as the inter-ionic distance lengthens and therefore it is suggested that the EFP errors should reduce on the absolute scale, while keeping the relative error relatively constant. To demonstrate this argument we generated relaxed potential energy surfaces for two types of ionic liquid ion pairs, [C1mim][BF4] and [C1mpyr][BF4] by increasing the interionic distance by 0.6 and 1 Å. The absolute and relative differences between EFP and SAPT for each fundamental component are given below in Table 1 & 2, respectively. In this case Re refers to the equilibrium distances in the ion pairs whose structures were used in the manuscript. The CT energy was not calculated due to expense of SAPT2+3 calculations.

As one can see that absolute differences between EFP and SAPT reduce significantly going to longer interionic distances for each energetic component without exception. At the same time, the relative errors as shown in Table 2 below reduce to a lesser extent, with errors being still > 10% for the exchange, induction and dispersion terms even at Re+0.6 Å. Therefore, it is not expected that the relative errors will change drastically for longer interionic distances observed in the bulk of ionic liquids as shown in MD simulations.

Table 1. Absolute differences between SAPT and EFP terms (in kJ mol-1).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Differences (kJ/mol) | Elst | Exch | Ind | Disp | Total |
| [C1mim][BF4] (Re) | -38.3 | 91.5 | -17.3 | -3.4 | 35.0 | |
| [C1mim][BF4] (Re+0.6) | 5.4 | 7.8 | -3.9 | -0.7 | 9.1 | |
| [C1mim][BF4] (Re+1.0) | 4.4 | 2.4 | -1.9 | -0.2 | 4.8 | |
| [C1mpyr][BF4] (Re) | -38.6 | 94.8 | -23.6 | -10.1 | 26.7 | |
| [C1mpyr][BF4] (Re+0.6) | 1.6 | 7.6 | -3.8 | -2.6 | 4.0 | |
| [C1mpyr][BF4] (Re+1.0) | 1.0 | 1.7 | -1.8 | -1.1 | 0.2 | |

Table 2. Relative differences between SAPT and EFP terms (in %)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Relative Differences (%) | Elst | Exch | Ind | Disp | Total |
| [C1mim][BF4] (Re) | 8.9 | 56.1 | 34.6 | 5.7 | 9.3 |
| [C1mim][BF4] (Re+0.6) | 1.6 | 27.6 | 13.9 | 2.7 | 2.5 |
| [C1mim][BF4] (Re+1.0) | 1.4 | 28.4 | 9.9 | 1.2 | 1.4 |
| [C1mpyr][BF4] (Re) | 9.3 | 60.0 | 38.6 | 19.1 | 7.2 |
| [C1mpyr][BF4] (Re+0.6) | 0.5 | 31.1 | 12.6 | 12.6 | 1.1 |
| [C1mpyr][BF4] (Re+1.0) | 0.3 | 26.2 | 8.8 | 10.2 | 0.0 |

4. It would be helpful to indicate the amount of charge transfer between the ion pairs, in terms of some population analysis such as Weinhold's NPA. The authors noted that this is of great concern for the development of classical and coarse-grained potentials.

#The reviewer raises another excellent point. Our group has previously published Weinhold’s NPA charge-transfer calculations on ionic liquids in PCCP, 2013, 15, 1632. The results indicated that NPA gives very small net charge transfer (NCT), except for the chloride anion. Due to the localised orbitals used in NPA, it treats covalent interactions well, but not so much for systems the orbital overlap is reduced due to the delocalized nature of ions. The reason the chloride anion performs better is because of the small size of the monoatomic anion which leads to greater orbital overlap. This renders the interaction semi-covalent, and hence NPA produces non-negligible charge-transfer comparable with other atomic partial charge schemes. In the same work it was established the Geodesic scheme produced the best trends in NCT and therefore this scheme was subsequently used on the ion pairs studied the current manuscript.