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Self-interaction error in DFT-based modelling of ionic liquids[†]

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The modern computer simulations of potential green solvents of the future, involving the room temperature ionic liquids, heavily rely on density functional theory (DFT). In order to verify the appropriateness of common DFT methods, we have investigated the effect of the self-interaction error (SIE) on the results of DFT calculations for 24 ionic pairs and 48 ionic associates. The magnitude of the SIE is up to 40 kJ mol^{-1} depending on the anion choice. Most strongly the SIE influences the calculation results of ionic associates that contain halide anions. For these associates, the range-separated density functionals suppress the SIE; for other cases, the revPBE density functional with dispersion correction and triple-ζ Slater-type basis is suitable for computationally inexpensive and reasonably accurate DFT calculations.

1 Introduction

Ionic liquids (ILs) – salts with low melting point – attract considerable research interest in the fields of surface science and physical chemistry, due to combinations of physicochemical properties that make them excellent candidates for a wide range of applications.[1,2] These properties include negligible vapour pressure at room and elevated temperatures, high thermal and (electro)chemical stability, a broad liquid range, ionic conductivity, catalytic activity, and also good solvent and miscibility properties for chemical compounds. A particular combination of properties results from a subtle balance of Coulomb and van der Waals interactions, donor–acceptor bonds, conformational flexibility, and steric effects. Therefore, a task-specific set of properties can be achieved by structural variations and by selection of the right combination of ions.

Molecular physics and computational chemistry are playing a significant role in the exploration of the ILs properties-landscape depending on the chemical composition.[3] In particular, because of continuing increases in computer power, the use of quantum chemical methods becomes more and more attractive for studying ILs electronic structure and reactivity. Due to the favourable accuracy-to-computational cost ratio, density functional theory (DFT) methods are most actively used for the electronic structure calculations of ILs as well as for parametrization of molecular dynamics (MD) force fields.[4,5] However, common density functionals, mostly in generalized-gradient approximation (GGA), suffer from a known set of intrinsic errors, which for certain systems could lead to a wrong description of the electronic structure and the interactions between the ions. Such functionals are often employed without verification of the results reliability.[6–16] Only in a few studies of ILs, DFT methods were examined in comparison to more accurate post Hartree–Fock (HF) methods, such as Møller–Plesset perturbation method, e.g. MP2, and couple cluster technique, e.g. CCSD(T).[17–20] The authors of these studies emphasized the importance of the dispersion correction which considerably improves the results of DFT calculations in comparison to CCSD(T) and MP2 results for anion–cation interaction energies[19–23].

The interaction energies along with ionic charges were evaluated in numerous works, using DFT methods.[24–36] In this kind of calculations, the self-interaction error (SIE) plays a central role in electronic polarization. The SIE is the spurious interaction of an electron with itself, and it is related to Coulomb energy of the Kohn–Sham Hamiltonian. It is an intrinsic error of the DFT approach, in contrast to the HF approach where self-interaction is explicitly and totally cancelled by the exchange contribution.[37] This well-known problem leads to an over stabilization. To our best knowledge, only in two works the effect of SIE on the ILs calculations were investigated. Grimme *et al.* estimated the impact of the SIE for three ionic pairs showing how this error is

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responsible for the artificial charge transfer and inaccurate interaction energies.[20] Weber *et al.* demonstrated the SIE effect on calculated interaction energies and structural properties of an adsorption process of two ionic pairs at anatase surface.[38]

The use of the hybrid functionals, including a portion of the HF exchange, is known to suppress the SIE and thereby reaches the accuracy of SIE-free post-HF methods.[39] For example, the ionic charges obtained with B3LYP hybrid density functional and MP2 method are almost identical for [BMIm]Cl.[40] On the contrary, charge analyses confirm that the value of Cl⁻ ionic charge in [MMIm]Cl is lower by 0.05–0.10e in MP2-level calculations than in pure GGA DFT calculations.[41,42] Accordingly, as the ionic charge is sensitive to the inclusion of the HF exchange, a range of ionic charge values varying from $-0.6e$ to $-0.8e$ was obtained for chloride in ILs using similar charge analysis methods, but with different GGA density functionals.[5,6,26,29,32,43]

The ionic charges are important parameters in MD simulations of ILs. Their values are usually estimated with quantum chemical calculations and are known to have a strong effect on the modelled structural and dynamical parameters of ILs.[27] Particularly, an application of a range of chloride ionic charge values obtained with DFT leads to markedly different MD simulations results. Simulations of [MMIm]Cl performed using force fields with ionic charges of $\pm 1e$ give good results for the static properties, but too low conductivity in comparison to the experimental data.[44,45] Better dynamics can be obtained with ionic charges of $\pm 0.8e$.[46] Note that on the absolute scale the ionic charge is lower from the discrete value due to polarization, and charge analysis of DFT results does provide a value of $\pm 0.8e$ for ionic charges in most ionic pairs.[26,32] However, according to the pure GGA DFT results it may be concluded that the ionic charge for chloride is $-0.6e$,[32,33,46] which implies a significant partial charge transfer between the ions of opposite charge.

The question then arises: "Is the polarization between cation and (halide) anion in an ionic liquid (pair) so strong that can be treated as the partial charge transfer, or is it artificially induced by the SIE?" Previous studies of the SIE effect on the DFT calculations revealed that the error is common for both molecular and ionic substances, like halides.[47–49] Grimme and co-workers demonstrated how the SIE influences the potential energy curves and molecular orbitals for three ionic pairs, hence, indicating the need for a detailed study of the SIE in DFT-based modelling of ILs.[20] In this work, we qualitatively evaluate the magnitude of the SIE for 24 ionic pairs and 48 ionic associated by applying the counterpoise method to the basis set superposition error (BSSE),[50] Perdew–Zunger (PZ) SIE correction,[51–54] Grimme's dispersion correction,[55] as well as global hybrid and range-separated functionals.

2 Computational methods

All DFT calculations were run using ADF 2013 program.[56–58] MP2 calculations were performed using the ORCA program.[59] Figures for orbitals and structures were prepared using Avogadro software.[60]

The computations were divided into three case studies:

1. We investigated the effect of HF exchange inclusion on the dipole moment in [BMIm]Cl ionic pair by using GGA and meta-GGA (BLYP,[61,62] PBE,[63] revPBE,[64] TPSS[65]), global hybrid (B3LYP,[66] revPBE38,[20] PBE0,[67] TPSSh[65]), the family of Minessota functionals (M06[68]) as well as range-separated functional LCY-revPBE and its variations.[69]

2. In order to determine the relationship between chemical composition and the SIE, we studied a set of 24 ionic pairs formed by combination of three cations (1-butyl-3-methylimidazolium = [BMIm]⁺, N-butylpyridinium = [BPy]⁺ or N-methyl-N-butylpyrrolidinium = [BMPyr]⁺) with eight anions (tetrafluoroborate = [BF₄]⁻, chloride = Cl⁻, tris(pentafluoroethyl)trifluorophosphate = [FEP]⁻, iodide = I⁻, dicyanamide = [N(CN)₂]⁻, hexafluorophosphate = [PF₆]⁻, thiocyanate = SCN⁻* and bis(trifluoromethylsulfonyl)imide = [TFSI]⁻), see Figure 1. For most ionic pairs, the initial configuration was taken from the work by Rigby and Izgorodina[26] and re-optimized using the revPBE functional in combination with a triple-ζ Slater-type basis set (TZ2P) and with Grimme's dispersion correction.[55] Core potential was only used in calculations involving iodide anion. Self-interaction corrected optimized effective potential for the TZ2P basis set was used for sulphur atom in SCN⁻ and halogen atoms in calculations with the PZ correction. The optimized geometries were used in all consequent calculations of the ionic pairs properties. The geometries are available at the NaRIBaS repository.[70]

   Zahn *et al.*[19] found small differences (from 2 to 6 kJ mol⁻¹) between MP2 and CCSD(T) energies for a set of 236 ionic pairs. Izgorodina *et al.*[18] suggested to use the triple-ζ Pople type basis set including diffusion and polarization for comparing DFT results obtained with triple-ζ Slater-type basis sets. Therefore, the MP2/6-311+G(3df) level with the BSSE correction was used for the qualitative evaluation of the DFT calculations results.

   The 24 ionic pairs are divided into three groups; SET1 includes ionic pairs containing [FEP]⁻, SET2 includes ionic pairs containing Cl⁻, I⁻, SCN⁻ anions, and SET3 consists of ionic pairs containing [BF₄]⁻, [N(CN)₂]⁻, [PF₆]⁻ and [TFSI]⁻ anions.

3. Single point calculations for associates consisting of four anions and four cations were performed with revPBE and LCY-revPBE density functionals[64,69] in combination with DZP basis set. The set of ions was extended with tetracyanoborate = [B(CN)₄]⁻, bromide = Br⁻, tricyanomethanide = [C(CN)₃]⁻, bis(fluorosulfonyl)imide = [FSI]⁻ anions, and N,N,N-triethyl-N-propylammonium = [TEPA]⁺ cation. The associates were prepared using NaRIBaS scripting framework[70] and packmol[71] as follows: four cations were placed into four 7 Å× 7 Å × 7 Å boxes situated in the corners of a tetrahedrom inside a cube; each anion was placed in

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* below referred as a pseudohalide anion

the unoccupied space of the cube according to the Pack-mol algorithm so that ions of opposite charge form the distorted tetrahedron inside the cube. The cube edge length was chosen to be 10 Å for associates containing halide and CN-group anions, and 14 Å for all other associates. Figure 2 displays the geometry of a [TEPA][B(CN)$_4$] associate. Smaller cubes were selected because of convergence problems that arise for revPBE density functional when anion–cation distance is increased (see detailed discussion in the work by Grimme *et al.*[20]). The associate geometry resembles NaCl type unit cell; it corresponds neither to solid nor liquid phase, yet allows us to evaluate the effect of the inclusion of HF exchange for ionic systems that are more complex than an ionic pair.

The 48 ionic associates are divided into three groups; SET1 includes ionic associates containing [FEP]$^-$ anion, SET2 includes ionic associates containing (pseudo)halide anions (Cl$^-$, Br$^-$, I$^-$, SCN$^-$), and SET3 consists of ionic associates containing [BF$_4$]$^-$, [B(CN)$_3$]$^-$, [C(CN)$_3$]$^-$, [N(CN)$_2$]$^-$, [PF$_6$]$^-$, [FSI]$^-$, and [TFSI]$^-$ anions.

Interaction energy was calculated as:

$$\Delta E_{\text{int}} = E_{n\text{CA}} - nE_A - nE_C \qquad (1)$$

where $E_{n\text{CA}}$ is the total energy of the ionic associate consisting of n anions and n cations, E_A and E_C are the energies of the anion and the cation in the associate geometry, respectively.

In the range-separated (RS) functionals the Coulomb operator is separated into short-range and long-range regions:[69]

$$\frac{1}{r_{12}} = \frac{1 - \alpha - \beta[1 - f(r_{12})]}{r_{12}} + \frac{\alpha + \beta[1 - f(r_{12})]}{r_{12}} \qquad (2)$$

where α is the ratio of the global mixing of the HF exchange and $\alpha + \beta$ is the mixing ratio of the HF exchange in $r_{12} = \infty$. In this work the Yukawa potential was used to express $f(r_{12})$ as $\exp(-\gamma r_{12})$ where γ is the Yukawa parameter. The amount of HF exchange was varied by changing the α parameter and keeping $\alpha + \beta = 1$. For calculations in the set of 24 ionic pairs and 48 ionic associates we have used $\alpha = 0$ and $\beta = 1$, that is range-separated functional LCY-revPBE.[69]

The dispersion contribution to the interaction energy was accounted using the third version of the Grimme's dispersion correction to the density functional used.[55] The BSSE was evaluated by application of the counterpoise method to the interaction energy.[50] The SIE was addressed i) by applying the PZ SIE correction,[51–54] and ii) by using range-separated density functionals. In the first case, the SIE correction was applied self-consistently using the Krieger–Li–Iafrate approximation.[47–49] The scaled version of the PZ correction proposed by Vydrov *et al.*[72] was also applied.

3 Results

For the set of 24 ionic pairs, the analysis of interacction energies, BSSE and dipoles at the revPBE level increasing the size of the basis set (DZ, DZP, TZP, TZ2P, QZ4P) was carried out in order to determine the influence of the basis set on interaction energies

and dipoles (see tables S1, S2 and S3 in the ESI). The BSSE was evaluated by application of the counterpoise method to the interaction energy. BSSE was found to be negligible from TZ2P, except for ionic pairs containing Cl$^-$ and I$^-$. For these cases QZ4P basis set is needed to suppress BSSE. The addition of diffuse functions (ATZ2P) was also evaluated. According to the analysis of interaction energies and dipoles presented (see Tables S4 and S5 in the ESI), the difference found in calculations with and without the diffuse functions is in general small. There are some ionic pairs where marked differences are seen, but still they are much smaller than those produced by the SIE.

3.1 Case study of [BMIm]Cl

As aptly noted by Perdew and co-workers, there are the "road more traveled" and the "road less traveled" towards the elimination of the SIE.[73] The roads correspond to the application of hybrid density functionals and PZ SIE correction, respectively.

The PZ correction of the SIE is expected to give highly accurate results at low computational cost. However, in practice the results are worse. In case of [BMIm]Cl pair, application of the full PZ correction leads to a significant overcorrection of the dipole moment and interaction energy values (12.4 D and $-247.8 \, \text{kJ mol}^{-1}$) in comparison to the MP2 results (9.2 D and $-378.2 \, \text{kJ mol}^{-1}$). However, the agreement between PZ corrected DFT and MP2 results can be improved by scaling the PZ correction by ($\Delta E_{\text{int}}^{\text{sPZ}} = -368.4 \, \text{kJ mol}^{-1}$).

The application of hybrid density functionals is computationally more demanding than pure GGA DFT methods but leads to marked improvement of the calculated properties. As an illustration, Figure 3 shows dipole moment value dependence on the portion of the HF exchange that suppress the SIE. The amount of HF exchange was varied by changing the α parameter and keeping $\alpha + \beta = 1$ as well as varying the Yukawa parameter γ from the default value of 0.75 to 0.50. It can be seen that the addition of HF exchange improves the agreement between the DFT and MP2 values. For GGA (BLYP) and meta-GGA (TPSS) functionals the use of the corresponding hybrid functionals (B3LYP, TPSSh) only slightly improves the results. For PBE and M06 an amount of almost 100% is needed to achieve the MP2 quality. The results obtained with range-separated version of revPBE functional with variable α, β and γ parameters (Eq. 2) are in much better agreement with the MP2 results even at low HF exchange addition (see Figure 3).

3.2 Case study of 24 ionic pairs

Table 1 shows the interaction energy values obtained in DFT calculations with BSSE, dispersion and SIE corrections. The correlation with MP2 results is displayed in Figure 4. It can be seen that, in general, the dispersion correction significantly improves the agreement between the DFT and MP2 results. However, for SETS 1 and 2 the deviation from the MP2 results remains significant and is comparable to the average magnitude of the dispersion correction (on average 37 kJ mol^{-1}) that in turn is much larger than the average BSSE (5 kJ mol^{-1}). Application of range-separated functionals and scaled PZ correction results are in a

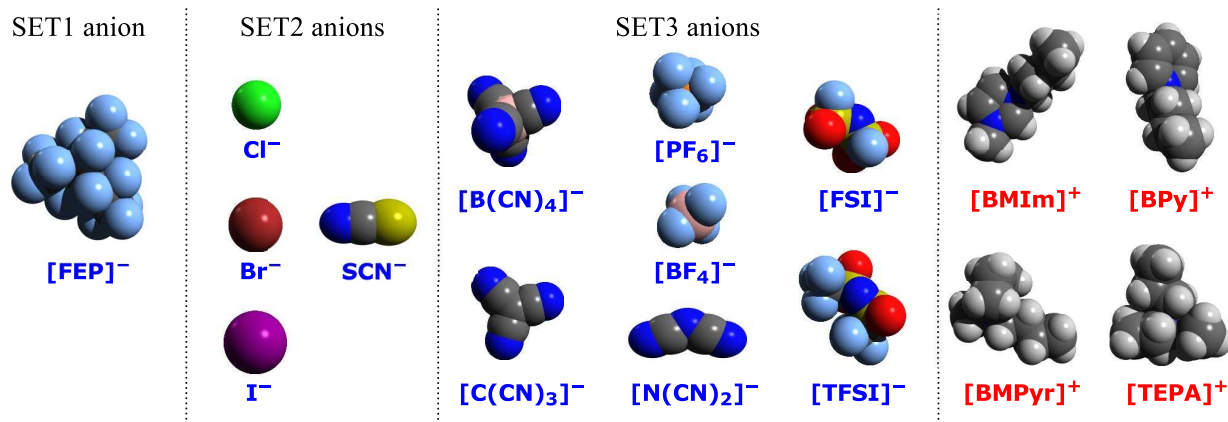SET1 anion | SET2 anions | SET3 anions

Fig. 1 van der Waals space-filling representation of anions and cations used in this work. H – white, C – grey, N – dark blue, O – red, F – light blue, S – yellow. All studied ionic associates were divided into sets: SET1 includes ionic associates containing [FEP]$^-$, SET2 includes ionic associates containing (pseudo)halide anions (Cl$^-$, Br$^-$, I$^-$, SCN$^-$), and SET3 consists of ionic associates containing [BF$_4$]$^-$, [B(CN)$_4$]$^-$, [C(CN)$_3$]$^-$, [N(CN)$_2$]$^-$, [PF$_6$]$^-$, [FSI]$^-$, and [TFSI]$^-$ anions.
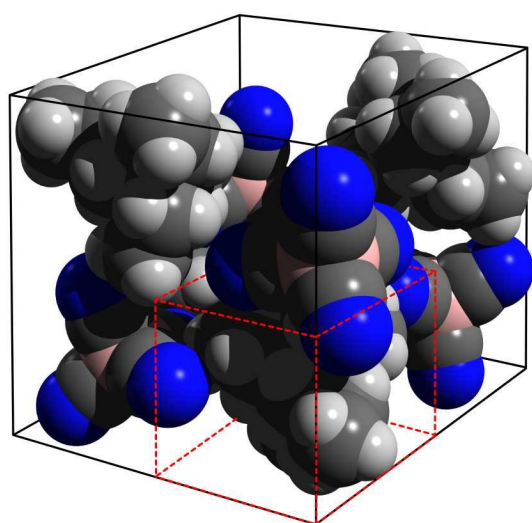
Fig. 2 van der Waals space-filling representation of a [TEPA][B(CN)$_4$] associate. H – white, B – pink, C – grey, N – dark blue. The cube borders are drawn with black lines, and the box borders are drawn with red lines.
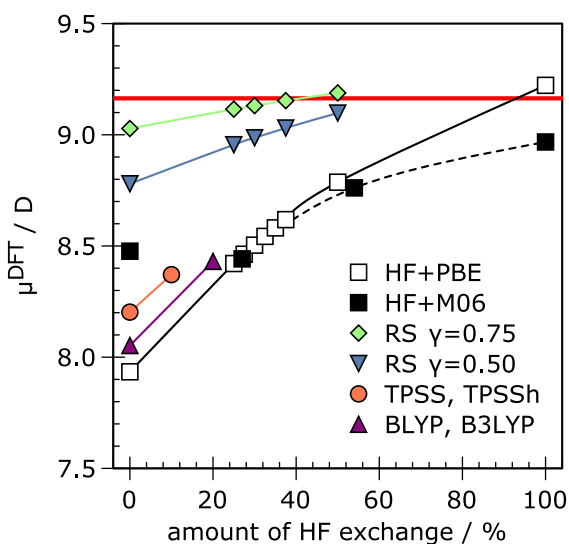

Fig. 3 Dependence of dipole moment on the amount of HF exchange for [BMIm]Cl ionic pair and comparison with the MP2 value (red line). Calculations were performed using PBE and M06 functionals with variable amount of the HF exchange. RS stands for range-separated revPBE functional with variable α, β and γ parameters (see text for details).

reasonable agreement with the MP2 results, lowering the interaction energies by 10–40 kJ mol^{-1} for SETS 1 and 2.

Table 2 shows mean absolute deviation (MAD) of various revPBE/TZ2P calculations (including BSSE and dispersion corrections) from the BSSE corrected MP2 level for the interaction energies. As can be seen, application of the PZ correction scaled by $\frac{1}{5}$ results in reduction of the MAD in comparison to the revPBE/TZ2P calculations. A comparison between calculations with full PZ and scaled PZ corrections is given in Table S6 in the ESI. Similar decrease of the MAD was obtained for the whole set of ionic pairs in LCY-revPBE calculations. Inclusion of diffuse functions into the basis set only slightly reduces the MAD for SETS

1 and 2 while markedly increasing it for the SET3. Qualitatively these results indicate the crucial effect of the SIE on the energetic characteristics of the ionic associates and indicate a minor role of diffuse functions in case of Slater-type basis sets. Similarly, a clear impact of the SIE is seen for the electronic characteristics such as dipole moment of ionic pairs.
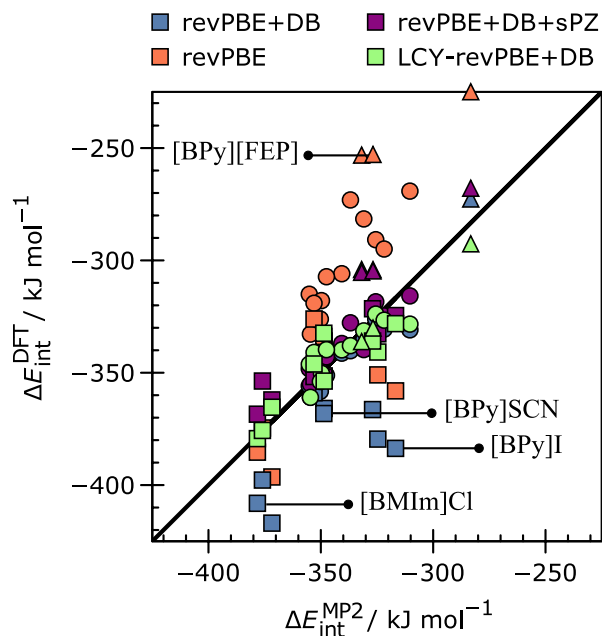

Fig. 4 Correlation plot for 24 ionic pairs showing revPBE/TZ2P vs. MP2/6-311+G** interaction energy values. Triangles denote ionic pairs from SET1, Squares – SET2, and Circles – SET3. Applied dispersion, BSSE, scaled PZ SIE corrections, and range-separated HF exchange addition are denoted with D, B, sPZ and LCY, respectively.

Figure 5 plots the dipole moment values for all studied ionic pairs using different variations of revPBE functional (pure GGA, with addition of 38% of HF exchange and range-separated) versus the values obtained at the MP2 level of theory. It can be seen that for the SET3 (circles) and SET1 (triangles) the three methods provide similar results that are in good agreement with the MP2 results. However, for ionic pairs containing Cl^-, I^- and SCN^- anions (SET2, squares) the use of range-separated functionals (LCY-revPBE, green marks) or global hybrid functional (revPBE38, blue marks) is required to obtain similar results to those of MP2.

3.3 Case study of 48 ionic associates

Figure 6 illustrates the lower unoccupied molecular orbital (LUMO) of the [BMIm]Cl ionic associate obtained with revPBE and LCY-revPBE density functionals. In the revPBE LUMO (Figure 6A) there is a mixing of the cation and anion orbitals. If LCY-revPBE functional is used no mixing can be seen (Figure 6B). This mixing can be interpreted as an artificial charge-transfer between ions, so it can be stated that the inclusion of range-separated functionals almost suppress the effect of SIE.

It can be shown that the established relationship between the chemical structure of ionic pairs and the magnitude of the SIE holds true also for larger associates by comparing interaction en-
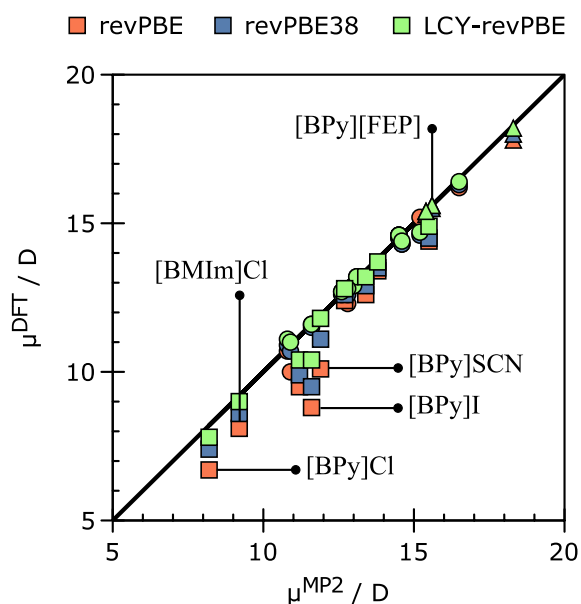

Fig. 5 Correlation plot for 24 ionic pairs showing DFT/TZ2P vs. MP2/6-311+G(3df) dipole moment values. Triangles denote ionic pairs from SET1, Squares – SET2, and Circles – SET3.

ergies in 48 associates calculated with revPBE and LCY-revPBE functionals. As can be seen in Figure 7, there is a clear deviation between the revPBE and LCY-revPBE results for ionic associates from SET1 and SET2. For ionic associates from SET3 the deviation is small ($< 2\%$), therefore in calculations of similar systems there is no need using hybrid functionals unless a higher precision is required.

As expected, application of the PZ correction scaled by $\frac{1}{5}$ results in reduction of the deviation from the LCY-revPBE/DZP results. However, the utilization of PZ correction in calculations of larger associates is obstructed by particular implementation of this correction in a given code, e.g. by availability of specific basis sets and parallelization. In Figure 7 we show the improvement for selected associates. Note that, as has been recently marked by Perdew and co-workers,[73] the success of the scaling approach and the failure of the full PZ SIE correction is probably related to the imperfection of commonly used density functionals. Perdew *et al.*[73] suggested that novel strongly constrained density functionals could be compatible with the PZ correction and thus would open a straightforward way to more efficient and more accurate SIE-free DFT calculations. As the studied ionic pairs and larger associates demonstrate a clear dependence of the SIE effect on chemical structure, such associates could be used in order to verify novel methods for the SIE corrections in future.

4 Conclusions

The implication of the self-interaction error (SIE) on calculations involving ionics liquids has been systematically investigated. Due to this error common density functionals artificially favour the partial charge transfer between anions and cations and, hence, overestimate interaction energy and underestimate dipole moment values. Our investigation of 24 ionic pairs and 48 larger

Table 1 Interaction energy (kJ mol^{-1}) calculated at the revPBE/TZ2P level of theory in combination with the dispersion, BSSE, scaled PZ SIE corrections, and range-separated HF exchange addition (denoted with D, B, sPZ and LCY, respectively). MP2/6-311+G(3df) results with BSSE correction are given in the last column

Ionic Pair	revPBE	revPBE+D	revPBE+DB	LCY-revPBE+DB	revPBE+DB+sPZ	MP2
[BMIm]Cl	−385.4	−408.1	−398.6	−379.3	−368.4	−378.2
[BMIm]I	−351.0	−379.5	−368.7	−340.8	−332.7	−335.8
[BMIm]SCN	−335.9	−365.9	−363.1	−353.7	−351.4	−348.5
[BMIm][BF$_4$]	−332.8	−360.9	−357.0	−361.0	−355.1	−354.6
[BMIm][N(CN)$_2$]	−315.1	−355.9	−352.4	−346.2	−348.2	−355.1
[BMIm][PF$_6$]	−305.9	−341.3	−339.5	−339.8	−337.0	−340.7
[BMIm][TFSI]	−273.1	−340.2	−335.7	−337.9	−327.8	−336.8
[BMIm][FEP]	−253.1	−304.1	−300.6	−336.1	−305.3	−331.8
[BPy]Cl	−396.4	−416.9	−401.0	−365.4	−362.1	−371.8
[BPy]I	−358.1	−383.7	−367.0	−328.2	−324.5	−329.1
[BPy]SCN	−333.8	−368.2	−364.8	−332.4	−352.1	−348.7
[BPy][BF$_4$]	−317.9	−350.0	−346.0	−350.2	−344.3	−349.7
[BPy][N(CN)$_2$]	−319.1	−359.6	−355.3	−341.0	−349.2	−343.4
[BPy][PF$_6$]	−290.8	−326.2	−322.1	−323.9	−318.4	−325.6
[BPy][TFSI]	−281.5	−335.2	−332.0	−331.4	−339.7	−330.9
[BPy][FEP]	−252.8	−304.1	−300.5	−330.1	−304.7	−326.8
[BMPyr]Cl	−374.6	−397.8	−383.9	−375.7	−353.7	−376.0
[BMPyr]I	−339.0	−366.4	−349.5	−335.9	−321.5	−334.4
[BMPyr]SCN	−326.1	−358.9	−355.8	−346.1	−351.7	−353.0
[BMPyr][BF$_4$]	−326.1	−358.3	−354.9	−353.9	−342.5	−350.2
[BMPyr][N(CN)$_2$]	−307.3	−351.2	−347.9	−339.7	−342.9	−347.5
[BMPyr][PF$_6$]	−294.9	−330.6	−328.9	−326.6	−324.7	−321.8
[BMPyr][TFSI]	−269.2	−330.9	−314.4	−328.4	−315.8	−310.4
[BMPyr][FEP]	−224.9	−272.7	−269.0	−292.6	−267.9	−284.1

Table 2 MAD (kJ mol^{-1}) of revPBE+DB/TZ2P interaction energy values from the MP2 results. In addition to BSSE and dispersion corrections, the calculations included diffuse functions (A), scaled PZ correction (sPZ) and range-separated HF exchange addition (LCY)

	SET1	SET2	SET3
revPBE+DB	24	26	3
revPBE+DB+A	19	20	9
revPBE+DB+sPZ	21	9	5
LCY-revPBE+DB	6	8	5

ionic associates demonstrates that range-separated density functionals effectively suppress the SIE and provide dipole moment, ionic charge and interaction energy values that are comparable to those obtained at the MP2 level of theory. The magnitude of the SIE is negligible for SET3 but it is large for SETS 1 and 2; from 24 kJ mol^{-1} on average up to 40 kJ mol^{-1} for [BPy]I. For comparison, the magnitude of the basis set superposition error is less than 5 kJ mol^{-1} for triple-ζ Slater-type basis, and the Grimme's dispersion correction is on average 37 kJ mol^{-1}.

Therefore, we suggest to be cautious in the analysis of the previous and the future DFT calculations of ionic liquids with (pseudo)halide or [FEP]$^-$ anions. Besides, we recommend the presented set of ionic associates for testing the Perdew–Zunger correction with novel strongly constrained density functionals.

Acknowledgements

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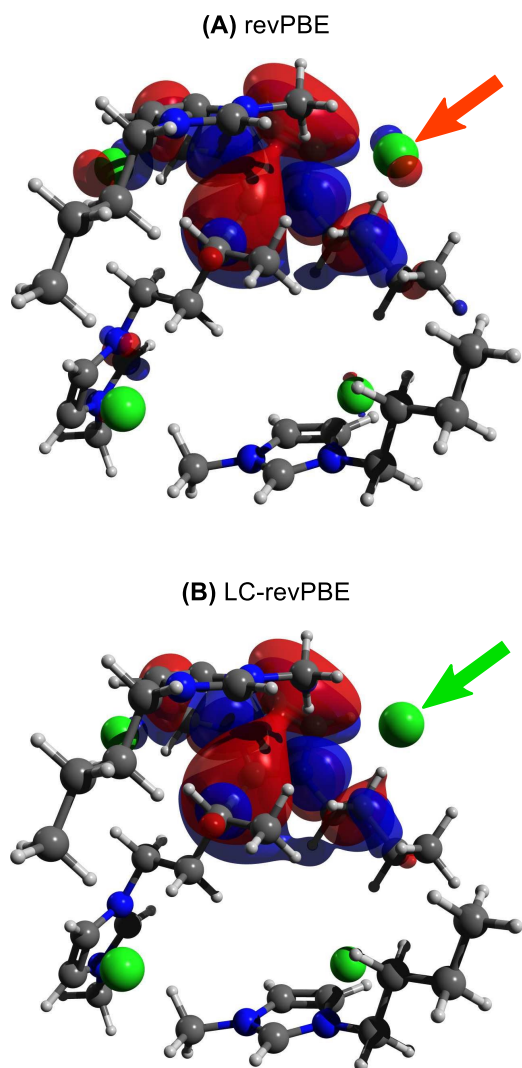
(A) revPBE

(B) LC-revPBE

Fig. 6 Contour plot of the LUMO of the [BMIm]Cl ionic associate at the revPBE/DZP (A) and LCY-revPBE/DZP (B) levels. Red arrow points at the mixture in cation and Cl⁻ orbitals. Green arrow indicates the absence of such mixture. Contour isosurface values are ± 0.02 a.u.

Fig. 7 Correlation plot for 48 ionic associates showing revPBE/DZP vs. LCY-revPBE/DZP interaction energy values. Triangles denote ionic pairs from SET1, Squares – SET2, and Circles – SET3. Blue diamonds indicate results obtained using revPBE/DZP calcualtions with scaled PZ correction.

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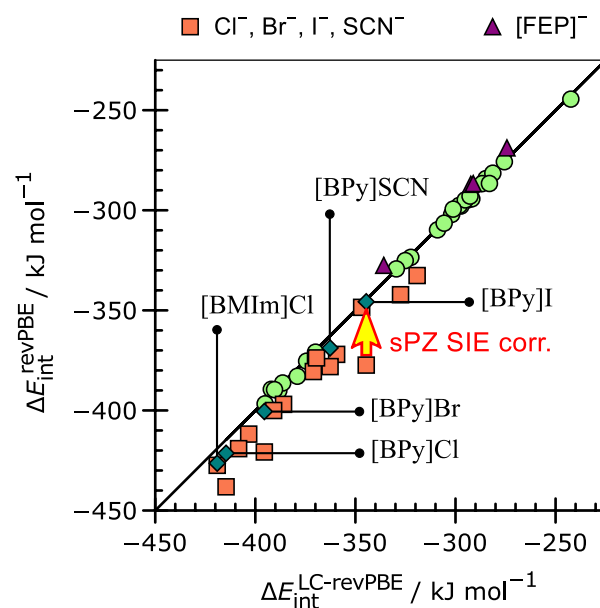19 S. Zahn, D. MacFarlane and E. I. Izgorodina, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13664–13675.

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