Novel SCS-IL-MP2 and SOS-IL-MP2 Methods for Accurate Energetics of Large-Scale Ionic Liquid Clusters

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Ⓢ *Supporting Information*

ABSTRACT: Accurate energetics of intermolecular interactions in condensed systems are challenging to predict using highly correlated quantum chemical methods due to their great computational expense. Semi-Coulomb systems such as ionic liquids, in which electrostatic, dispersion, and induction forces are equally important, represent a further challenge for wave function-based methods. Here, the application of our recently developed SCS-IL-MP2 and SOS-IL-MP2 methods is reported for ionic liquid clusters of two and four ion pairs. Correlation interaction energies were found to be within 1.5 kJ mol^{-1}, on average, per ion pair of the CCSD(T)/CBS benchmark, thus introducing a marked improvement by a factor of 4 to conventional MP2 within the complete basis set. The fragment molecular orbital (FMO) approach in combination with both SCS-IL-MP2 and SOS-IL-MP2 has been shown to provide a reliable and computationally inexpensive alternative to CCSD(T)/CBS for large-scale calculations of ionic liquids, thus paving the way toward feasible *ab initio* molecular dynamics and development of reliable force fields for these condensed systems.

■ INTRODUCTION

Ionic liquids (ILs) have become increasingly relevant in a diverse set of applications, including as electrochemically superior electrolytes in energy storage devices,[1] "green" solvents in synthetic catalysis,[2] effective mechanical lubricants,[3] and pharmaceutically active ingredients,[4] to name just a few. Liquids qualifying as ILs (i.e., those with melting points below 100 °C) are said to number in the trillions, given common anion and cation combinations and mixtures thereof.[5] This incredibly large number of potential IL formulations means that the existence of suitable candidates for any given application would not be an unreasonable assumption; however, identification of such a candidate is a formidable task. The uniqueness of ionic liquids stems from equally important electrostatic, induction, and dispersion forces among ions.[6,7] The latter have been recently shown to play a significant role in governing thermodynamic and transport properties of ionic liquids.[6]

Although some progress has been achieved in the last 5 years,[8] classical force fields are still predominantly considered to be of "post"-predictive power for studying essential physical properties of ILs such as viscosity and melting point.[9] More expensive polarizable force fields produce more reliable results,[10] with their expense becoming on par with that of *ab initio* (DFT) MD simulations. The lack of development of more accurate classical force fields reflects an absence of highly accurate correlated quantum chemical methods that predict energetics of condensed systems such as ionic liquids.[7] Consequently, efforts to reduce the notorious computational

cost associated with correlated levels of theory are critical for the development of an *a priori* design methodology for novel ILs with tuned properties.

Dispersion interactions have been shown to be far from negligible in ionic liquids, contributing between 30 and 60 kJ mol^{-1} in single ion pairs.[11] The dispersion contribution increases nonlinearly with the increasing number of ions present in the system.[12] In some ionic liquids, the delocalized nature of anions may further induce specific dispersion-driven interactions such as $\pi-\pi$ stacking, as was observed in crystal structures of methanide-based ionic liquids and confirmed by quantum chemical calculations.[13] Large contributions of dispersion to total interaction energy further emphasize that the issue of basis set superposition error (BSSE) in wave function-based methods can no longer be ignored in these systems. For example, for single ion pairs, BSSE can reach 20 kJ mol^{-1} at what is considered to be a reliable and appropriate level of theory, MP2/aug-cc-pVTZ.[11] It is, therefore, not surprising that a combination of two factors, non-negligible dispersion and BSSE, makes application of currently available correlated levels of theory an insurmountable computational challenge for systems consisting of more than two ions.

The silver lining comes from the fragment molecular orbital (FMO) approach[14−16] that has been demonstrated to produce accurate interaction energies of large-scale calculations of archetypical ionic liquids when two-body (FMO2) and three-

body (FMO3) effects were included in the formulation.[12] Three-body effects were identified as being important for electrostatic and induction forces, whereas dispersion forces were already well-treated through pairwise interactions. Due to its near-linear scalability with increasing cluster size, the FMO approach in combination with the MP2 method paves the way toward fully *ab initio* large-scale calculations of existing and novel ionic liquids.

Previously, we reported an extension[11] to the widely used spin-component scaled MP2, SCS-MP2,[17] and scaling opposite-spin MP2, SOS-MP2,[18] approaches in electronic structure theory, where the opposite-spin (α) and same-spin (β) components of the MP2 correlation energy are scaled to reproduce that of the benchmark level of theory such as coupled-cluster with single, double, and noniterative triple excitations, CCSD(T), in combination with the complete basis set (CBS).

$$E^{corr}_{CCSD(T)/CBS} \approx \alpha(E_{OS}(MP2)) + \beta(E_{SS}(MP2)) \tag{1}$$

This new method, termed SCS-IL-MP2, was parametrized for correlation interaction energies of ion pairs via multiple linear regression techniques to identify the ideal basis set and spin component coefficients for an extensive set of 174 IL ion pairs, which reproduced benchmark energies within 1.0 kJ mol^{-1}, on average. The main difference from the original SCS-MP2 method lies in the fact that such excellent agreement was achieved by excluding the BSSE correction that is commonly accounted for via the counterpoise (CP) method.[19] SCS-IL-MP2 involves scaling the opposite- and same-spin components by 1.05 and 0.68, respectively, for MP2 energies calculated with the relatively small Dunning's correlation-consistent triple-ζ quality basis set, cc-pVTZ.[20] For the SOS-IL-MP2 method, only the opposite-spin component is scaled by 1.64 using the same basis set, cc-pVTZ. As SCS-IL-MP2 and SOS-IL-MP2 can be coupled with efficient algorithms for integral evaluation (e.g., the resolution-of-identity approximation[21]) and do not require CP correction, exceptional accuracy can be achieved at just a fraction of the computational cost compared to that of CP-corrected MP2 calculations, let alone the benchmark method, CCSD(T), which scales as N^7 with respect to molecular size.

In this study, we show that, in addition to achieving high accuracy for ionic clusters consisting of multiple ions of routinely used ionic liquids, the SCS-IL-MP2 and SOS-IL-MP2 methods supersede conventional CP-corrected MP2 for these semi-Coulombic systems. We also demonstrate that omission of the CP correction makes SCS-IL-MP2 and SOS-IL-MP2 ideal quantum chemical methods to determine accurate energies of large ionic clusters in combination with the FMO approach.[15,22,23] Both methods, FMO3-SCS-IL-MP2 and FMO3-SOS-IL-MP2, produce results comparable to those of original SCS-IL-MP2 and SOS-IL-MP2, with mean absolute errors not exceeding 2.6 kJ mol^{-1} with respect to CCSD(T)/CBS. This excellent performance of SCS- and SOS-IL-MP2 methods in combination with FMO arises from the fact that the dispersion energy is primarily accounted for as a two-body effect.[12] The newly proposed SCS-IL-MP2 and SOS-IL-MP2 methods[11] were originally constructed for single ion pairs that included all possible energetically favorable ion-pair configurations between either imidazolium or pyrrolidinium cations and a number of routinely used anions. Since BSSE is expected to be a localized source of error,[11] the SCS-IL-MP2 method seems to be suited to account for its effect through the scaled opposite- and same-spin components.

THEORETICAL PROCEDURES

Two- and four-ion-pair structures were optimized with the two-body FMO approach at the MP2/cc-pVDZ level of theory using the GAMESS-US software package.[24] Benchmark CCSD-(T)/CBS-quality correlation interaction energies were computed by adding the counterpoise (CP) corrected interaction energy difference between MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ to two-point-extrapolated MP2/CBS energies calculated using the cc-pVTZ (abbreviated as VTZ) and cc-pVQZ (abbreviated as VQZ) basis sets, as shown in eqs 2 and 3.[25,26] We have previously shown that the use of augmented basis functions (denoted by the aug- prefix) is unnecessary for CBS extrapolation.[11]

$$\Delta E^{corr}_{MP2/CBS} = \frac{X^3 \Delta E_{MP2/X} - Y^3 \Delta E_{MP2/Y}}{X^3 - Y^3} \tag{2}$$

$$\Delta E^{corr}_{CCSD(T)/CBS} = \Delta E^{corr}_{MP2/CBS} + (\Delta E^{corr}_{CCSD(T)/ACCD} - \Delta E^{corr}_{MP2/ACCD}) \tag{3}$$

The MP2/CBS extrapolation scheme shown in eq 1 follows the standard Helgaker approach,[27] in which MP2/X and MP2/Y represent MP2 correlation energies at two correlation-consistent basis sets, VTZ and VQZ, and X and Y are corresponding cardinal numbers ($X = 3$ and $Y = 4$). All energies were calculated with density-fitting, and CCSD(T) calculations were calculated either using the frozen natural orbital approximation[28] or, where unfeasible, the domain-based local pair natural orbital coupled cluster approximation (DLPNO-CCSD(T)).[29] All single-point MP2 energies were performed with the Psi4 software package[30] except for the DLPNO-CCSD(T) energies, which were calculated using ORCA.[31] Counterpoise correction was calculated using the conventional approach by Boys and Bernardi.[19] When the CP correction was used method/basis set abbreviations were followed by (CP), e.g., SCS-MP2/VTZ(CP).

Single-point FMO3 calculations in combination with the MP2 level of theory were performed on optimized geometries of two- and four-ion-pair clusters using the cc-pVTZ basis set and the RI approximation for computation of two-electron integrals, as implemented in the GAMESS-US software package.[24] No cutoff restraints were used on the inclusion of two- and three-body ion fragments. The same- and opposite-spin components were scaled for one-, two-, and three-body contributions to correlation energy, as described above, to produce SCS-IL-MP2 and SOS-IL-MP2 correlation interaction energies denoted here as FMO3-SCS-IL-MP2 and FMO3-SOS-IL-MP2, respectively.

Correlation interaction energies were calculated as the difference between electron correlation contribution of an ionic cluster and electron correlation contributions of constituting ions in their cluster geometry. Correlation interaction energy represents a good estimation of the dispersion component of interaction energy; therefore, correlation interaction energy and dispersion energy are used as synonyms throughout the text. Total interaction energies are calculated by adding counterpoise-corrected HF/VQZ inter-action energies and correlation interaction energies. In the text, these energies are also referred to as interaction energies.

For statistical analysis, the following quantities were used: mean absolute errors (MAE), mean (unsigned) errors (referred
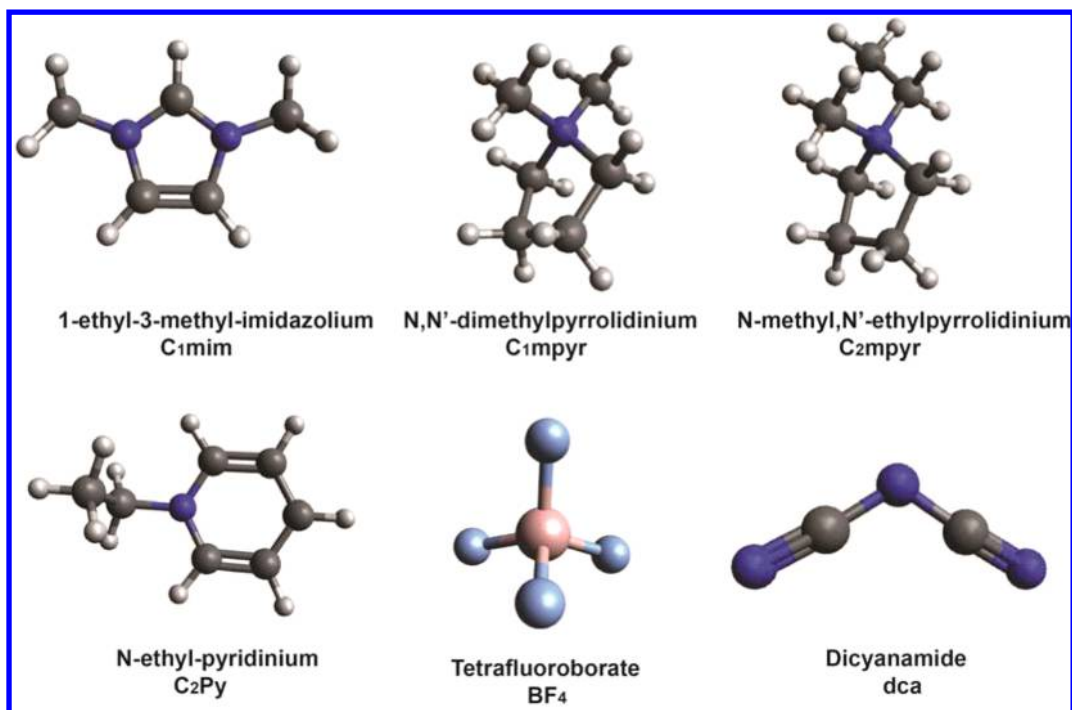
Figure 1. Structures of cations and anions used in the study.

to as mean errors), standard deviation (abbreviated as SD and shown in eq 4), and relative error (see eq 5).

$$\text{SD} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N - 1}} \qquad (4)$$

$$\text{relative error} = \frac{|(E_{corr}^{X} - E_{corr}^{benchmark})|}{E_{corr}^{benchmark}} \cdot 100\% \qquad (5)$$

where $\bar{x}$ is the mean absolute error.

■ RESULTS AND DISCUSSION

Construction of Ionic Liquid Clusters. Two- and four-ion-pair IL clusters consisting of 1,3-dimethylimidazolium (C_1mim), N-methyl-N-methylpyrrolidinium (C_1mpyr), N-methyl-N-ethylpyrrolidinium (C_2mpyr), and N-ethylpyridinium (C_2Py) cations and tetrafluoroborate (BF_4), dicyanamide ($N(CN)_2$), bromide (Br), and chloride (Cl) anions (see Figure S1) were constructed in an recursive way. Energetically favorable ion-pair configurations were assembled into ion-pair dimers, and these dimer units were duplicated and then assembled as ion-pair tetramers, followed by geometry optimization.

It has to be noted that the specific geometries used in this study are not of particular importance, as fully optimized minima (and not necessarily global minima) on the potential energy surface are already sufficient to generate a robust set of benchmark energies to assess the performance of both SCS-IL-MP2 and SOS-IL-MP2. In doing so, the versatility and robustness of these methods may be verified in a more diverse set of situations, such as those that may be found in condensed-phase molecular dynamics simulations, for example.

Figure 1 shows structures of cations and anions used in the study, whereas examples of the IL clusters used are given in Figure 2. The bromide anion is chosen to be representative of the positions of all other anion types in this series. A number of

interaction modes are observed in these clusters: in clusters (b) and (c), alkyl chains are positioned such that dispersion interactions between these nonpolar regions of the ions interact. In clusters (a) and (c), $\pi-\pi$ stacking interactions between cations is present, further contributing to the non-negligible dispersion contribution found typically in ionic liquids.[12,32] All clusters show multiple ion binding sites on the cation; the imidazolium clusters exhibit interactions inline with and on either side of the plane of the imidazolium ring; pyrrolidinium clusters have several exposed faces about the nitrogen atom, in which the anion may interact; and the pyridinium clusters have interaction sites on either face of the ring and in the plane near the nitrogen atom. The SCS-IL-MP2 and SOS-IL-MP2 methods were fitted in view of accounting for the variety of interaction modes with multiple ion-pair configurations used in the fitting procedure. It has to be emphasized that the N-ethyl-pyridinium cation was not included in the original study for scaling the opposite- and same-spin components. Therefore, clusters with the C_2Py cation represent the ultimate test for the performance of SCS-IL-MP2 for ionic liquid clusters.

Importance of Dispersion and BSSE in Ionic Liquid Clusters. To emphasize the significance of the two factors, dispersion and BSSE, that contribute to the challenge of developing accurate quantum chemical methods for ionic liquids, the dispersion contribution per ion is presented for two- and four-ion-pair clusters, as calculated at the CCSD(T)/CBS and MP2/VTZ(CP) levels of theory (Figure 3a). It is obvious that the dispersion component increases nonlinearly regardless of the cation–anion combination, contributing −68 and −81 kJ mol⁻¹, on average, to the total interaction energy in two- and four-ion-pair clusters, respectively. With respect to the total interaction energy, dispersion contributes in the range of 11−26%, which is not negligible, as might be assumed for systems consisting of charged species. It is not surprising that BSSE also increases with increasing cluster size (as shown in
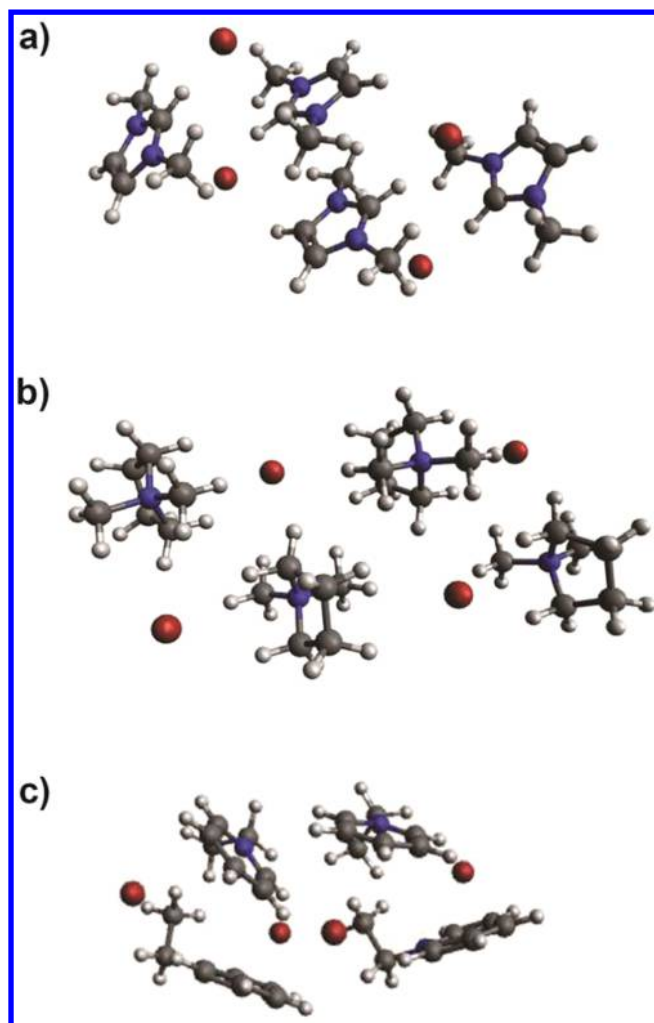
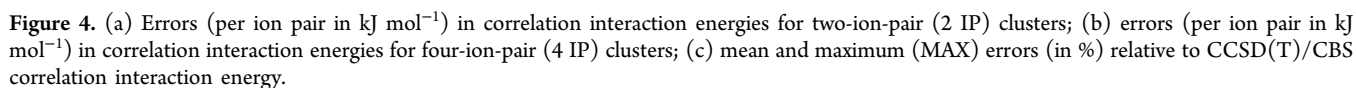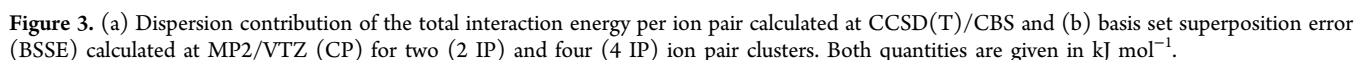**Figure 2.** Four-ion-pair cluster examples: (a) $[C_1mim]Br$, (b) $[C_2mpyr]Br$, and (c) $[C_2Py]Br$.

Figure 3b), ranging between 56 and 90 kJ mol^{-1} for four-ion-pair clusters, further highlighting its importance in these semi-Coulombic systems.

Performance of SCS-IL-MP2 and SOS-IL-MP2 for Ionic Liquid Clusters. The overall performance of SCS-IL-MP2 and SOS-IL-MP2 (see Figure 4a,b and Table S1) is excellent, producing the lowest mean absolute errors (MAE) compared to those of the other methods applied. The standard deviation of just 0.9 kJ mol^{-1} indicates a narrow error distribution regardless of the size of the ionic cluster and the chemical nature of the constituent cations and anions. For comparison, MP2/CBS predicts correlation interaction energies with MAEs of 5.4 and 8.2 kJ mol^{-1} for two- and four-ion-pair clusters, respectively (see Table S2, Supporting Information). The standard deviation for both sizes of clusters falls between 3.3 and 3.8 kJ mol^{-1}, on average, indicating a broad distribution of errors. A comparison of two other modifications of the original SCS-MP2 methods, SCS-(MI) and SCSN, is also included in Figure 4a,b. These methods were developed to study intermolecular interactions for the S22 data set[18] and stacked nucleobases,[33] respectively. Both methods underperform compared to that of both the SCS- and SOS-IL-MP2 methods when combined with VTZ and counterpoise correction. The mean errors (for more detail, see Table S2) are twice that of MP2/CBS, approaching 16.1 kJ mol^{-1} for SCS-(MI) and four-

ion-pair clusters. It has to be noted that, although both methods, SCS-(MI) and SCSN, were scaled for the counterpoise-corrected interaction energies, these also perform slightly better when the counterpoise correction was excluded. In this case, the mean errors are similar to those of MP2/CBS for two-ion-pair clusters and stay unchanged for four-ion-pair clusters, thus slightly outperforming MP2/CBS. When relative errors (eq 5) are expressed in terms of the percentage of the correlation interaction energy, as shown in Figure 4c, SCS-IL-MP2 gives the lowest average and maximum errors among all methods studied in both two- and four-ion-pair systems. SCS-IL-MP2 produces errors as low as 2.3% for two-ion-pair systems and 1.9% for four-ion-pair systems. An analogous trend is observed for SOS-IL-MP2, with errors reducing from 2.6% for two-ion pairs to 2.4% for four-ion pairs. This indicates that the error relative to the interaction energy of the cluster is largely invariant with cluster size. Indeed, a decrease in percentage error is observed due to the increased interaction energy resulting from the many-body effects present in IL clusters.[12]

Figure 5a,b shows the errors for all of the systems studied, given on a per ion pair basis. It can be seen that SCS-IL-MP2 consistently outperforms the original SCS-MP2 formulation for both the triple- and quadruple-ζ quality basis sets for the clusters studied. Of particular note are the results from the C_2py series that was not part of the original SCS-IL-MP2 fitting set. Here, SCS-IL-MP2 gives errors that are sub-kilojoules/mole per ion pair for the two-ion-pair set and less than 2 kJ mol^{-1} per ion pair for the four-ion pair-set. SOS-IL-MP2 gives only marginally larger errors (within sub-kilojoules/mole) compared to those of SCS-IL-MP2. The previous modifications, SCS-(MI) and SCSN, have mean relative errors that fall between 16.7 and 23.3% when the counterpoise correction is included, with SCSN performing slightly better than SCS-(MI). The same trend is observed here: the exclusion of the counterpoise correction improves the relative errors that still fall 4−6% short of the developed SCS- and SOS-IL-MP2 methods. These results show that the fitted SCS- and SOS-IL-MP2 coefficients are likely to be suitable to a broad range of semi-Coulomb systems, in which electrostatic, dispersion, and induction forces are non-negligible and play an equally important role.

The vast majority of the presented clusters are described with increased accuracy and consistency by the SCS- and SOS-IL-MP2 methods, with the performance exceeding that of MP2/CBS-extrapolated correlation energies. Notable outliers for the standard MP2 methods in general are the dicyanamide-based ILs, which often have a substantially overestimated correlation energy contribution that increases with the size of the basis set, as was previously shown for ion pairs with the $N(CN)_2$ anion.[11] For these systems, both SCS-IL-MP2 and SOS-IL-MP2 are able to provide a consistently high level of accuracy that is superior to that of the standard MP2 method. To this end, three conclusions can be drawn: (1) although CP-corrected MP2/VQZ may reproduce CCSD(T) energies in the majority of cases, outliers such as ILs with the $N(CN)_2$ anion cannot be corrected and *a priori* knowledge that some anions/cation sight be computationally challenging is usually not possible; (2) SCS- and SOS-IL-MP2 can provide comparable accuracy while minimizing the likelihood of outliers at only a fraction of the computational expense due to the exclusion of counterpoise correction; and (3) SCS- and SOS-IL-MP2 were independently
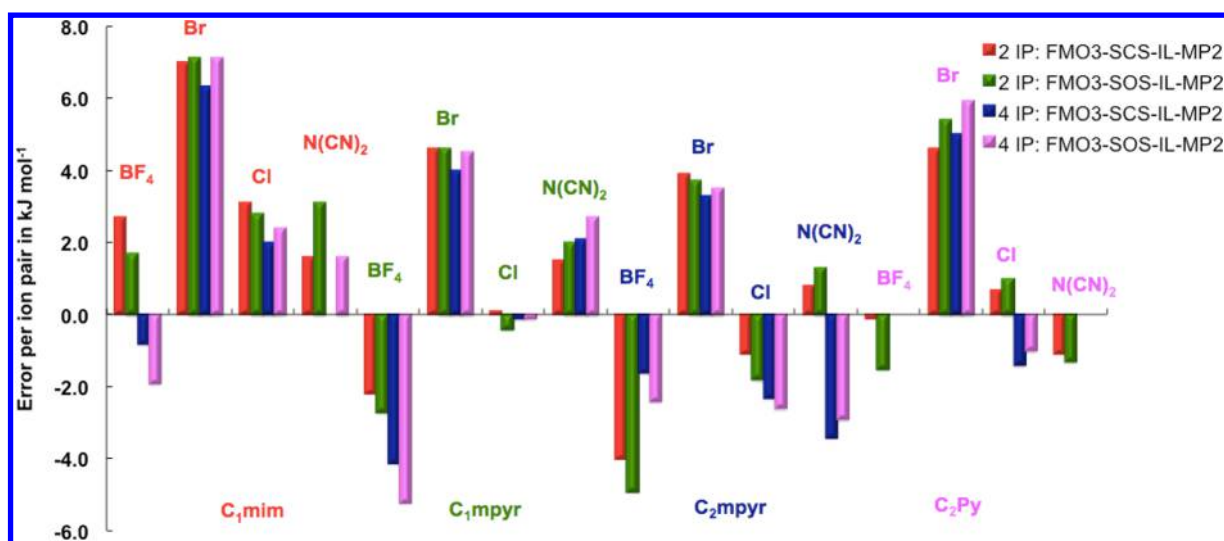
Figure 3. (a) Dispersion contribution of the total interaction energy per ion pair calculated at CCSD(T)/CBS and (b) basis set superposition error (BSSE) calculated at MP2/VTZ (CP) for two (2 IP) and four (4 IP) ion pair clusters. Both quantities are given in kJ mol^{-1}.

Figure 4. (a) Errors (per ion pair in kJ mol^{-1}) in correlation interaction energies for two-ion-pair (2 IP) clusters; (b) errors (per ion pair in kJ mol^{-1}) in correlation interaction energies for four-ion-pair (4 IP) clusters; (c) mean and maximum (MAX) errors (in %) relative to CCSD(T)/CBS correlation interaction energy.

Figure 5. Errors (in kJ mol^{-1}) for FMO3-SCS-IL-MP2 and FMO3-SOS-IL-MP2 correlation interaction energies of two- and four-ion-pair clusters.

tested for a set of ionic liquids that were not included in the original data set.

A key property of both methods involves its avoidance of CP correction. Indeed, CP correction for the original SCS-MP2 has been shown to have a detrimental effect on the quality of the correlation interaction energies produced, whereas CP correction for standard MP2 energies are essential (e.g., see Table S1).[11] The precise origin of this effect is not well-known. It is hypothesized that there is a favorable balance between the basis set incompleteness and rate of correlation energy recovery that results in a uniquely well-fitting regression when MP2 spin components calculated using the VTZ basis set (picked out of 17 popular basis sets) are fitted to a CP-corrected set of CCSD(T)/CBS benchmark correlation energies.[11] Recently, the conventional way of accounting for CP correction has been questioned,[34] further emphasizing the significance of departing from CP calculations for large-scale condensed systems.

Applications of SCS-IL-MP2 and SOS-IL-MP2 within the FMO Approach. In a practical sense, the absence of CP correction means that the analysis of IL clusters becomes even more computationally accessible, especially when combined with the FMO approach. Figure 5 shows errors of FMO3-SCS-IL-MP2 and FMO3-SOS-IL-MP2 correlation interaction energies with respect to the CCSD(T)/CBS benchmark ones. The largest errors are generally observed for the bromide anion, which is not surprising because bromide (with four electron shells) requires larger basis sets. FMO3-SCS-IL-MP2 produces mean absolute errors of 2.6 kJ mol^{-1}, with the mean error reducing from 1.4 kJ mol^{-1} for two-ion-pair clusters to 0.6 kJ mol^{-1} for four-ion-pair clusters. Without bromides, the MAE drops to around 1.7 kJ mol^{-1} for both sizes of clusters. In this respect, FMO3-SCS-IL-MP2 behaves nearly as accurately as SCS-IL-MP2. FMO3-SOS-IL-MP2 does not fall far behind, with a MAE of 3.1 kJ mol^{-1} and standard deviation of 0.8 kJ mol^{-1} for four-ion-pair clusters. It has to be noted that the absolute differences in the correlation energies per ion pair between two- (FMO2) and three-body (FMO3) combined with SCS-IL-MP2 and SOS-IL-MP2 range from 0.1 to 1.0 kJ mol^{-1}, on average, for two- and four -ion-pair clusters (for more detail, see Table S3). This observation in itself is a clear justification for the excellent performance of both methods when correlation energy is partitioned through two- and three-

body effects, with two-body effects clearly being much more important than three-body effects. It has to be noted that the HF energy of IL clusters still requires at least a three-body treatment. The beauty of the FMO approach is that it can be made of near-linear scalability for large-scale clusters of ionic liquids.[12] For example, four-ion-pair clusters presented here required between 1 and 4 h on 128 cores (i.e., 128 and 512 CPU hours, respectively) on the Raijin supercomputer within the National Computational Infrastructure facilities in Australia. Analogous eight-ion-pair clusters used the same amount of computing time when the number of cores was quadrupled. We have now demonstrated that, in combination with the FMO approach, both SCS-IL-MP2 and SOS-IL-MP2 are powerful methods for studying large-scale clusters of semi-Coulombic systems such as ionic liquids.

■ CONCLUSIONS

The new SCS-IL-MP2 and SOS-IL-MP2 methods for calculating the interaction energies of ionic liquid clusters represent a remarkably accurate and efficient route by which the bulk properties of ILs can be characterized. By leveraging an already well-established framework, SCS-MP2 and SOS-MP2, it has been shown that by fine-tuning the scaling factors applied to the spin components of the MP2 correlation interaction energy scaled without counterpoise correction and with the relatively small basis set, VTZ, accuracy approaching that of CCSD(T)/CBS quality can be achieved both for ion pairs as well as large-scale clusters of ionic liquids. The latter represents a tremendous achievement, as it allows not only for accurate calculations of energetics of novel ionic liquids to be made through highly parallel techniques such as the FMO approach but also development of more accurate forces fields that are extremely needed for molecular dynamics simulations with predictive power.[35] Applications of SCS-IL-MP2 and SOS-IL-MP2 within the FMO framework will provide invaluable insight into intermolecular interactions in mixtures of ionic liquids with traditional molecular solvents and various solutes (e.g., molecular gases such as CO_2 and charge carriers in batteries, fuel, and solar cells) that are already considered to be powerful replacements for traditional organic electrolytes in various sectors of multiscale industry.

■ ASSOCIATED CONTENT

S Supporting Information

Figure S1: Structures of polyatomic ions used to construct large-scale clusters. Table S1: Total and correlation interaction energies calculated at CCSD(T)/CBS for all clusters studied. Table S2: MAEs, mean errors, and standard deviations for a number of methods studied including SCS-IL-MP2 and SOS-IL-MP2. Table S3: Relative mean and maximum errors for the methods studied. Table S4: Energetic differences between FMO3 and FMO2 methods in conjunction with SCS-IL-MP2 and SOS-IL-MP2. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00551. Optimized structures of large-scale clusters used in this work can be made available upon request.

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■ ABBREVIATIONS

FMO, fragment molecular orbital; FMO3, combination of two- and three-body corrections with the fragment molecular orbital approach; SCS, spin-component scaling; SOS, scaling opposite spin; MP2, second-order Møller–Plesset perturbation theory; CCSD(T), a coupled cluster theory method with single and double excitations and noniterative triple excitations; CBS, complete basis set; IL, ionic liquid; CP, counterpoise correction; BSSE, basis set superposition error

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