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Effect of Basis Sets on the Selection of the Level of Theory Toward the Development of Quantum-Based Force Field Equation for Ionic Liquids

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The chemical industry is under considerable pressure to replace many of the volatile organic compounds. Volatile organic compounds are a major contributor to air pollution, but out of necessity, they are still frequently used in many chemical and industrial processes. A new class of solvents, referred to as ionic liquids, may offer at least a partial solution to the pollution problem caused by volatile organic compounds. Ionic liquids are generally considered "green" solvents because of their environment-friendly properties. However, the main problem that hinders the chemical industry from using ionic liquids is that, compared to conventional organic solvents, relatively little is known about their thermodynamic and transport properties. Since there are large possible combinations of ionic liquids, it would be very expensive if the study were conducted in the laboratory. The more appropriate approach in studying the properties of ionic liquids is to engage in a computational method, which uses a computer software that evaluates ionic liquids' thermophysical quantities via quantum mechanical and molecular mechanical simulations. In this study, a computer simulation, with the aid of SPARTAN '02 software, is used to study the effect of basis sets on the selection of the appropriate level of theory, which would be employed later in developing a quantum-based force field equation for predicting the properties of ionic liquids. Using the Hartree-Fock self-consistent filled (HF-SCF) molecular orbital model with different basis sets, a single point energy calculations were carried out for the chosen ionic liquid. With the exception of the minimal basis set, the SCF total energies for the other basis sets agree with each other in terms of magnitude. The SCF total energy is not affected as the basis set varies from minimal to split valence and as it polarizes. The most appropriate basis set was found to be 6-31G*.

Keywords: Basis sets, Hartree-Fock, ionic liquids, force field equation, level of theory, *and* SPARTAN '02.

INTRODUCTION

The chemical industry is under considerable pressure to replace many of the volatile organic compounds (VOCs), which are currently used as solvents in organic synthesis, because of the toxic and/or hazardous properties of many of these compounds—their use is prohibitive as far as serious environmental issues are concerned. This issue can be solved through the use of clean technology, which is concerned with the reduction of wastes from industrial chemical processes to a minimum. The technology requires rethinking and redesigning the current chemical processes available, and this can be done by assessing possible alternative raw materials, which can be used as a substitute for the conventional ones, or by modifying the equipment to reduce pollution outputs.

VOCs are a major contributor to air pollution, but out of necessity, they are still frequently used in many chemical and industrial processes. Solving this fugitive emission problem is a daunting task. A new class of solvents, referred to as ionic liquids (ILs), may offer at least a partial solution to this problem.

ILs are composed of organic cation and inorganic anion. Variation in cations and anions can produce literally billions of ILs. This large possible combination of ILs allows fine tuning the ionic liquid properties for specific applications (Abraham et al. 2002). ILs are generally considered "green" solvents because of their immeasurably low vapor pressure. With low vapor pressure, the tendency for solvent escape to the atmosphere is essentially eliminated. Apart from that, ILs have attracted much attention in many chemical process industries due to their properties such as high ionic conductivity, low volatility, non-flammability, high thermal stability, and high solvation capacity. With these properties of ILs, they are capable of reducing or eliminating related costs, disposal requirements, and hazards associated with the use of VOCs.

However, the main problem that hinders the chemical industry from using ILs is that, compared to conventional organic solvents, relatively little is known about their thermodynamic and transport properties. Since there are large possible combinations of ILs, it would be very expensive if the study, considering all cost-related parameters, were conducted in the laboratory. The more appropriate approach in studying the properties of ILs is to engage in a computational method, which uses a computer software that evaluates ILs' thermophysical quantities via quantum mechanical and molecular mechanical simulations. Molecular simulations have made enormous strides in recent years and are gradually becoming a ubiquitous tool in many fields of science and engineering. This is partly due to the ever-increasing speed of computers and, perhaps to a larger extent, to the development of new methods of complex fluids and materials (Pablo et al., 2002).

Aside from some experimental efforts to determine the thermodynamic and transport properties of ionic liquids, there have been very few theoretical and computational studies (Katritzky *et al.*, 2001; Morrow *et al.*, 2002; Margulis 2004).

Basis sets are combinations of mathematical functions which are used to represent atomic orbitals. These functions are used to have a mathematical picture of the molecular orbital which is used in the estimation of the solution of the Schrödinger equation. This study focuses on the effect of basis sets on the selection of the appropriate level of theory to be used as an initial assumption for quantum mechanical computation *(ab-initio)* of ILs. A computer simulation, with the aid of SPARTAN '02 software, is used to study the effect of basis sets.

The evaluation of the effect of basis sets is divided into three modifications: the effect of increasing the size of the basis functions, the effect of split valence basis sets, and the effect of polarized basis sets. The effect of increasing the size of the basis functions is evaluated with the computational cost, which is attributed to the simulation time. The effects of split valence and polarized basis set are evaluated with un-split and un-polarized basis sets as reference.

Table 1. Basis Sets Used in this Study

Basis Sets	Number of Basis Functions	Type of Basis Set
STO-3G	104	Minimal
3-21G*	193	Split valence
6-31G*	289	Double Zeta Split valence, polarization on 'p' orbitals
6-31G**	334	Double Zeta Split valence, polarization on 'p' and 's' orbitals
6-31+G*	357	Double Zeta Split valence, polarization on 'p' orbitals, diffused
6-311G*	359	Triple Zeta Split valence, polarization on 'p' orbitals
6-311+G**	472	Triple Zeta Split valence, polarization on 'p' and 's' orbitals, diffused

Minimal basis sets approximate all orbitals to be of the same shape. For a split valence basis set, a function is added to treat all valence orbitals separately when conducting Hatree-Fock calculation. While in polarization basis sets, functions are added to take into account charge distribution.

The results of this study would contribute to the development of the quantum-based force field equation, which would eventually be useful in predicting thermodynamic and transport properties of ILs.

COMPUTATIONAL METHODOLOGY

The theoretical method in this study was carried out using Spartan '02 for Windows (Wavefunction, Inc. 2002), which comprises a series of independent modules tightly connected via a graphical user interface.

Using the Hartree-Fock self-consistent filled (HF-SCF) molecular orbital model with different basis sets, a single point energy calculations were carried out for the chosen ionic liquid. Table 1 shows the different types of basis sets with their corresponding number of basis functions used in this study.

The following computational assumptions are set on the given system. Cation and anion charges were set at +1 and –1, respectively. The default (1.0×10^{-6}) convergence limit for the computation of the SCF energy and the default (50) maximum number of iterations were used.

The ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate, the structural formula of which is shown in Figure 1, was used in the evaluation of the effect of basis sets on the determination of optimum level of theory.

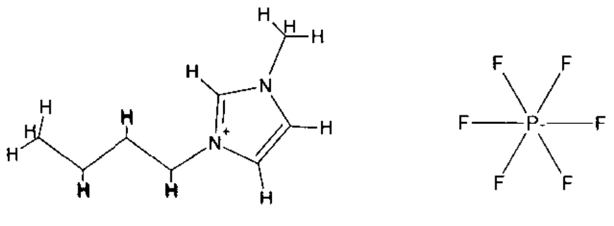

Figure 1. The Structural Formula of 1-n-butyl-3-methylimidazolium hexafluorophosphate

RESULTS AND DISCUSSION

The calculated self-consistent filled (SCF) total energies employing HF calculation are summarized in Table 2. The STO-3G (minimal) basis set gave the minimum SCF total energy, whereas 6-311+G** basis set gave the maximum total energy. With the exception of the minimal basis set, the SCF total energies for the other basis sets agree with each other in terms of magnitude. This points out that the minimal basis set cannot be a choice for the determination of the optimum basis set.

Table 2. Summary of Hartree-Fock Calculation

Basis Sets	Number of Basis Functions	SCF total energy (KJ/mol) / 10^6	Simulation time (second)
STO-3G	104	-3.5186	48
3-21G*	193	-3.5465	220
6-31G*	***289***	***-3.5650***	***1156***
6-31G**	334	-3.5651	1992
6-31+G*	357	-3.5651	3431
6-311G*	359	-3.5657	7062
6-311+G**	472	-3.5658	13178

The percentage deviation of SCF total energies, as basis sets vary from minimal to split valence to double-zeta split valence to triple-zeta split valence, is tabulated in Table 3. The deviation increases as the level of split valence increases, although this deviation is not significant. This is an indication that the SCF total energy is not affected as the basis set varies from minimal to split valence.

Table 3. Percentage Deviation of SCF Total Energy with Respect to the Minimal Basis Set

Basis Sets	Number of Basis Functions	SCF total energy (KJ/mol) / 10^6	Simulation time (second)
STO-3G	104	-3.5186	48
3-21G*	193	-3.5465	220
6-31G*	***289***	***-3.5650***	***1156***
6-31G**	334	-3.5651	1992
6-31+G*	357	-3.5651	3431
6-311G*	359	-3.5657	7062
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The percentage deviation of SCF total energies, as basis sets vary from un-polarized to polarized on 'p' and on 's' orbital, is tabulated in Table 4. The SCF total energies are not significantly different from each other, as indicated by almost equal percentage deviations, as shown in Table 4. This is an indication that the SCF total energy is not affected by the polarization on 'p' and on 's' orbital.

Table 4. Percentage Deviation of SCF Total Energy with Respect to the Un-polarized Basis Set

Basis Sets	Type of Polarization	% deviation
6-31G*	polarization on 'p' orbitals	0.52
6-31G**	polarization on 'p' and 's' orbitals	0.52
6-31+G*	polarization on 'p' orbitals, diffused	0.52
6-311G*	polarization on 'p' orbitals	0.54
6-311+G**	polarization on 'p' and 's' orbitals, diffused	0.54

The computational cost is attributed to the simulation time. The plot of the number of basis functions versus simulation time is shown in Fig. 2. It can be seen that the simulation time increases almost exponentially as the number of basis functions increases.

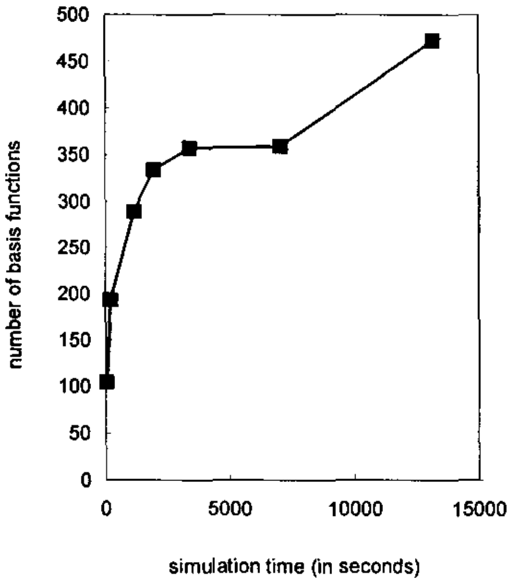

Figure 2. Number of Basis Functions versus Simulation Time (Curve-fitted Using Logarithmic Regression)

The choice of the appropriate level of theory can be based on the accuracy of computed SCF total energy and simulation time. On these regard, 6-31G* (Double Zeta Split valence, polarization on 'p' orbital) is the most appropriate level of theory.

CONCLUSIONS

Single point calculations using the Hartree-Fock self-consistent filled (HF-SCF) molecular orbital model were done to study the effect of basis set on the selection of the appropriate level of theory. Using the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate, the following conclusions were drawn:

1. With the exception of the minimal basis set, the SCF total energies for the other basis sets agree with each other in terms of magnitude.
2. The SCF total energy is not affected as the basis set varies from minimal to split valence.
3. The SCF total energy is not affected by the polarization on 'p' and on 's' orbital.
4. The most appropriate basis set was determined to be 6-31G* (Double Zeta Split valence, polarization on 'p' orbital).

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