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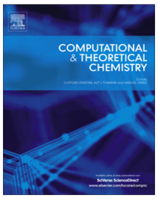

Applying group functions to description of ionic liquids

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ABSTRACT

Concept of group functions (GF) in quantum chemistry explicates chemical idea of ‘chromophores’ – fragments of molecules responsible for their physical properties and chemical reactivity. This concept permits to construct quantum chemical methods which provide correct qualitative and quantitative results for complex systems being unpretentious in computer resources. This is achieved by basing the form of the trial electronic wave function on adequate ’chromophores’ present in the system under study. If it can be said so, substantial percentage of needs in computational resources are switch on the researcher’s mind which should be able to realize what parts of the molecule are adequate ’chromophores’ at given conditions by this giving a chance to a “new concept of semi-empirism”.

In our previous studies group functions were applied to transition metal complexes of 3d-elements (effective Hamiltonian crystal field – EHCF) and to organic molecules with single and isolated multiple bonds (antisymmetrized product of strictly localized geminals – APSLG). It was shown that these methods can be successfully applied for theoretical study of complex systems which represent considerable difficulties for standard quantum chemistry methods. For organic molecules deductive molecular mechanics which represents a simplified version of the APSLG method was also proposed.

In the present paper recent results obtained with use of the GF theory are discussed. Deductive molecular mechanics force field stemming from the APSLG method is adopted for many-particle molecular assemblies and possibility of its application for modeling liquid state is demonstrated on an example of binary mixtures of hydrophobic-hydrophilic ionic liquids with water.

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1. Introduction

For the long history of progress in understanding nature of chemical compounds theoretical concepts which allow to explain and predict experimentally observed relations between properties and structure of the system have been developed. These concepts are based on the idea of picking out fragments of the molecule responsible for its specific properties like reactivity within a class of chemical transformations and to focus on this fragment, considering the rest to be inert at present conditions and taking its influence into account as ’perturbation’. This approach – dividing into parts is the most general way of studying the reality which was formulated as philosophic maxima yet by Rene Decartes: ’to divide each of the difficulties under examination into as many parts as possible, and as might be necessary for its adequate solution’ [1].

Creation of such concepts was decisive for the development of chemistry. The most convincing example is the concept of atom which allows chemists to understand nature and reactivity of matter and to provide a huge number of substances, materials and methods of their synthesis. Similar paradigm applies to physical properties of molecules as well. *E.g.,* color of substances is explained with use of the concept of chromophore proposed by Witt [2]. To emphasize the correctness of the idea to pick out the fragment responsible for the system’s properties we generalize term ’chromophore’ and use it for any distinguishable part of the system responsible for its properties following the suggestion of Ruedenberg [3] (see [4] for a detailed elaboration on this topic).

Unfortunately in quantum chemistry (QC) as we know it now there are no general approaches to explicate the idea of ’chromophores’ in QC (excluding several examples which explicate it in an intuitive way: crystal field theory [5] and Hückel theory [6]). The main reason which causes such state of affairs is that most ‘chromophores’ which are observable in chemistry are considered not to exist in QC. For example, chemical bonds are considered

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not to be observable, because there is no operator for them [7]; atoms are not existing in most the purist *ab initio* point of view, rather nuclei and electrons. Thus it is important to notice that all entities proposed by human are objects in mind which form the foundations of some symbolic systems (languages) describing the reality. And the only criterion of entity existence is the comparison of such description and reality itself (more detailed discussions can be found in [4]). At this point of view, atoms and bonds are observable entities, thus they should be somehow expressed in terms of QC.

We abstract the idea of 'chromophores' can come back to quantum chemistry if one takes the trial wave function (WF) [4] in the McWeeny's group functions approximation (GF) [8] as proposed in [9] assuming the groups to represent (generalized) chromophores. According to the group functions approximation total electronic wave function has the general form (see Appendix A also):

$$\Psi(x_1 \ldots x_N) = \widehat{A}\left\{\Phi^A(x_1 \ldots x_{N_A}) \cdot \Phi^B(x_{N_A+1} \ldots x_{N_B}) \cdot \ldots\right\}$$

$$N = N_A + N_B + \cdots$$

where A, B refer to subsystems in which the original system is divided,Φ^K are their electronic wave functions and N_K are numbers of electrons at these subsystems. $\widehat{A}$ is projection operator to the antisymmetric irreducible representation of the symmetric group S_N. When total WF Ψ is expressed that way, it is called *'group function'* [8]. SCF-like wave function is obviously a special case of group function which is obtained when all N_K are equal to unity.

Applying GF approach to transition metal complexes (containing 3d-elements) and organic molecules with single and isolated multiple bonds, two methods were performed n our previous studies: Effective Hamiltonian of Crystal Field (EHCF) [11] and Antisymmetrized Product of Strictly Local Geminals (APSLG) [10,12] respectively. Discussions of EHCF method is beyond the scope of this paper, further information may be found in [11,13,14]. In the present study we are going to focus on APSLG method and its descendants.

In the APSLG method the trial WF may be expressed as:

$$\Psi = \widehat{A}\prod_m g_m$$

where g_m are two-electronic functions which correspond to chemical bonds and lone electronic pairs in organic molecules, so called 'geminals'. This form of trial function takes chemical bonds as (generalized) 'chromophores' – observable entities – which is a natural choice for organic molecules with single and isolated multiple bonds [15–24]. In the second quantization formalism they can be expressed as:

$$g_m^+ = u_m r^+_{m\alpha} r^+_{m\beta} + v_m l^+_{m\alpha} l^+_{m\beta} + w_m (r^+_{m\alpha} l^+_{m\beta} + l^+_{m\alpha} r^+_{m\beta})$$

where u_m, v_m – amplitudes of ionic contributions; w_m – amplitude of covalent contributions; $r^+_{m\sigma}, l^+_{m\sigma}$ are Fermi-operators creating an electron with spin projection σ in the one-electronic states (OES) $|r_m\rangle$ and $|l_m\rangle$, respectively. For the lone pairs only one contribution remains:

$$g_m^+ = r^+_{m\alpha} r^+_{m\beta}.$$

As it was discussed previously [16] significant success of MM as applied to organic molecules is based on underlying representation of molecular electronic structure: in all MM schemes chemical bonds are assumed to be local and transferable pretty much independent on their surrounding. Chemical bonds are 'chromophores' in this case and using, say, APSLG approximation for the underlying wave function is a good starting point to deduce rather than simply parameterize an MM force field. Truly, strictly localized hybrid orbitals and transferable of one- and two electronic density matrix elements coming from APSLG permit to present the energy of a molecule in the classical form as combination of additive potentials with parameters determined from QC calculations (see Appendix B). Such alternative molecular mechanics dubbed as 'deductive molecular mechanics' (DMM) [20,21] was constructed in our previous works. In [18] it was shown that DMM is successful for organic molecules.

In present work we investigate a possibility of using DMM for molecular modeling of more complex system: hydrophobic-hydrophilic ionic liquids (HHILs) and their binary mixtures with water. HHILs are the new class of room temperature ionic liquids [25]. Binary biphasic systems containing HHILs and water are perspective for the heavy metal extraction because of HHILs' unusual property – they have high content of water being almost insoluble in it at the same time. Specifically, we address the HHIL *tetra*-octylammonium lauroylsarcosinate (TOALS) [25] in the framework of Monte-Carlo approach using the APSLG based force field with parameters having clear QC source. It is shown that such an approach gives acceptable results in molecular modeling of such complex system as a ionic liquid and its mixture with water. All presented results were obtained with use of our library CARTESIUS FORT implementing the GF concept and containing tools for modeling complex system of different composition and structure.

2. Is there nanostructural organization in ionic liquids? – APSLG based study

2.1. Force field

Force fields (FF) based on the assumption of transferability and additivity of various intra- and intermolecular interactions are widely used for modeling of liquids. Such an assumption allows one to represent the potential energy surface (PES) as a combination of some additive potentials with empirical parameters:

$$E = E^{bond} + E^{bend} + E^{torsion} + E^{Coulomb} + E^{vdW}$$

First three terms correspond to intramolecular interactions of bonded atoms (elongation of valence bonds, deformation of valence and torsion angles, respectively); the last two correspond to interactions of nonbonded atoms (electrostatic and van der Waals interactions). Each energy contribution depends on atomic coordinates and may have different functional forms. The quality of molecular simulations substantially depends on the functional form of potentials and values of parameters in force field.

Being successfully used for modeling of huge number of molecular systems (specifically, for ionic liquids [26–35]), these molecular mechanics FFs do not have their own charge distributions rather use interpolated ones obtained through training against QC calculations. Substantial advantage of DMM force field used in present study is that it has its own charge distribution and at the same time requires much less computational resources then any QC method.

It should be noted that additional terms in the total energy appear because of the mutual influence of the atomic charge distributions (known as van der Waals interactions). In principle they can be obtained in APSLG by using perturbation theory [15], but it is beyond the scope of this paper. Thus we take the van der Waals interactions into account by applying Lennard-Jones potential in its classical (6–12) form with parameters given in [27]. In conclusion, the form of the force field used in present work is:

$$E = E^{SLG}_{total} + E^{VDW}$$

(for complete expression for E^{SLG}_{total} see Appendix B) with MINDO/3 [17] parametrization used for APSLG part. The single molecule

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