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Application of the reference interaction site model self-consistent field method based on the Dirac–Hartree–Fock wave function to a chemical reaction

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Abstract. The reference interaction site model self-consistent field (RISM-SCF) method is a combined method of the electronic structure theory of molecules and the integral equation theory of molecular liquids. The RISM-SCF method based on the Dirac–Hartree–Fock wave function, recently proposed, is applied to a chemical reaction, specifically, a Menshutkin reaction in aqueous solution. The Helmholtz energy profile along the reaction coordinate is calculated and the characteristics of the reaction are discussed based on energy component analysis.

1. Introduction

Relativistic effects play an important role in the electronic structure of molecules containing heavy elements. It is now well known that both the scalar and spin–orbit effects are important for the geometry and properties of molecules. There are several methods to treat these relativistic effects theoretically. Among them, the four-component method [1] based on the Dirac equation is one of the most suitable methods for treating relativistic effects because it is based on the basic equation of relativistic quantum mechanics. Therefore, many methods for describing the electronic structure, including electron correlation methods, have been transferred to the relativistic four-component level.

For molecules in the solution phase, solvent effects also play an important role. Among the various solvation models, the polarizable continuum model (PCM) [2,3] is one of the most widely used approaches. In the PCM approach, the solvent molecules are considered as a continuum medium. In 2015, Di Remigio et al. [4] presented a formulation of a four-component relativistic self-consistent field (SCF) theory for a molecular solute described within the PCM for solvation, and successfully applied it to systems containing heavy elements. The PCM method is very effective, yet it does not include microscopic solute–solvent interactions such as hydrogen bonds. A method that can handle such microscopic interactions is the reference interaction site model self-consistent field (RISM-SCF) method [5,6], which combines the electronic structure theory with the reference interaction site model [7,8], an integral equation theory of molecular liquids.



Recently, we have proposed the RISM-SCF based on the Dirac–Hartree–Fock (DHF) method, one of the four-component relativistic molecular orbital (MO) methods [9]. This method can simultaneously calculate the precise electronic structure of molecules, including relativistic effects, with the DHF method and the solvent structure with the RISM theory. In the original article, the theoretical structure of the DHF/RISM-SCF method and its energy derivative is presented and applied to several molecular systems. In the present article, we present the application of this method to a chemical reaction involving heavy atoms—a Menshutkin reaction in aqueous solution, $\text{NH}_3 + \text{CH}_3\text{I} \rightarrow \text{NH}_3\text{CH}_3^+ + \text{I}^-$.

2. Method

2.1. DHF/RISM-SCF method

The DHF/RISM-SCF method [9] was obtained as a variational problem for free energy, as initially proposed by Sato et al. [10] for a multiconfiguration SCF wave function. Consider a system in which a quantum mechanical solute molecule is immersed in a solvent composed of classical molecules at infinite dilution. In the variational formulation, the basic equations are derived from the stationary conditions for the Helmholtz energy Lagrangian:

$$L(\mathbf{C}, \boldsymbol{\zeta}^U, c, h, t) = E^U(\mathbf{C}) + \Delta\mu(\mathbf{C}, c, h, t) + \boldsymbol{\zeta}^U \cdot \mathbf{e}^U(\mathbf{C}). \quad (1)$$

The first term of the right-hand side in Eq. (1) represents the electronic energy of the solute molecule and \mathbf{C} is the set of variational parameters in the wave function. The second term represents the excess chemical potential of solvation, and c , h , and t are the direct, total, and indirect correlation functions describing the solvent structure around the solute molecule, respectively. The third term corresponds to constraints on the parameters \mathbf{C} in the solute wave function, i.e., the orthonormality of orbitals and/or the normalization of the wave function. The symbols \mathbf{e}^U and $\boldsymbol{\zeta}^U$ are the sets of constraints and multipliers, respectively. Taking variations of the Lagrangian with respect to the correlation functions and MO coefficients, we obtain the basic equations for RISM-SCF from the stationary conditions.

The resulting RISM-SCF equation is given as

$$\mathbf{F}^{\text{solv}} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\epsilon}, \quad (2)$$

where \mathbf{F}^{solv} is the four-component solvation Fock matrix

$$\mathbf{F}^{\text{solv}} = \begin{bmatrix} \mathbf{F}^{\text{LL,gas}} + \mathbf{V}^{\text{LL,solv}} & \mathbf{F}^{\text{LS,gas}} \\ \mathbf{F}^{\text{SL,gas}} & \mathbf{F}^{\text{SS,gas}} + \mathbf{V}^{\text{SS,solv}} \end{bmatrix}, \quad (3)$$

and \mathbf{C} , \mathbf{S} , and $\boldsymbol{\epsilon}$ are the four-component coefficient, overlap, and eigenvalue matrices, respectively. The matrices \mathbf{F}^{gas} and \mathbf{V}^{solv} in Eq. (3) are the conventional Fock matrix in the DHF method and the potential matrix due to the solvent. By solving Eq. (2) coupled with the RISM equations, the electronic structure of the solute molecule and the solvation structure of the solvent are obtained simultaneously.

2.2. Computational details

The DHF/RISM-SCF method was applied to a Menshutkin reaction, $\text{NH}_3 + \text{CH}_3\text{I} \rightarrow \text{NH}_3\text{CH}_3^+ + \text{I}^-$, in aqueous solution. The Helmholtz energy profile was drawn along a reaction coordinate. The reaction coordinate was defined as the difference between the C–I and C–N distances. The basis sets used were the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis sets for C, N, and H, and Dyal’s double-zeta with polarization basis set for I. For CH_3I , the parameters for RISM were the same as given in our earlier paper [9]. For NH_3 , the pairs of Lennard-Jones parameters (σ in Å, ϵ in kcal mol⁻¹) were (3.250, 0.1700) for N and (1.069, 0.0157) for H. The reaction path was determined by constrained optimization at the Hartree–Fock/cc-pVDZ-PP level.

3. Results and discussion

Figure 1(A) shows the Helmholtz energies A along the reaction coordinate $d = r(\text{C–N}) - r(\text{C–I})$ by the DHF/RISM-SCF and DHF/PCM-SCF methods, where A is shifted so that the energy of the reactant $\text{NH}_3 + \text{CH}_3\text{I}$ in the gas phase is zero. RISM-SCF gives a higher Helmholtz energy than PCM-SCF on

the reactant side while giving a lower Helmholtz energy on the product side. The reaction is exergonic, and the reaction free energies are $-47.37 \text{ kcal mol}^{-1}$ and $-33.42 \text{ kcal mol}^{-1}$ for RISM-SCF and PCM-SCF, respectively. This is because the solutes are ionized in the product state due to charge separation, which enhances the solute–solvent interaction and stabilizes the product state. RISM describes hydrogen bonds between solutes and solvents well, however, PCM underestimates them. RISM, therefore, has a greater stabilization of the product state compared with the PCM case. Because of the larger reaction free energy, the transition state (TS) of RISM-SCF is located more on the reactant side than in the case of PCM-SCF, at $d = 0.0 \text{ \AA}$ for RISM-SCF and at 0.3 \AA for PCM-SCF. The activation free energies are 7.23 and $12.94 \text{ kcal mol}^{-1}$ for RISM-SCF and PCM-SCF, respectively. Note that an activation energy of $23.5 \text{ kcal mol}^{-1}$, determined by kinetic analysis, was reported for this reaction by Okamoto et al. [11,12]; it is different from the activation *free* energy, however, and therefore cannot be directly compared.

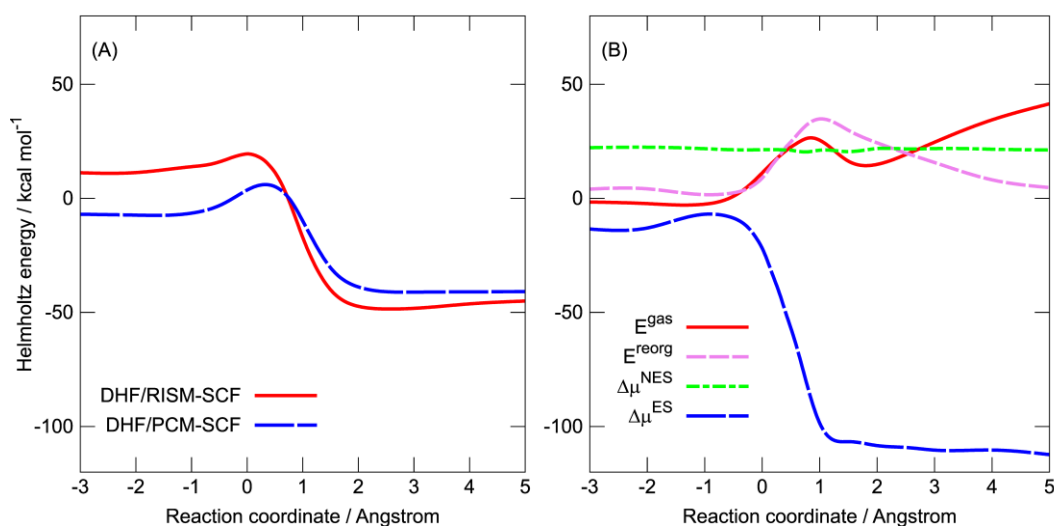


Figure 1. (A) Helmholtz energy profiles of RISM-SCF and PCM-SCF and (B) energy components of RISM-SCF.

The Helmholtz energy A can be decomposed into the solute energy in the gas phase E^{gas} , the reorganization energy E^{reorg} , and the nonelectrostatic and electrostatic parts $\Delta\mu^{\text{NES}}$ and $\Delta\mu^{\text{ES}}$ of the excess chemical potential, as $A = E^{\text{gas}} + E^{\text{reorg}} + \Delta\mu^{\text{NES}} + \Delta\mu^{\text{ES}}$. Figure 1(B) shows the components of A by RISM-SCF, where E^{gas} is shifted so that E^{gas} of the reactant is zero. E^{gas} has a very shallow first minimum and a second minimum, corresponding to the dipole compound and ion pair, respectively, as the typical Menshutkin reaction profiles in the gas phase show. The very shallow first minimum is due to the very small dipole moment of CH_3I . This energy is destabilized by the nearly constant $\Delta\mu^{\text{NES}}$ and by E^{reorg} , although stabilized by $\Delta\mu^{\text{ES}}$. The stabilization by $\Delta\mu^{\text{ES}}$ is particularly pronounced after the TS, where the charges are separated.

Table 1 shows the Helmholtz energies A by RISM-SCF and their components at the reactant, TS ($d = 0.0 \text{ \AA}$), and the product. In the reactant, which is a pair of neutral molecules, E^{reorg} and $\Delta\mu^{\text{ES}}$ are relatively small (3.88 and $-13.55 \text{ kcal mol}^{-1}$, respectively) and $\Delta\mu^{\text{NES}}$ is dominant ($21.93 \text{ kcal mol}^{-1}$). In the TS, E^{gas} increases relative to the reactant ($11.17 \text{ kcal mol}^{-1}$) and E^{reorg} also increases in response to the increase in charge bias ($8.89 \text{ kcal mol}^{-1}$). $\Delta\mu^{\text{ES}}$ also becomes large ($-21.90 \text{ kcal mol}^{-1}$), as in E^{reorg} , but is still comparable to $\Delta\mu^{\text{NES}}$ ($21.33 \text{ kcal mol}^{-1}$) because the charges are not sufficiently well separated. This may be because the TS is on the reactant side in the Helmholtz energy profile. In contrast,

in the product, E^{gas} increases significantly (95.27 kcal mol⁻¹) due to charge separation, whereas E^{reorg} is relatively small (0.87 kcal mol⁻¹) because the system has already been separated into ions. In the product, which is a pair of ions, $\Delta\mu^{\text{ES}}$ is very large (-152.50 kcal mol⁻¹) and greatly stabilizes the system, outweighing the destabilization of E^{gas} .

Table 1 Helmholtz energies and their components at the reactant, TS, and product (kcal mol⁻¹)

	Reactant		TS	Product	
	Total	NH ₃ + CH ₃ I	NH ₃ -CH ₃ -I	Total	NH ₃ CH ₃ ⁺ + I ⁻
A^a	12.26	-0.34 + 12.60	19.49	-35.11	
Component					
E^{gas} ^a	0.00		11.17	95.27	
E^{reorg}	3.88	3.15 + 0.73	8.89	0.87	0.87 + 0.00
$\Delta\mu^{\text{NES}}$	21.93	7.46 + 14.47	21.33	21.25	13.95 + 7.30
$\Delta\mu^{\text{ES}}$	-13.55	-10.95 - 2.60	-21.90	-152.50	-57.60 - 94.89

^a The values of A and E^{gas} are shifted so that the energy of the reactant in the gas phase $E^{\text{gas}}(\text{R})$ is zero. $E^{\text{gas}}(\text{R}) = -4525521.55$ kcal mol⁻¹

Overall, the data in the figure and the table well illustrate the characteristics of the Menshutkin reaction, which is endergonic in the gas phase due to the ion dissociation, resulting in a late TS, but exergonic in the aqueous phase due to the large stabilization of the ionic product by the solvent, resulting in an early TS.

4. Conclusions

We have presented an application of the RISM-SCF method, based on four-component relativistic electronic structure theory, to a chemical reaction. We created Helmholtz energy profiles of a Menshutkin reaction $\text{NH}_3 + \text{CH}_3\text{I} \rightarrow \text{NH}_3\text{CH}_3^+ + \text{I}^-$ and conducted a component analysis. The reaction profile based on method well described the characteristics of the Menshutkin reaction. Component analysis revealed the contributions of the effects of electron reorganization, and electrostatic and nonelectrostatic interactions. The DHF/RISM-SCF method has proven to be an effective method for analyzing chemical reactions of systems containing heavy atoms such as iodine. The current method does not include the electron correlation effect in molecules. However, the development of RISM-SCF based on four-component electron correlation methods is currently underway.

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