Calculation of NMR chemical shift combined with RISM-SCF-SEDD method

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We propose a new method for calculating NMR chemical shifts in solutions based on the reference interaction site model self-consistent field spatial electron density distribution (RISM-SCF-SEDD) method. In the RISM theory, we solve the integral equations of molecular liquids. By combining this method with electronic structure theory, the description of solvent effects is expected to be better than those with implicit solvent models such as the PCM method.

In order to obtain the Fock operator of the RISM-SCF method, we variationally minimize the Helmholtz free energy A

$$A = E_{\mathrm{solute}} + \Delta\mu,$$

which is the sum of the electronic energy of the solute molecule and the excess chemical potential of solute-solvent interaction [J. Chem. Phys. 105, 1546 (1996)]. The component of the nuclear magnetic shielding tensor of a nuclei X is described as second derivative of A with respect to the external magnetic field B and the nuclear magnetic moment m

$$\sigma^X_{\alpha\beta} = \left.\frac{\partial^2 A(\mathbf{B},\mathbf{m})}{\partial B_\alpha \partial m^X_\beta}\right|_{\mathbf{B}=\mathbf{0},\mathbf{m}=\mathbf{0}} \qquad (\alpha,\beta = x,y,z).$$

Yamazaki et al. reported this formulation, and the calculation of NMR chemical shifts with the RISM-SCF method was performed [J. Chem. Phys. 115, 8949 (2001)]. However, in the conventional RISM-SCF theory, the electrostatic potential of a solute is described with the distribution of point charges located on atoms. This treatment often results in ill-description of buried atoms and polarizable molecules.

Yokogawa et al. proposed the RISM-SCF-SEDD method by introducing new description of coulomb interaction with spatial electron density distribution (SEDD) [J. Chem. Phys. 126, 244504 (2007)]. This method overcame the defects of the conventional RISM-SCF method and significantly improved numerical stability. In this study, we combine the RISM-SCF-SEDD method with the NMR calculation. It is expected that we can accurately evaluate the chemical shifts of buried atoms such as carbon or nitrogen. This new method is also applicable to the chemical shift of a strongly polarizable molecule in solution. The results of numerical calculation will be discussed in poster presentation.