

I-R Analysis Method of Electronic Structure

Understanding of chemical bond has been one of the main subjects in physical chemistry since its foundation. Nowadays, it is easy for the modern quantum-chemical technique to compute bond energy, length or detailed information on wave functions. However, it is difficult to directly bridge between these results and traditional chemical concepts (or chemical intuition), because the wave function of a molecule is usually described in terms of molecular orbitals (MO) being de-localized over whole molecule. Even obtaining the wave function of the molecule, it is numerical description of the molecule, and is often far from chemical intuition. Various methods have been developed to make up for the deficiencies in MO method. One good example is population analysis, which provides the information on an atom in a molecule. In this project, we have developed new analysis methods abstracting chemical concepts from computational results of standard MO.

I-R-1 Analysis on Solvated Molecule with a New Energy Partitioning Scheme for Intra- and Intermolecular Interactions

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A new partitioning scheme for the total energy of molecules is presented. In the scheme, the Hartree-Fock total energy of a molecular system is represented as the sum of one- and two-center terms exactly. The present method provides physically reasonable behavior for a wide range of interactions, and intermolecular interaction is treated equivalently with intramolecular interaction. The method is applied to analysis on the inter- and intramolecular interactions of molecular complexes both in gas phase and in aqueous solution. The results strongly indicate that the present method is a powerful tool to understand not only the bonding nature of molecules but also interaction between molecules.

I-R-2 A New Analysis of Molecular Orbital Wavefunctions Based on Resonance Theory

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A new method to evaluate the weights of resonance

structures from molecular orbital wave function is proposed, which is based on the second quantization of singlet-coupling. The present method is useful to analyze molecules of which the electronic structures are well localizable. The evaluation is carried out through localization of molecular orbitals followed by algebraic calculation of density matrices. This method is applied to H₂O, H₃O⁺, and BH₃. The calculated weights of covalent and ionic structures are in excellent agreement with those of the previous works and our chemical intuition.

I-R-3 Solvation Effect on Resonance Structure. Extracting Valence Bond-Like Character from Molecular Orbitals

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We have analyzed the resonance structure in the electronic structure for solvated molecules, which are computed by the RISM-SCF method. The analysis offers a bridge between modern quantum computational results and chemical intuitions. As expected, the contribution from the ionic structure tends to be enhanced in aqueous solutions on the electronic structure polarization due to solvation. The present procedure offers understanding of the nature of chemical bonds in a solvated molecule.

I-S Solvation Structure and Its Effect on Electronic Structure

It is well known that the electronic structure of a molecule considerably changes when the molecule is dissolved in solvent. Understanding the essential of this complex event requires three points of view, namely, the electronic structure of the molecule, solvation structure around it and these coupling. In this project, we have developed various types of methods to describe solvation processes and applied them to real systems.

I-S-1 A New Method to Reconstruct Three-Dimensional Spatial Distribution Function from Radial Distribution Function in Solvation Structure

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Three-dimensional spatial distribution function SDF of solvent is a fundamental quantity for analysis of solvation. However, its calculation has been very limited because long computational time is required. We here developed a novel and robust method to construct approximated SDFs of solvent sites from radial distribution functions. In this method, the expansion of SDFs in real solid harmonics around atoms of solute leads to a linear equation, from which SDFs are evaluated with reasonable computational time. This method is applied to the analysis of the solvation structure of liquid water, as an example. The successful results clearly show that this method is very powerful to investigate solvation structure.

I-S-2 New Evaluation of Reconstructed Spatial Distribution Function from Radial Distribution Functions

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Although three dimensional (3D) solvation structure is much more informative than one dimensional structure, its evaluation is difficult experimentally and theoretically. In our previous communication [Yokogawa *et al. J. Chem. Phys.* **123**, 211102 (2005)], we proposed a new method to present reconstructed spatial distribution function (RC-SDF) from a set of radial distribution functions (RDFs). In this article, we successfully extended the method more accurately with new basis sets. This new method was applied to two liquid solvation structures, methanol and DMSO, as examples. Their RC-SDFs evaluated here clearly show that the former solvation structure is well-defined while the latter one is broad, which agrees well with the SDFs calculated directly from MD simulations. These results indicate that the method can reproduce well these 3D solvation structures in reasonable computational cost.