I-K Simulation and Dynamics of Real Molecular Systems

Accurate quantum computational chemistry has evolved dramatically. The size of molecular systems, which can be studied accurately using molecular theory is increasing very rapidly. Theoretical chemistry has opened up a world of new possibilities. It can treat real systems with predictable accuracy. Computational chemistry is becoming an integral part of chemistry research. Theory can now make very significant contribution to chemistry. The project focuses on the theoretical development in methodologies for the study of molecular electronic structures. We are aiming at developing accurate molecular theory on systems containing hundreds of atoms. We have continued our research in the following three directions: (i) development of new *ab initio* theory, particularly multireference based perturbation theory, (ii) development of exchange and correlation functionals in density functional theory, and (iii) development of molecular theory including relativistic effects.

I-K-1 UTChem—A Program for *Ab Initio* Quantum Chemistry

YANAI, Takeshi[1]; NAKANO, Haruyuki[2];
NAKAJIMA, Takahito[2,3]; TSUNEDA, Takao[2];
HIRATA, So[4]; KAWASHIMA, Yukio; NAKAO,
Yoshihide[2]; KAMIYA, Muneaki[2]; SEKINO, Hideo[5];
HIRAO, Kimihiko[6]
(*[1]Oak Ridge Natl. Laboratory, USA; [2]Univ. Tokyo,
[3]PREST; [4]William R Wiley Environmental Molecular
Sci. Laboratory Battelle, USA; [5]Toyahashi Univ. Tech.;
[6]IMS and Univ. Tokyo*)

Present molecular quantum theory is highly sophisticated, and has evolved dramatically. Software forms a basis for computational chemistry. However, it is not an easy task for an individual/group to develop a comprehensive new program package in *ab initio* quantum chemistry from scratch. Several years ago, we decided to accept this challenge. In view of the availability of such good programs as Gaussian, Gamess, Molcas, NWChem, *etc.*, one may question the relevance of a new program package. We have three arguments for our project. (1) First, we believe that healthy competition is very important in science. (2) Second, we can have a good harvest by doing research using other programs, but it is an abortive flower. We could not make a true breakthrough if we were circumscribed by current software limitations. (3) Third, in spite of the excellent performance of other programs, there are important and powerful methods that others cannot yet handle. We have developed new methodologies in quantum chemistry, particularly the multireference-based perturbation theory for describing chemical reactions and excited states, relativistic molecular theory to treat heavy elements, parameter-free (less) exchange and correlation functionals in DFT, highly efficient algorithms for calculating molecular integrals over generally contracted Gaussians, *etc*. UTChem is a research product of our work to develop new and better theoretical methods in quantum chemistry. Most of the codes have been developed recently by Hirao's group at the University of Tokyo. The basic philosophy behind UTChem is to develop methods that allow an accurate and efficient computational chemistry of electronic structure problems for molecular systems in both the ground and excited states. UTChem also contains codes for well-developed methods such as MPn, CI, CC, *etc.*, which are standard in most quantum chemistry programs. We are aiming ultimately at better performance than other programs. UTChem will soon be ready for distribution. Here you will be able to see the features of UTChem. UTChem contains a large number of improvements and some interesting new features, which others cannot match.

I-K-2 Douglas-Kroll Transformation to the Relativistic Many-Electron Hamiltonian

NAKAJIMA, Takahito[1,2]; HIRAO, Kimihiko[3]
(*[1]Univ. Tokyo; [2]PREST; [3]IMS and Univ. Tokyo*)

A new generalized Douglas-Kroll (DK) approach has been proposed for the relativistic many-electron Hamiltonian including the electron-electron interaction. In order to consider the higher-order DK transformation to the two-electron interaction, the present approach adopts the effective one-electron potential in the Dirac-Hartree-Fock (DHF)/Dirac-Kohn-Sham (DKS) operator as an expansion parameter in the DK transformation. Its numerical performance is tested for the atomic Hg and molecular HAt and At_2 systems. The third-order DK transformation to both one-electron and two-electron Hamiltonians, which is the highest level of theory treated in this study, gives excellent agreement with the four-component relativistic approach. The first-order DK correction to the two-electron interaction is proved to be satisfactory for both atomic and molecular systems.

I-K-3 A Four-Index Transformation in Dirac's Four-Component Relativistic Theory

ABE, Minori[1]; YANAI, Takeshi[2]; NAKAJIMA,
Takahito[1,3]; HIRAO, Kimihiko[4]
(*[1]Univ. Tokyo; [2]Oak Ridge Natl. Laboratory, USA;
[3]PREST; [4]IMS and Univ. Tokyo*)

A four-index transformation from atomic orbitals to molecular orbitals is an essential first step in any calculation that aims to account for correlation effects. An efficient integral transformation program based on the four-component spinors resulting from the Dirac-

Hartree-Fock method is implemented in our program package, *UTChem*. By adopting generally contracted spherical harmonic Gaussian-type spinors, the number of small-component basis functions is reduced to about one half compared with commonly used kinetically balanced basis sets. The decrease in basis functions permits an efficient integral transformation. The present integral transformation program is four to eight times faster than the pioneering programs of MOLFDIR and DIRAC. As illustrative examples, the singles and doubles coupled-cluster methods with and without perturbative triples [CCSD, CCSD(T)] are applied to the ground state of thallium hydride. The computed spectroscopic constants are in good agreement with experiment.

I-K-4 Recent Advances in Multireference-Based Perturbation Theory

NAKANO, Haruyuki[1]; HIRAO, Kimihiko[2]
(*[1]Univ. Tokyo; [2]IMS and Univ. Tokyo*)

Accurate *ab initio* computational chemistry has evolved dramatically. In particular, the development of multireference-based approaches has opened up a completely new area, and has had a profound impact on the potential of theoretical chemistry. Multireference-based perturbation theory (MRPT) is an extension of the closed-shell single reference Møller-Plesset method, and has been successfully applied to many chemical and spectroscopic problems. MRPT has established itself as an efficient technique for treating nondynamical and dynamical correlations. Usually, a complete active space self-consistent field (CASSCF) wave function is chosen as a reference function of MRPT. However, CASSCF often generates too many configurations, and the size of the active space can outgrow the capacity of the present technology. Many attempts have been proposed to reduce the dimension of CASSCF and to widen the range of applications of MRPT. This review focuses on our recent development in MRPT.