Relativistic Molecular Theory

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This brief review contains surveys of both four-component and two-component relativistic molecular theories. First the four-component relativistic approach is reviewed. Emphasis is placed on efficient computational schemes for the four-component Dirac-Hartree-Fock and Dirac-Kohn-Sham methods. Next, in the two-component relativistic framework, two relativistic Hamiltonians, RESC and higher-order Douglas-Kroll (DK), are introduced. An illustrative application is shown for the relativistic study on valence photoelectron spectrum of OsO_4. The developing four-component relativistic and approximate quasi-relativistic methods have been packed in a program suite named REL4D.

Key Words : Relativistic molecular theory, REL4D

Introduction

The relativistic effect has been considered as an essential factor to figure out molecular structures, chemical activities, or various properties of heavy-element systems theoretically. Recently many quantum chemists have dedicated a lot of efforts to the calculation and treatment of the electronic structures of polyatomic systems including heavy elements, which are involved in many interesting chemical and physical phenomena. They still present unique difficulties to the theoretical study. Until recently, the relativistic effect had ever been thought less important for chemical properties because the relativity appears primarily in the core electrons, which had been believed to be unlikely to affect chemically active valence regions dramatically. Recent studies, however, have revealed not only quantitatively but also qualitatively that the relativistic effect plays essential and comprehensive roles in total natures of molecular electronic structures for heavy-element systems. We are nowadays convinced that the relativistic effect is definitely important for the accurate theoretical treatment of heavy-element systems as well as the electron correlation effect.

We have recently developed several relativistic molecular theories including four-component relativistic and approximate quasi-relativistic approaches. For the four-component relativistic approach, which is the rigorous relativistic treatment using the four-component spinors explicitly, our development starts from derivation of the analytical form of the basis spinor. In the four-component case we have to manage to get rid of the variational collapse coming from using the finite basis sets. We have proposed the efficient four-component basis spinors using the generally contracted kinetically balanced Gaussian-type spinors, which are taken from the analytical spinor forms corresponding to the one-electron hydrogenic system, and maintain the variational stability through the kinetic balance condition. Furthermore, our contraction basis spinors have merits to give the correct behavior to the atomic limit, and require significantly less

number of small-component basis spinors than the conventional decoupled scalar spin-orbitals used in the pioneering four-component programs MOLFDIR and DIRAC. We have formulated and implemented Dirac-Hartree-Fock (DHF)[1] and Dirac-Kohn-Sham (DKS)[2] methods, which have been made computationally feasible by exploiting the highly efficient integral method for two-electron repulsion integrals over the two-component basis spinors. Adoption[1,3] of the ACE formula proposed by Ishida[4] and the transfer relation proposed by Head-Gordon and Pople[5] makes our algorithm efficient. It is shown that our REL4D program is about 60 times faster than an old style of four-component relativistic program, MOLFDIR, in the Au_2 case, and our algorithm is very efficient.[3]

Even though we have spent much effort to develop the four-component method, still, the relativistic method using four-component spinors demands severe computational efforts to solve, and has a lot of difficulties to be applied to the large-size molecules. Thus, we have proposed as the quasi-relativistic approximation instead of solving the Dirac equation with the fully four-component spinors. Chemists' interest is devoted to the electronic solution, although the four-component calculations provide the eigenstates for not only electronic states but also positronic ones. The motivation of two-component approximation is to obtain the electronic states without treating the positronic solution explicitly. However, since the relativistic effect appearing in the electronic states is closely related to the positronic states in the four-component language, the problem of two-component method is how we can effectively retrieve the effect lost by neglecting the positronic solutions within the framework of the two-component Hamiltonian. In our recent works, we have developed the two kinds of two-component quasi-relativistic method using the RESC[6,7] and higher-order Douglas-Kroll (DK)[8,9] Hamiltonian. The RESC Hamiltonian has been derived from the eliminating small component equation with the relativistic substitutive correction. The higher-order DK Hamiltonian is the effective Hamiltonian

obtained by transforming the Dirac Hamiltonian by an exponential-type unitary operator based on the philosophy of DK transformation.[10,11] The exponential-type operator, which we have proposed, can simplify the formulation and implementation of the higher-order transformation by taking full advantage of the Baker-Campbell-Hausdorff expansion. Both two-component methods have the excellent features that they contain no singularity, therefore, and variationally treat the relativistic effect on the same footing as the electron correlation.

We have also developed several related works that make practical calculations possible with the relativistic approaches mentioned so far: the relativistic Gaussian basis sets.[12,13] the relativistic effective core potentials.[14,15,16] the relativistic energy gradient method.[17]

The resulting four-component relativistic and approximate quasi-relativistic codes and their related works have been packed in a program suite named REL4D. The efficient ERI engine contributes to the performance for generating relativistic molecular integrals. In the self-consistent field (SCF) routine, several techniques have been implemented: the restricted open-shell treatment proposed by Davidson, the direct and conventional SCF methods, and the direct inversion in the iterative subspace (DIIS) method. The numerical grid-quadrature routine for the exchange-correlation potentials is implemented for our DKS scheme. The (SS|SS) integrals can be treated near the SCF convergence in the direct SCF approach. Using the REL4D program, we are now cultivating a way to clarify the importance of the relativity in chemistry.

We have applied our relativistic molecular theories to various chemical phenomena: the determination of the complicated spectra.[18,19] the determination of the spectroscopic constants.[20-23] the calculation of electric and magnetic properties.[24-26] and the pursuit of the chemical reaction.[27] In this review, we introduce the relativistic study on valence photoelectron spectrum of OsO4.[18]

The tetrahedral osmium oxide OsO4 has been extensively studied by the photoelectron spectroscopy (PES). The spectrum consists of five distinct band systems, called as peaks A, B, C, D, and E. Unfortunately, the band assignments proposed differ in each of these PES studies. Furthermore, numerous *ab initio* computational and DFT approaches have been applied to this molecule with the aim of assigning the upper five valence ionization bands. However, some uncertainties still remain for assigning these bands mainly due to occurrence of significant relativistic and correlation effects. There is no theoretical work studied by the method fully including both relativistic and correlation effects. In this study, we clarify the whole range of the observed PES of OsO4 by all-electron RESC-CASPT2 theory. Figures 1 and 2 show the non-relativistic and relativistic CASPT2 results, respectively. RESC-CASPT2 gives values for the peak positions and intensities in reasonable agreement with the resolved photoelectron spectrum data. It is expected that the Os valence 6s and 5p orbitals are stabilized while Os 5d orbitals are destabilized due to the relativistic effect. This
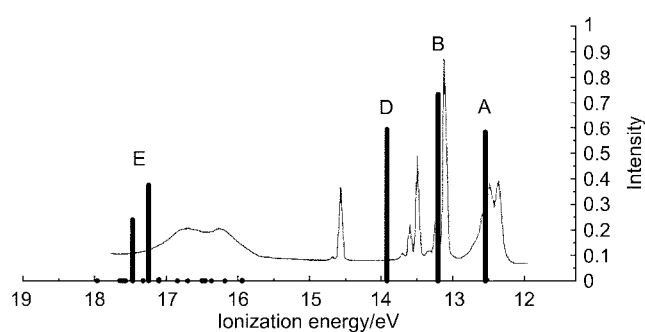

Figure 1. The theoretical ionization spectrum of OsO4 calculated by non-relativistic CASPT2.
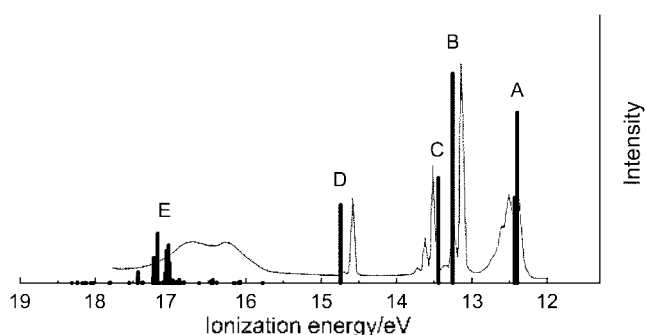

Figure 2. The theoretical ionization spectrum of OsO4 calculated by spin-orbit RESC-CASPT2.

change can be attributed to the change of the orbital (radial) part of the wave function, as known well. The A band originating from O 2p MOs remains almost unchanged with the relativity. We can see that the peak C cannot be obtained without the relativity. This study confirms that the peak C arises from the spin-orbit coupling in the ionic $^2T_2(3t_2)$ states originated from the Os 5p orbitals. The observed intensity ratio of the B and C peaks is approximately 2 : 1. This is fully supported by the present calculations. Peak positions and intensities suggest that there is no doubt that this splitting could be associated with the bands B and C observed in PES. The peak D moves by 0.8 eV to the high energy side by the spin-free relativistic effects due to the stabilization of Os 6s orbital. The band D is originated from Os 6s and the peak position and intensity are rather insensitive to the spin-orbit effects. Under the E band, there are many two-electron shake-up peaks commencing at *ca.* 16.0 eV in addition to the two one-electron ionization peaks. The broad feature of the E band is due to these satellite peaks.

In summary, the recent developments of our relativistic molecular theories are introduced in this brief review. Our approaches are expected to be useful and effective for various studies of electronic structures and spectroscopic properties of large-scale heavy-element systems.

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