Advanced Electronic Structure Theory in Quantum Chemistry

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Aiming at predictive computational modelings of molecular electronic structures with *ab initio* quantum chemistry calculations, our scientific exploration is to establish a cutting-edge theoretical methodology that allows one to compute accurately and efficiently the complex electronic structures, in which strongly-interacting electrons play a crucial role to characterize the nature of molecules. The complicated electronic structures can be handled accurately with the multireference theory, which deals with multiple important electronic configurations on equal footing. However, with the standard multireference methods such as the complete active space self-consistent field (CASSCF), the tractable size of the reference space is limited to small active space because the complexity of the calculations grows exponentially with the reference size. The existing multireference methods are nevertheless usefully applied to chemical theory problems such as exploring chemical reactions of bonding, dissociation and isomerization along the reaction coordinates, electronically excited states, unstable electronic structures of radical systems, and multiple covalent bindings in molecular metal complexes, *etc*. Our resultant works to be reported here are (1) to develop a type of the multireference correlation model named Canonical Transformation (CT) theory, which can efficiently describe short-range dynamic correlation on top of the multi-configurational staring wave function, (2) to construct the extensive complete active space self-consistent field (CASSCF) method combined with *ab initio* density matrix renormalization group (DMRG) method for making unprecedentedly larger active spaces available for the CASSCF calculations, and (3) to develop an efficient second-order perturbation theory that can use large active space with the DMRG-SCF reference wavefunction.

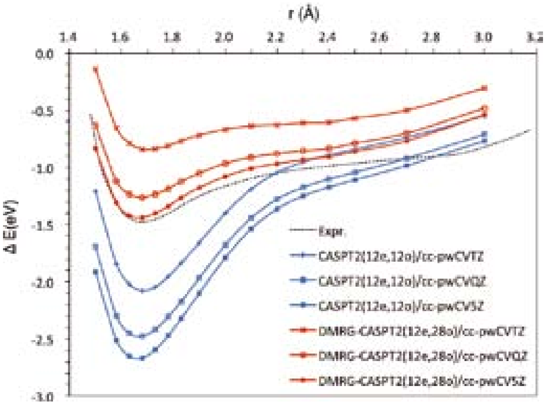

Figure 1. CASPT2(12e,12o)/$\mathbf{g}_1$ and DMRG-CASPT2(12e,28o)/$\mathbf{g}_1$/M = 512 potential energy curves of Cr_2 with a suite of cc-pwCXZ basis sets (X = T,Q,5). The energies ΔE are given relative to the isolated atoms. Experimental curve is included.

1. Second-Order Perturbation Theory with a DMRG Self-Consistent Field Reference Function: Theory and Application to the Study of Chromium Dimer[1)]

We have presented a second-order perturbation theory based on a density matrix renormalization group self-consistent field (DMRG-SCF) reference function. The method reproduces the solution of the complete active space with second-order perturbation theory (CASPT2) when the DMRG reference function is represented by a sufficiently large number of renormalized many-body basis, thereby being named DMRG-CASPT2 method. The DMRG-SCF is able to describe non-dynamical correlation with large active space that is insurmountable to the conventional CASSCF method,[2–3)] while the second-order perturbation theory provides an efficient description of dynamical correlation effects. The capability of our implementation is demonstrated for an application to the potential energy curve of the chromium dimer, which is one of the most demanding multireference systems that require best electronic structure treatment for non-dynamical and dynamical correlation as well as large basis sets. The DMRG-CASPT2/cc-pwCV5Z calculations were performed with a large (3*d* double-shell) active space consisting of 28 orbitals. Our approach using large-size DMRG reference addressed the problems of why the dissociation energy is largely overestimated by CASPT2 with the small active space consisting of 12 orbitals (3*d*4*s*), and also is oversensitive to the choice of the zeroth-order Hamiltonian. (**Figure 1**)

2. A Dual-Level Approach to Four-Component Relativistic Density-Functional Theory[4)]

This study presents an improvement that enhances the efficiency of the four-component density-functional theory (DFT) calculations by incorporating the dual-level approach proposed by Nakajima and Hirao into the Dirac-Kohn-Sham (DKS) method. At the heart of the dual-level approach is that high-cost hybrid DFT calculation using high-quality basis can be reproduced from a simple perturbation to much lower-cost DFT calculation that uses small basis and low-level pure exchange-correlation functional. The accuracy of this approach hinges on the insight that the description of total density is insensitive to the level of calculation. Significant computational saving arises in avoiding self-consistent field (SCF) procedure of iterating the time-consuming evaluation of Fock matrix in large basis representation as well as its large-dimensional diagonalization.

In the dual-level approach, a pair of the basis sets and exchange-correlation functionals is defined for specifying each level of the low- and high-cost calculations. We apply this scheme to four-component DFT calculations. Although this can be approached in a rather straightforward way, we attempt to mix an extra ingredient associated with the relativistic extension. In the present study, the duality of relativistic treatment is further invoked to achieve a further cost saving in the low-level calculations, for which the two-component relativistic approximation is employed.

There has been considerable progress in the development of a computationally less demanding two-component Hamiltonian which effectively neglects negative states. As the most suitable two-component method that allows for transparently bridging a gap between low- and high-level (*i.e.* four-component) descriptions, we employ a quasi-relativistic scheme proposed by Iliaš and Saue for implementing the Infinite-Order Two-Component (IOTC) relativistic Hamiltonian derived by Barysz and Sadlej. It is generated from a one-step decoupling transformation starting from the Dirac operator in the finite basis representation. The key reason for employing the IOTC Hamiltonian is that the decoupling matrix for the transformation is obtained as unitary. This unitarity is exploited, allowing for accurately retaining the description of the density matrix when it is similarity-transformed as frozen for the secondary high-level calculation. (**Figure 2**)

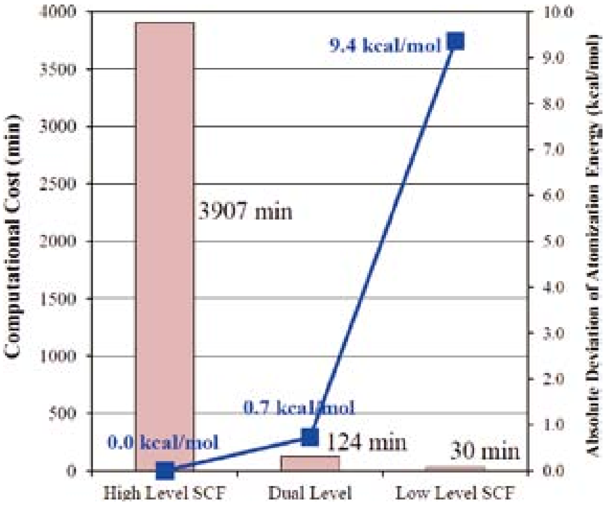

Figure 2. Computational times (bar) of the high- and low-level SCF calculations as well as the dual-level one for AuH at the equilibrium geometry, and the absolute deviations (square) of the atomization energies from the high-level result. The B3LYP functional is chosen as both high- and low-level functionals.

3. Canonical Transformation Theory for Multireference Dynamic Correlation Calculations

We have proposed a new class of explicit correlated theory on the basis of the effective Hamiltonian approach using the so-called canonical transformation (CT). The CT theory has been developed by Yanai, Chan, Neuscamman, and coworkers, in which dynamic electron correlation is described by a similarity transformation of the Hamiltonian H using a unitary exponential operator exp(A) with the excitation amplitude operator A = –A*. The central idea is to use the operator and cumulant decompositions to define a two-body effective Hamiltonian through an approximate Baker-Campbell-Hausdorff expansion,

$$\exp(-A)\,H\,\exp(A) = H + [H,A]_{1,2} + 1/2[[H,A],A]_{1,2} + \ldots$$

which can be evaluated recursively. Here $[\ldots]_{1,2}$ denotes that a commutator is approximated by an operator that contains only one- and two-body operators in the sense of generalized normal ordering of Mukherjee and Kutzelnigg.

We generalize this approach to F12 theory by introducing an A operator that depends on the interelectronic distances. In the present work, we use a Slater-type geminal function [$f(r_{12}) = -k^{-1}\exp(-k\, r_{12})$] and project it onto the two-body operator bases. The associated amplitudes are determined by the first-order cusp condition as Ten-no proposed in F12 theory (SP or "fixed" Ansatz), so that the A is determined *a priori*.

References

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