

## I-O Simulation and Dynamics of Chemical Systems

### I-O-1 Quasi-Degenerate Perturbation Theory with General Multiconfiguration Self-Consistent Field Reference Functions

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The quasi-degenerate perturbation theory (QDPT) with complete active space (CAS) self-consistent field (SCF) reference functions is extended to the general multiconfiguration (MC) SCF references functions case. A computational scheme that utilizes both diagrammatic and sum-over-states approaches is presented. The second-order effective Hamiltonian is computed for the external intermediate configurations (including virtual or/and core orbitals) by the diagrammatic approach and for internal intermediate configurations (including only active orbitals) by the configuration interaction matrix-based sum-over-states approach. The method is tested on the calculations of excitation energies of H<sub>2</sub>O, potential energy curves of LiF, and valence excitation energies of H<sub>2</sub>CO. The results show that the present method yields very close results to the corresponding CAS-SCF reference QDPT results and the available experimental values. The deviations from CAS-SCF reference QDPT values are less than 0.1 eV on the average for the excitation energies of H<sub>2</sub>O and less than 1 kcal/mol for the potential energy curves of LiF. In the calculation of the valence excited energies of H<sub>2</sub>CO, the maximum deviation from available experimental values is 0.28 eV.

### I-O-2 A Highly Efficient Algorithm for Electron Repulsion Integrals over Relativistic Four-Component Gaussian-Type Spinors

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A highly efficient computational scheme has been proposed for the Dirac-Hartree-Fock and the Dirac-Kohn-Sham solutions using the generally contracted kinetically balanced Gaussian-type spinors. Nevertheless, the calculations based on the full Dirac Hamiltonian are limited to small systems if they contain heavy elements. The bottleneck is the calculation of the two-electron repulsions over the four-component GTs. The present study presents an improved algorithm for evaluation of the four-component relativistic integrals.

### I-O-3 Accurate Relativistic Gaussian Basis Sets Determined by the Third-Order Douglas-Kroll Approximation with a Finite-Nucleus Model

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Highly accurate Gaussian basis sets with a finite-nucleus model are developed for the 103 elements from H to Lr. The present GTO sets augment the relativistic basis sets with a point-charge model proposed in the previous paper of this series. The relativistic third-order Douglas-Kroll approach is adopted in optimizing the orbital exponents of a basis set by minimizing the atom self-consistent field energy. The basis sets are designed to have equal quality and to be appropriate for the incorporation of relativistic effects.

### I-O-4 A Density Functional Study of van der Waals Interactions

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The applicability of density functional theory (DFT) to van der Waals (vdW) calculations are investigated by using the long-range exchange correction scheme and the Andersson-Langreth-Lundqvist vdW functional. By calculating bond energy potentials of rare-gas dimers, it was found that the present scheme gives much more accurate potentials for all dimers than conventional sophisticated DFT methods do. We therefore confirmed that vdW bonds are constructed under the balance of long-range exchange and vdW correlation interactions, although neither of these interactions are usually contained in pure exchange-correlation functionals. It was also found that calculated vdW potentials are obviously affected by functional forms for rapidly varying densities. Especially in vdW calculations, we must employ a correlation functional that satisfies the fundamental condition for rapidly varying density.