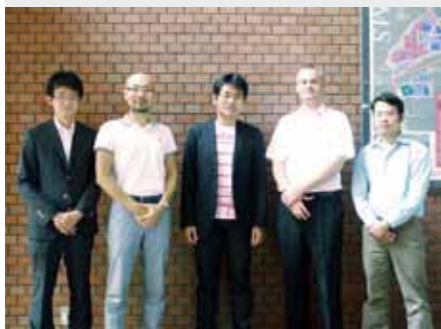


Advanced Electronic Structure Theory in Quantum Chemistry

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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 multi-reference 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 starting 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.

1. Canonical Transcorrelated Theory with Projected Slater-Type Geminals¹⁾

An effective Hamiltonian perturbed with explicit inter-

Canonical transcorrelated theory

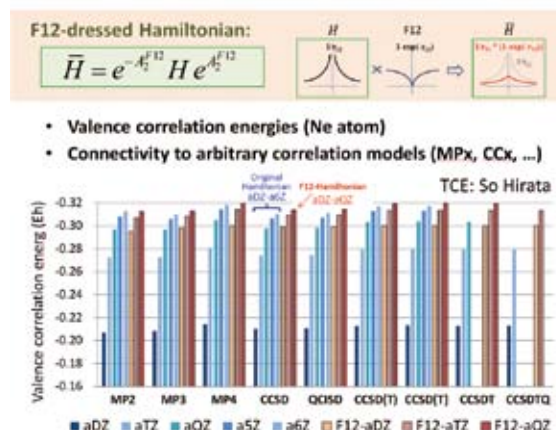


Figure 1. Canonical Transcorrelation method with F12 correlation factor.

electronic correlation is derived from similarity transformation of Hamiltonian using a unitary operator with Slater-type geminals. The Slater-type geminal is projected onto the excitation (and de-excitation) component as in the F12 theory. Simplification is made by truncating higher-body operators, resulting in a correlated Hamiltonian which is Hermitian and has exactly the same complexity as the original Hamiltonian in the second quantized form. It can thus be easily combined with arbitrary correlation models proposed to date. The present approach constructs a singularity-free Hamiltonian *a priori*, similarly to the so-called transcorrelated theory, while the use of the canonical transformation²⁾ assures that the effective Hamiltonian is two-body and Hermite. Our theory is naturally extensible to multireference calculations on the basis of the generalized normal ordering. The construction of the effective Hamiltonian is non-iterative. The numerical assessments demonstrate that the present scheme improves the basis set convergence of the post-mean-field calculations at a similar rate to the explicitly correlated methods proposed by others

that couple geminals and conventional excitations.

In this study, we propose a canonical transcorrelated Hamiltonian with the F12 operator:

$$\hat{H}^{F12} \equiv \hat{H} + \{\hat{H}, \hat{A}^{F12}\}_{1,2} + \frac{1}{2}[\{\hat{F}, \hat{A}^{F12}\}_{1,2}, \hat{A}^{F12}\}_{1,2}$$

which is derived in two ways of formal approximations: (i) terminating the expansion at the second order and (ii) replacing the uncorrelated Hamiltonian \hat{H} at the second order term (*i.e.*, the double commutator) by the Fock operator F . Note that F is the effective one-particle approximation to \hat{H} . This truncation of the infinite expansion is correct through the second order in perturbation.

We use an anti-Hermitian generator with projected geminal functions to make the transcorrelated H Hermite:

$$\begin{aligned} \hat{A}^{F12} &= \frac{1}{2} G_{ij}^{\alpha\beta} (\hat{E}_{ij}^{\alpha\beta} - \hat{E}_{ij}^{\beta\alpha}), \\ G_{ij}^{\alpha\beta} &= \frac{3}{8} \langle \alpha\beta | \hat{Q}_{12} F_{12} | ij \rangle + \frac{1}{8} \langle \alpha\beta | \hat{Q}_{12} F_{12} | j i \rangle, \\ F_{12} &= -\gamma^{-1} \exp(-\gamma r_{12}), \end{aligned}$$

in which we have fixed the amplitudes by those determined by the first-order cusp condition. The explicit electron correlation with the *projected* Slater-type geminals is built into a Hamiltonian through the canonical transformation. The present approach provides a formulation to effectively remove high-energy orbital components by using the F12 factor as a regulator for renormalizing them into the smaller-size orbital space. The features of the canonical transcorrelated theory are:

- (1) The resulting effective Hamiltonian is already perturbed with a considerable amount of the dynamic correlation associated with the interelectronic Coulomb singularity;
- (2) It remains Hermitian and has exactly the same size, dimension, and quartic complexity as the bare Hamiltonian;

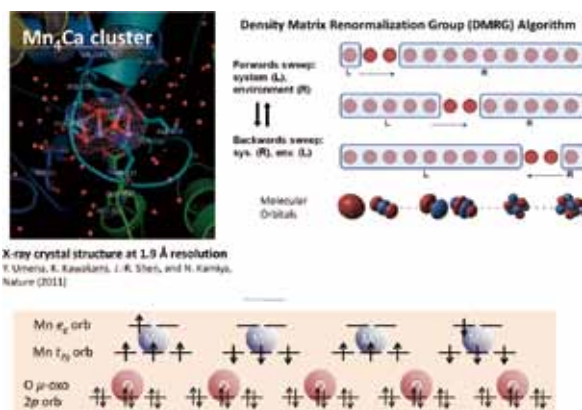


Figure 2. Determination of oxidation state of Mn_4CaO_5 cluster in photosystem II from a multireference wavefunction theory based on Density Matrix Renormalization Group method.

- (3) There is no adjustable parameter in the geminal excitations with Ten-no's fixed amplitude ansatz, since the F12 amplitudes for the present transformation are predetermined and calculated in a non-iterative manner;
- (4) The theory is extensible to multireference models on the basis of the generalized normal ordering of Mukherjee and Kutzelnigg;
- (5) In contrast to the standard F12 theories which couple the F12 and conventional excitations in the amplitude equations or Valeev's *a posteriori* F12 corrections, we have introduced an *a priori* F12 transformed Hamiltonian that can be readily used in conjunction with arbitrary correlation models to describe the remaining orbital correlation. We have demonstrated its applications to various solvers in quantum chemical methods, such as CCSD(T), QCISD, MP4, CCSDT, CCSDTQ, and so forth. The benchmarks on small molecules have revealed that the numerical performance of our explicit correlation scheme is comparable to that of other F12 theories. In our method, the F12 correction and the orbital correlation are treated separately at different steps, and thus it is indicated that they are more or less additively separable. (**Figure 1**)

2. Oxidation State of Mn_4Ca Cluster in Photosystem II: A Quantum-Chemical Density-Matrix Renormalization Group Study³

The X-ray diffraction (XRD) structure of photosystem II at a resolution of 1.9 Å was recently reported, entailing atomic-details of the Mn_4Ca cluster. Meanwhile, there is an earlier study suggesting that the high-valent Mn^{III-IV} ions of the cluster are potentially damaged by X-rays and reduced towards the lower-valent Mn^{II} , involving structural deformation. Thus, the record-resolution XRD measurement used a low-level X-ray dose to avoid such damage. We report a theoretical analysis identifying the oxidation states of the Mn ions as fingerprints to be compared with the widely-accepted oxidation state. Super high-dimensional multireference wavefunctions were calculated to account for nonperturbative interactions arising from four Mn 3d and five μ -oxo 2p shells. (**Figure 2**)

References

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