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 cuttingedge 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, and (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.

1. Discovery of New Quantum States of Electron Spins in Polycarbenes from *Ab Initio* Density Matrix Renormalization Group Calculations¹⁾

An investigation into spin structures of poly(m-phenylenecarbene)s, a prototype of organic magnetic molecules, is presented using the *ab initio* density matrix renormalization group method. It is revealed by achieving large-scale multi-



Figure 1. The spin correlation densities $\sigma_i^{\text{spin}}(r)$ of the CASSCF wave functions with respect to the non-bonding sp^2 orbital on the leftmost carbene site of polycarbene with n = 5 (solid red and blue color) for the singlet state. Crystal red and blue represent α spin ($\sigma_i^{\text{spin}}(r) > 0$) and β spin ($\sigma_i^{\text{spin}}(r) < 0$), respectively. The density visualizes the spin correlation against the α spin at the nonbonding orbital at the leftmost carbene site. The orbital and molecular geometry is superimposed.

reference calculations that the energy differences between high-spin and low-spin states (spin-gaps) of polycarbenes decrease with increasing the number of carbine sites. This size-dependency of the spin-gaps strikingly contradicts the predictions with single-reference methods including density functional theory. The wave function analysis shows that the low-spin states are beyond the *classical* spin picture, namely, much of multireference character, and thus are manifested as strongly correlated *quantum* states. The size dependence of the spin-gaps involves an odd-even oscillation, which cannot be explained by the model Hamiltonians with a single magneticcoupling constant (**Figure 1**).

2. Multireference Quantum Chemistry through a Joint Density Matrix Renormalization Group and Canonical Transformation Theory^{2–4)}

We presented the joint application of the density matrix

renormalisation group and canonical transformation theory to multireference quantum chemistry. The density matrix renormalization group provides the ability to describe static correlation in large active spaces, while the canonical transformation theory provides a high-order description of the dynamic correlation effects. We demonstrate the joint theory in two benchmark systems designed to test the dynamic and static correlation capabilities of the methods, namely (i) total correlation energies in long polyenes, and (ii) the isomerisation curve of the [Cu₂O₂]²⁺ core. The largest complete active spaces treated by the joint DMRG-CT theory in these systems correspond to a (24e,24o) active space in the polyenes and a (28e,32o) active space in [Cu₂O₂]²⁺.

3. *Ab Initio* Study of the Excited Singlet States of All-*trans* α, ω -Diphenylpolyenes with One to Seven Polyene Double Bonds: Simulation of the Spectral Data within Franck–Condon Approximation⁵⁾

Computational simulations of the electronic spectra with *ab initio* electronic structure calculations are presented for all*trans* α , ω -diphenylpolyenes with the polyene double bond number (*N*) from one to seven. A direct comparison of the fluorescence spectra of diphenylpolyenes was made between the results of highly accurate calculations and the experimental data for the systems with various chain lengths. For the realistic simulation of the emission, the total vibrational wave function was described approximately as a direct product of one-dimensional (1D) vibrational wave functions along the normal coordinates that are determined from the vibrational analysis of the ground state. The observed spectra can be reproduced in a computationally efficient way by selecting effective C–C and C=C stretching modes for the constructions of the 1D vibrational Hamiltonians. The electronic structure



Figure 2. Simulated fluorescence spectrum of the vibronic transitions $2A_g \rightarrow 1A_g$ of all-*trans* α, ω -diphenylhexatriene (DP3) with N = 3 (*N* is the number of double bond in the polyene chain). Inset: The observed spectrum measured by T. Itoh (the Joint Studies Program (2008~2009) of the Institute for Molecular Science).

calculations were performed using the multireference Møller-Plesset perturbation theory with complete active space configuration interaction reference functions (CASCI-MRMP). Based on the vertical excitation energies computed, the lowest singlet excited state of diphenylbutadiene is shown to be the optically forbidden 21Ag state. The simulations of fluorescence spectra involving vibronic coupling effects reveal that the observed strong single C=C band consists of two major degenerate vibrational C=C modes for the shorter diphenylpolyenes with N = 3 and 5. Further, the relative intensities of the C–C stretching modes in the fluorescence spectra tend to be larger than those of the C=C stretching modes for the systems with Nover 5. This indicates that the geometric differences of the energy minima between the ground (1^1A_g) and 2^1A_g states grows larger towards the direction of the C-C stretching mode with increasing N (Figure 2).

4. Tensor Factorizations of Local Second-Order Møller-Plesset Theory⁶⁾

Efficient electronic structure methods require efficient tensor representations of the wavefunction. Here we describe a general way to view tensor factorization. We use these ideas to construct low-complexity representations of the doubles amplitudes in local second order Møller-Plesset perturbation theory. We introduce two approximations-the direct factorized virtual approximation and the complete factorized virtual approximation. Conceptually, these lie between the projected atomic orbital representation used in the Pulay-Saebo local correlation theories and pair natural orbital correlation theories. We have tested the factorized virtual approximations on a variety of systems and properties including total energies, reaction energies, and potential energy curves. Compared to the Pulay-Saebo ansatz, we find that these approximations exhibit favourable accuracy and computational timings, while yielding smooth potential energy curves.

References

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