Abstract

The recent development of the density matrix renormalization group (DMRG) method in multireference quantum chemistry makes it practical to evaluate static correlation in a large active space, while dynamic correlation provides a critical correction to the DMRG reference for strong-correlated systems and is usually obtained using multi-reference perturbation (MRPT) or configuration interaction (MRCI) methods with internal contraction (ic) approximation. These methods can use active space scalable to relatively larger size references than has previously been possible. However, they are still hardly applicable to systems with active space larger than 30 orbitals and/or large basis set because of high computation and storage costs of high-order
reduced density matrices (RDMs) and the crucial dependence of the MRCI Hamiltonian dimension on the number of virtual orbitals. In this work, we propose a new effective implementation of DMRG-MRCI, in which we use re-constructed CASCI-type configurations from DMRG wave function via the entropy-driving genetic algorithm (EDGA) [Luo et. al., J. Chem. Theory Comput., 2017, 13, 4699–4710.], and integrate it with MRCI by an external contraction (ec) scheme. This bypasses the bottleneck of computing high-order RDMs in traditional DMRG dynamic correlation methods with ic approximation and the number of MRCI configurations is not dependent on the number of virtual orbitals. Therefore, DMRG-ec-MRCI method is promising for dealing with larger active space than 30 orbitals and large basis sets. We demonstrate the capability of our DMRG-ec-MRCI method in several benchmark applications, including the evaluation of potential energy curve of Cr$_2$, single-triplet gaps of higher n-acene molecules and the energy of Eu-BTBP(NO$_3$)$_3$ complex.

1 Introduction

The theoretical evaluation of the structures and energies of molecules is a primary goal of quantum chemistry. In most *ab initio* approaches, the first step to evaluate the electronic structure of a molecule is using mean-field models such as Hartree-Fock self-consistent-field theory to obtain a starting point for further calculations and account for the bulk of the total energy. There is still an amount of energy that is not included in Hartree-Fock calculation, which results from the neglect of instantaneous interactions between electrons and is called electronic correlation energy. One of the most common ways to account for the correlation energy in strongly correlated systems (e.g. conjugated molecules or transition metal complexes) is to perform multi-configurational quantum chemical calculation by complete active space configuration interaction (CASCII) and completely active space self-consistent-field (CASSCF) methods. However, the computational costs of CAS calculations scale exponentially with respect to the numbers of active orbitals and electrons
and so these approaches can hardly be applied to active spaces larger than (16e, 16o). In this case, one can turn to density matrix renormalization group (DMRG)\textsuperscript{1–21} method, which was originally introduced by White et al.\textsuperscript{12} for solid state physics, emerges as a promising quantum chemical approach in recent years. DMRG reduces the freedom of full configurational space by constituting a renormalized basis with $M$ eigenvectors with the largest eigenvalues of sub-systems’ reduced density-matrix (RDM), which makes its computational cost to scale only polynomially,\textsuperscript{6} i.e. \(O(k^3 M^3) + O(k^4 M^2)\), where $k$ is the number of active orbitals. Note that DMRG is just an efficient full-CI solver for large active spaces. The significantly high computational efficiency and accuracy of DMRG-based approaches makes it possible to explore larger configuration-interaction spaces.

DMRG approaches have already been applied by theoretical chemists in the researches of transition metal complexes,\textsuperscript{22,23} catalytic metalloenzymes\textsuperscript{24} and aromatic excimers.\textsuperscript{25} Along with these applications, quantum chemists have successively developed many DMRG-based multi-configuration (MC) or multi-reference (MR) approaches, including DMRG-based CASSCF (DMRG-CASSCF)\textsuperscript{26–32} method. Using DMRG-CASCI/DMRG-CASSCF methods, the electronic correlation in the large active space can be measured up to the FCI level since the wave function is constructed by all possible distribution of a given number of electrons to a selected set of orbitals. This part of electronic correlation is usually referred to as non-dynamic or static correlation. For example, a (46e, 46o) active space is explored by Mizukami et al.’s DMRG-CASSCF calculation,\textsuperscript{33} and their results illustrated the intriguing quantum spin states in long chain poly(\textit{m}-phenylenecarbene)s. However, electron correlation is far more complicated than a restricted active space calculation can handle, and dynamic correlation in the external space needs to be considered in order to get more quantitative results. The popular implementations for calculating dynamic correlation after a DMRG-CASCI/DMRG-CASSCF calculation are based on perturbation theory, including DMRG-CASPT2 and DMRG-NEVPT2 methods\textsuperscript{34–37} based on internal contraction approximation. Besides the internally-contracted MRCI method\textsuperscript{38,39}
is also available. These approaches reduce their computational costs by contracting all of the configurations in the reference active space. Nevertheless, because the computational costs also increase steeply with the number of virtual orbitals and it is not easy to obtain and store higher-order reduced density matrices (RDMs), the practicability of these internally contracted methods is limited to much smaller systems than DMRG-CASCI/DMRG-CASSCF can handle. For example, Shirai et al.\textsuperscript{25} use DMRG-CASPT2 calculations with full $\pi$ valence reference CAS(20e, 20o) to investigate the excited states of the naphthalene dimer and theoretically confirm the inversion of energy levels of $^1L_a^-$ and $^1L_b^-$ excited during the excimer formation. Therefore, one has to notice that usually these internally-contracted approaches can hardly be applied to reference active spaces larger than (30e, 30o). Recently, Legeza and Pittner proposed “post-DMRG” treatment of dynamic correlation based on the tailored coupled cluster (TCC) theory\textsuperscript{40}. The computation of higher-order RDMs is avoided in this method by using a reference wave function of only the singly and doubly excited configurations in DMRG wave function within the active space, and DMRG-TCCSD calculations for oxo-Mn(Salen) with an active space (34e, 25o) are illustrated in their paper.

Another contraction scheme for reducing the degrees of freedom for the new excitations outside the active space is the external contraction (ec) approximation proposed by Meyer\textsuperscript{41} and Siegbahn.\textsuperscript{42} As the name of this approach suggests, the external space is contracted in this scheme and the combination coefficients of different external space configurations are determined using perturbation method. As a result, the computational cost of externally contracted method is not sensitive to the size of the external space or the number of external orbitals, while the number of reference configurations has a great influence on the calculation cost. In general, the reference configurations come from the preceding MCSCF calculation, and the number of configurations obtained from the MCSCF procedure rapidly increases with the size of the active space, which makes the traditional externally contracted methods underperform in comparison with the internally
contracted methods when applied to small molecular systems. However, if a small set of
determinants rather than the whole active space is used as the reference wave function,
the computational cost of ec-MRCI method would be greatly reduced, making it possible
to compute the dynamic correlation of large systems.

Considering the fact that the contribution of an electronic configuration to an elec-
tronic state is positively correlated with the magnitude of its CI coefficient, one can pick
out a relatively small number of the configurations with large absolute value of CI coef-
ficient to approximate the entire FCI wave function. This idea is used by Thomas et al.\textsuperscript{13} in
their stochastic multi-configurational self-consistent field theory. Besides, the specific
structure of wave functions is helpful to understand many of chemical processes such
as electron excitation and bond breaking. Unfortunately when dealing with large active
spaces, one should notice that the DMRG wave functions are usually considered to be
not intuitively comparable with traditional single reference (SR) or MR wave functions
based on CI electronic configurations. That is because the expansion items in DMRG
wave function are the so-called matrix-product states (MPSs),\textsuperscript{44–47} which are renormal-
ized throughout the DMRG “sweep” procedure, rather than the distinguishable electronic
configurations in forms of Slater determinants (SDs). In 2007, Moritz et al.\textsuperscript{48} rationalized
a method to decompose MPS into a SD basis, however the full CI expansion for a DMRG
wave function in large active space with more than 20 active orbitals would be prohibitive
since the number of SDs would be easily larger than $10^{10}$. Two different schemes for ef-
ciently searching for the important configurations are practical, the early one of which
is the Monte-Carlo based sampling-reconstructed CAS (SR-CAS) algorithm\textsuperscript{49} proposed
by Boguslawski et al.\textsuperscript{49} and another one is the entanglement-driving genetic algorithm
(EDGA) proposed by us.\textsuperscript{50} The analyses in these works suggest that only a comparatively
small amount of SDs within the entire large active space has to be considered to construct
an efficient CASCI-type wave function, and these SDs could already represent the main
feature for a specific electronic state.
In this paper we propose an implementation of DMRG-ec-MRCISD method based on the reference configurations collected by our EDGA scheme from a DMRG-CASCI/DMRG-CASSCF wave function. By using a limited number of reference configurations selected in a DMRG wave function using EDGA, our method can be used to effectively evaluate electron correlations with large active spaces and large basis sets. The paper is organized as following: In Sec. II, we present a brief description of 1) the DMRG-MPS ansatz, CI re-construction under such ansatz, and the EDGA scheme; as well as 2) the theory of externally contracted MRCISD method using a given set of selected reference configurations. Examples of Chromium dimer (Cr$_2$), higher n-acene molecules and transition metal compounds Eu-BTBP(NO$_3$)$_3$ are presented in Sec. III. Finally, we draw our conclusions in Sec. IV.

2 Theory and Methodology

2.1 MRCI method

The CI method is conceptually a very general and simple procedure to compute approximate solutions to the quantum many-electron Schrödinger equation. Starting from one or more configurations as the reference wave function, CI methods generate more additional configurations by exciting electrons from the doubly occupied and/or active space(s) into active and/or external space(s). In order to reduce computational costs while ensuring accuracy, usually the number of the excited electrons is no more than 2. Thus, the scheme starting from one reference configuration is called single-reference CISD (SRCISD) method, while the one starting with multiple reference configurations is called multi-reference CISD (MRCISD) method. The MRCISD wave function can usually
be written as

$$|\Psi\rangle = \sum_m c(m)|\phi(m)\rangle + \sum_m \sum_{i,a} c_{ia}^a(m)|\phi(m)_{ia}\rangle + \sum_m \sum_{i>j,a>b} c_{ij}^{ab}(m)|\phi(m)_{ij}^{ab}\rangle$$  \hspace{1cm} (1)$$

where the terms $|\phi(m)\rangle$ are reference configurations and usually obtained from a preceding MCSCF calculation; and the terms $|\phi(m)_{ia}^a\rangle$ and $|\phi(m)_{ij}^{ab}\rangle$ are single and double excitation configurations respectively, as

$$|\phi(m)_{ia}^a\rangle = a^\dagger_a a_i|\phi(m)\rangle$$  \hspace{1cm} (2)$$

and

$$|\phi(m)_{ij}^{ab}\rangle = a^\dagger_a a^\dagger_b a_j a_i|\phi(m)\rangle.$$  \hspace{1cm} (3)$$

c(m), c_{ia}^a(m)$ and $c_{ij}^{ab}(m)$ are CI coefficients and need to be determined by diagonalizing CI matrix, in which the matrix element can be obtained by

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle$$  \hspace{1cm} (4)$$

where $H$ is the Hamiltonian operator and can be written as

$$H = \sum_{pq,\sigma} h_{pq} a^\dagger_p a_{q\sigma} + \frac{1}{2} \sum_{pqrs,\sigma\tau} g_{pqrs} a^\dagger_p a^\dagger_r a_{s\tau} a_{q\sigma}$$  \hspace{1cm} (5)$$

in which the summation indices $p, q, r$ and $s$ represent molecular orbitals, $\sigma$ and $\tau$ represent spins, and the terms $h_{pq}$ and $g_{pqrs}$ are one- and two-electron integrals respectively.

Obviously the number of configurations determines the dimensions of the CI matrix and most significantly affects the computational cost. One way to reduce the number of configurations is contraction, that is, to determine the numerical relationship of the CI coefficients between certain configurations before constructing the CI matrix, and to treat these configurations as one group when building the matrix. One of the general methods
is internal contraction approximation,\textsuperscript{[25],[54]} where all the excited configurations with the same excitation pattern are contracted and considered as one group, and their relative weights are determined from the CASCI coefficients of their reference configurations in preceding CASCI/CASSCF calculations. Another contraction scheme is external contraction approximation.\textsuperscript{[55]} In this scheme, the configurations in external space are contracted. The wave function of ec-MRCISD can be written as

$$|\Psi\rangle = \sum_{m} c(m)|\phi(m)\rangle + \sum_{m,i} c_i(m)|\tilde{\phi}_i(m)\rangle + \sum_{m,i>j} c_{ij}(m)|\tilde{\phi}_{ij}(m)\rangle \quad (6)$$

where $|\tilde{\phi}_i(m)\rangle$ are the contracted singly-excited configurations

$$|\tilde{\phi}_i(m)\rangle = \sum_{a} c_i^{a}(m)|\phi(m)^{a}_i\rangle \quad (7)$$

and $|\tilde{\phi}_{ij}(m)\rangle$ are the doubly-excited ones

$$|\tilde{\phi}_{ij}(m)\rangle = \sum_{a>b} c_{ij}^{ab}(m)|\phi(m)^{ab}_{ij}\rangle \quad (8)$$

Since the diagonalization of large matrix in variational computations is costly and difficult, external contraction methods merge all the external configurations with the same internal form into one term, and determine the contraction coefficients using perturbation method

$$c_i^{a}(m) = \frac{\langle\Psi_0|H|\phi(m)^{a}_i\rangle}{E_0 - \langle\phi(m)^{a}_i|H|\phi(m)^{a}_i\rangle} \quad (9)$$

for single excitation terms, and

$$c_{ij}^{ab}(m) = \frac{\langle\Psi_0|H|\phi(m)^{ab}_{ij}\rangle}{E_0 - \langle\phi(m)^{ab}_{ij}|H|\phi(m)^{ab}_{ij}\rangle} \quad (10)$$

for double ones, where $\Psi_0 = \sum_{m} c(m)|\phi(m)\rangle$ is the reference wave function and $E_0$ is the corresponding reference energy usually obtained from a previous CASCI/CASSCF
calculation. Therefore, only \( c(m), c_i(m) \) and \( c_{ij}(m) \) in Eq. 6 need to be determined using variational calculation, and the number of configurations in external space does not affect the size of the CI matrix. Therefore, the ec-MRCISD method is particularly suitable for the calculations using large basis sets if the number of reference configurations is not too large.

### 2.2 Construction of DMRG Reference Wave Function

As mentioned above, MRCI methods usually use the multi-configurational wave function from a preceding CASCI/CASSCF calculation as reference state. Traditional CASCI/CASSCF methods are usually applicable to active spaces not larger than \((16e, 16o)\) because complete construction of such large CI spaces exceeds the capability of modern computer. DMRG is a good way to handle large active space. Here we give a brief presentation of a modern derivation of the DMRG algorithm using the MPS representation of a wave function. Considering an arbitrary electronic state \(|\Psi\rangle\) spanned by \(L\) orbitals, in traditional CI language one can express the wave function as a linear combination of occupation number vectors \(|\sigma\rangle\), with the CI coefficients \(c_{\sigma_1...\sigma_L}\) as expansion coefficients,

\[
|\Psi\rangle = \sum_{\sigma} c_{\sigma} |\sigma\rangle = \sum_{\sigma_1,...,\sigma_L} c_{\sigma_1...\sigma_L} |\sigma_1...\sigma_L\rangle .
\]  

For the \(l\)-th spatial orbital, the basis states \(|\sigma_i\rangle\) has four possible occupation status as \(|\uparrow\downarrow\rangle, |\uparrow\rangle, |\downarrow\rangle\) and \(|0\rangle\). Note that the number of electron configurations of the full-CI wave function will be exponentially large depending on the size of active space. Turning to the MPS ansatz, the CI coefficients \(c_{\sigma_1...\sigma_L}\) can be encoded as products of \(m_{l-1} \times m_l\)-dimensional matrices \(M^{\sigma_i} = \{M^{\sigma_i}_{a_{l-1}a_l}\}\) via singular value decomposition (SVD) procedure

\[
|\Psi\rangle = \sum_{\sigma_1,...,\sigma_L} \sum_{a_1,...,a_{L-1}} M^{\sigma_1}_{1a_1} M^{\sigma_2}_{a_1a_2} \cdots M^{\sigma_L}_{a_{L-1}1} |\sigma_1...\sigma_L\rangle = \sum_{\sigma} M^{\sigma_1} M^{\sigma_2} \cdots M^{\sigma_L} |\sigma\rangle ,
\]
where the first matrix is $1 \times m_1$-dimensional row vector and the last one is $m_L-1 \times 1$-dimensional column vector, respectively. Collapsing the summation over the $a_l$ indices as matrix-matrix multiplications results in the last equality. The wave function can be optimized by iteratively optimizing these matrices $M^{\sigma_i}$. Furthermore, we can make the matrix dimension $m_i$ not to always be less than a given value $M$ by ignoring the configurations with very small singular values in SVD decompositions in DMRG sweeps. Thus, the total degrees of freedom in the wave function of Eq. 12 scale as $O(4M^2L)$.

The connection between the matrices $M^{\sigma_i}$ and the CI coefficients $c_{\sigma_1...\sigma_L}$ is clear and one can obtain the weight of a certain determinant by contracting all these matrices by

$$c_{\sigma_1...\sigma_L} = M^{\sigma_1}[^1\sigma_1]M^{\sigma_2}[^2\sigma_2]...M^{\sigma_L}[^L\sigma_L]$$

where $M$ matrices for basis transformations are obtained and kept in DMRG sweeps. Moritz et al.\textsuperscript{48} presented a method for the calculation of all determinants weights by multiplying all the matrices $M^{\sigma_i}$ after the convergence of the DMRG-CASCI/DMRG-CASSCF calculation.

However, obtaining the coefficients of all determinants in a large active space is almost impossible because of the large number of configurations. Our EDGA scheme\textsuperscript{50} can be used to efficiently explore the Hilbert space and collect the most important configurations. This scheme is based on the concept of orbital entanglement entropy\textsuperscript{56} from quantum information theory and the genetic algorithm. In short, starting from a given set of determinants, the algorithm generates new determinants through "crossover" and "mutation" operations and compute the corresponding CI coefficients, repeats this evolution process and collects all the determinants whose absolute values of CI coefficients are greater than a given threshold. Orbital entanglement entropy plays an important role in the process of "mutation" because the greater the value of entanglement between a pair of orbitals, the easier electrons will transfer between them. The details of EDGA scheme
can be found in Ref.\textsuperscript{50}

### 2.3 DMRG-ec-MRCI method

From Eq.\textsuperscript{6} we can see that the main computational costs of the external contraction methods come from the number of reference configurations and the number of electrons in the active space. If we use a DMRG wave function as the reference state, ec-MRCISD calculations for large systems are challenging because the number of reference configurations will be very large due to the large active space. As mentioned above, we can often approximate the DMRG wave function with a small amount of configurations. In the next step we can use these selected configurations as the reference state for further ec-MRCISD calculations. In this way, we combine our EDGA scheme and the traditional externally-contracted MRCISD method to propose a new ec-MRCISD algorithm using a truncated DMRG-CASCI/DMRG-CASSCF wave function as reference state for large systems.

It must be mentioned that the CI coefficients of reference configurations in the truncated DMRG wave function and the corresponding reference energy $E_0$ must be recalculated before using these values in Eq.\textsuperscript{9} and Eq.\textsuperscript{10}. Besides, since the lack of size-consistency is a serious deficiency of truncated CI expansions, a posteriori Davidson correction\textsuperscript{57,58} has been added into the final results. The correction energy is computed by

$$E_{\text{Davidson}} = (1 - \sum_m c_m^2)(E_{\text{MRCISD}} - E_0)$$  \hspace{1cm} (14)$$

where $c_m$ is the CI coefficients of the $m$-th reference configuration in ec-MRCISD wave function, $E_{\text{MRCISD}}$ is the energy of ec-MRCISD calculation and $E_0$ is the same energy of reference state as we use in Eq.\textsuperscript{9} and Eq.\textsuperscript{10}. Then the final energy with this correction is labeled as MRCISD+Q and obtained by

$$E_{\text{MRCISD+Q}} = E_{\text{MRCISD}} + E_{\text{Davidson}}$$  \hspace{1cm} (15)$$

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The complete work flow for DMRG-ec-MRCISD+Q is shown below.

1. Perform a DMRG-CASCI/DMRG-CASSCF calculation using OPENMOLCAS.\textsuperscript{39}

2. Collect the most important determinants in the DMRG wave function using EDGA.

3. Reconstruct CI matrix using the collected determinants, diagonalize the matrix and obtain refined CI coefficients of these determinants and the reference energy $E_0$.

4. Generate singly- and doubly-excited configurations based on the selected determinants.

5. Compute the contraction coefficients of singly- and doubly-excited configurations using Eq. 9 and Eq. 10.

6. Construct the Hamiltonian matrix, diagonalize the matrix and obtain energy for the specified states.

7. Compute Davidson correction energy using Eq. 14.

8. Compute the ec-MRCISD+Q energy using Eq. 15.

3 Numerical Examples

3.1 The Potential Energy Curve of Cr$_2$

The chromium dimer Cr$_2$ molecule is a challenging system for accurate theoretical computations. Its electronic structure is highly multi-configurational and both static and dynamic correlations need to be carefully taken into account. Many quantum chemists have made attempts to compute the ground state singlet potential energy curve of Cr$_2$\textsuperscript{34,60–67} Roos et al.\textsuperscript{60,61} use a (12e, 12o) active space derived from the 3d and 4s atomic orbitals of the two chromium atoms and ANO basis sets\textsuperscript{68} including up to f -type function in
their CASPT2 calculations. This (12e, 12o) active space is a minimal requirement for describing bond stretching and breaking between the two chromium atoms, while Angeli et al.\textsuperscript{[63]} indicate that the CASSCF(12e, 12o) wave function is not a sufficient reference of the perturbation theory since the third-order perturbation shows a significantly large fluctuation. It is also mentioned that the dissociation energy of the 3d-3d bond with increasing the size of basis sets is largely overestimated in CASPT2 calculations.\textsuperscript{[69]} However, the size of (12e, 12o) active space nearly reaches the applicable limit for the conventional implementation of the CASSCF method. A larger active space (12e, 28o) derived from 3d, 4s, 4p, and 4d atomic orbitals is used in the DMRG-CASPT2 calculations by Kurashige et al.\textsuperscript{[34]} Accurate theoretical results have been achieved by Müller,\textsuperscript{[64]} using the robust multi-reference averaged quadratic coupled cluster (MR-AQCC) method\textsuperscript{[70]} and ANO-RCC basis sets including h-type functions and utilizing up to 512 processors.

Since large active space is necessary for correctly describing the electronic structure of Cr\textsubscript{2} molecule, we use a (12e, 42o) active space consisting of the 3d, 4s, 4p, 4d and 4f atomic orbitals of chromium in this work. We start our calculations with the (12e, 12o) active space in CASSCF calculations using \textsc{OpenMolcas} package and obtain the optimized molecular orbitals. In order to evaluate static correlations with reasonable computational costs, then we perform DMRG-CASCI calculations with the QC\textsc{M}A\textsc{Q}\textsc{u}\textsc{i}\textsc{s} DMRG software package\textsuperscript{[71–73]} and $M = 1000$ reserved states using these CASSCF molecular orbitals and the larger active space (12e, 42o). For each chromium-chromium distance value, we use our EDGA program to analyze the DMRG-CASCI wave function, pick up the most important configurations and make sure the sum of CI coefficients of these selected determinants is not less than 0.97. Finally, we use these selected determinants as reference configurations and perform ec-MRCISD+Q calculations. The “exact two-component” (X2C) method\textsuperscript{[74,75]} in combination with ANO-RCC basis set and a quadr-ζ contraction scheme (ANO-RCC-VQZP) are used for the Cr\textsubscript{2} for a good description of relativistic effect.

The potential energy curve of singlet ground state is presented in Fig.\textsuperscript{[1]} The shape of
our curve is similar to the experimental one while the calculated values are about 0.08 eV lower, and our calculated dissociation energy $D_e$ is 0.06 eV lower than the experimental value. This may be because the basis sets we use here are not complete, or the measurement of relativistic effects is not accurate enough. On the other hand, there are different reports on the experimental values of dissociation energy $D_e$, one of which is listed in Tab. I and another one is 1.47 eV measured by Casey and Leopold.\footnote{76,77}

Equilibrium bond length $R_0$ and vibrational frequency $\omega_e$ also have been calculated and are listed in Tab. I. The calculated equilibrium distance between the two chromium atoms is 0.03 Å longer than experimental value, while our calculated vibrational frequency agrees very well with the experimental value. Although large active space always means very expensive computational costs, our method can still handle such calculations. And to our knowledge, our work in this paper is the first time that a DMRG-based dynamic correlation evaluation method deals with active space larger than 30 orbitals.

Figure 1: The potential energy curve of Cr$_2$. The experimental curve is taken from Ref.\textsuperscript{76} The energetical zero point is set as the energy of two Cr atoms with an infinite inter-atom distance.
Table 1: Spectroscopic Constants for the Ground State of \( \text{Cr}_2 \).

|                  | \( D_e \) (eV) | \( R_0 \) (\( \text{Å} \)) | \( \omega_e \) (cm\(^{-1}\)) |
|------------------|----------------|-----------------------------|-----------------------------|
| DMRG-ec-MRCISD+Q | 1.62           | 1.71                        | 476.8                       |
| experiment       | 1.56\( ^a \)   | 1.68\( ^b \)                | 480.6\( ^c \)              |

\( ^a \) Data taken from Ref.\(^{78}\)

\( ^b \) Data taken from Ref.\(^{79}\)

\( ^c \) Data taken from Ref.\(^{76}\)

3.2 The Singlet-Triplet Energy Gap of Higher Acenes

The nature of the ground state of higher acenes (Fig. 2) still remains controversial because of the instability and the absence of accurate experimental characterization of the higher acenes. It has been predicted that the ground state of higher acenes is singlet rather than triplet; while the size of the aromatic system grows, the ground singlet state exhibits more and more open-shell free radical properties, and the singlet-triplet energy gap, which refers to the transition energy from the lowest \( ^1A_g \) state to the lowest \( ^3B_{2u} \) state, becomes smaller and smaller.\(^{80-87}\)

![Figure 2: Structure of higher \( n \)-acene in Kekule resonance form.](image)

In this work, we calculated the \( S_0-T_1 \) energy gaps of higher acenes for the number of benzene rings \( n = 2 \) to 9. For the adiabatic S-T gaps, we compute the energies using optimized geometries of the two states respectively. The vertical S-T energy gaps are obtained with the optimized geometry of the lowest \( ^1A_g \) state. All the geometries of higher acenes are optimized in \( D_{2h} \) symmetry at UB3LYP/6-31G(d) level for \( S_0 \) and \( T_1 \) states respectively using GAUSSIAN16\(^{88}\) package. DMRG-CASCI calculations with \( M = 1000 \) states reserved in DMRG sweeps are performed for \( n = 4 \) to 9 using OPENMOLCAS and the QCMAQUIS DMRG software package\(^{71,73}\) with the active spaces ((\( 4n+2 \))e, (\( 4n+2 \))o), which are consisting of all the valence \( \pi \) orbitals and electrons. For naphthalene (\( n = 2 \))
and anthracene \((n = 3)\), since the \(\pi\) valence active spaces are not too large, we perform traditional CASCI calculations instead of DMRG-CASCI. The ec-MRCISD+Q calculations are performed using truncated reference wave functions constructed with EDGA with completeness as 0.97. ANO-L-VTZP and ANO-S-MB basis sets are used for C and H atoms, respectively. The results are illustrated in Fig. 3.

![Figure 3: The \(S_0-T_1\) energy gaps (eV) of higher \(n\)-acenes. Experimental values are from Ref. 89–92](image)

Compared with experimental data, our theoretical predictions of S-T gaps differ from experimental values by around 0.07 eV for \(n = 2\) to 5. It is clear that dynamic correlation is necessary to correctly describe the electronic structure of higher acenes, since DMRG-CASCI calculations with \(M = 1000\) reserved states overestimate the S-T energy gaps since only static correlation is considered. For \(n = 6\) to 9, our results are about 0.1 eV higher than the results reported by Yang et al.\(^{87}\) with the method of particle–particle random-phase approximation (pp-RPA) B3LYP functional. Our calculation supports the conclusion that the ground state is singlet, and larger acene has smaller S-T energy gap. It also can be seen from Fig. 3 that the experimental values are closer to adiabatic gaps.
rather than vertical ones evaluated at fixed geometries of $S_0$ states. This may be because the electron transitions between the singlet and triplet states are forbidden, which provides the opportunity for geometric structural relaxation.

### 3.3 Eu-BTBP(NO$_3$)$_3$ complex

In this section, we turn to the europium complex Eu-BTBP(NO$_3$)$_3$. Since the BTBP is one of the popular ligands for selectively extract trivalent actinides (An) over lanthanide (Ln) fission products by solvent extraction via nitric acid solutions to organic solvents, it has been considered as one of the most promising species for partitioning the minor actinides from radioactive waste.$^{93-95}$ In this work we are focusing on its electronic structure rather than selectively. The geometry we used (cf. Fig. 4) in this paper is from Ref.$^{96}$ with the two far-end ethyls removed and the symmetry constrained to $C_2$ group. The same X2C Hamiltonian is used in the calculation with the OPENMOLCAS package. ANO-RCC with double-$\zeta$ basis sets (ANO-RCC-VDZP) are used for Eu, N, and O elements; while the ANO-RCC-MB basis sets are used for C and H elements.

![Figure 4: The geometry of Eu-BTBP(NO$_3$)$_3$ complex.](image)

Since we are focusing on the ground state of this complex at present, several DMRG(38e, 36o)-CASSCF calculations with $M = 1000$ states reserved in DMRG sweeps have been employed with carefully selected orbitals before further ec-MRClSD+Q calculations and
the conclusion is that the maximum spin multiplicity state $^7\text{B}_1$ is the lowest energy electronic state, as reported by Narbutt and Oziminski.\textsuperscript{[96]} We perform ec-MRCISD+Q calculations with different completeness of the reference space and the results are listed in Tab.\textsuperscript{2}

Table 2: The energies of Eu-BTBP(NO$_3$)$_3$ complex computed using different completeness of reference space.

| completeness of reference state | 0.90       | 0.92       | 0.95       | 0.97       |
|--------------------------------|------------|------------|------------|------------|
| Number of Reference Configurations | 777       | 3965       | 15417      | 86343      |
| DMRG-ec-MRCISD+Q Energy (Hartree)     | -12720.7495 | -12721.0153 | -12721.0314 | -12721.0327 |

From Tab.\textsuperscript{2} one can clearly see that the DMRG-ec-MRCISD+Q energy is gradually converging upon using more and more reference configurations, and the energy difference for the completeness of 0.95 and 0.97 is only around 0.001 Hartree. One reason for the good convergence behavior of DMRG-ec-MRCISD+Q is that, the Davidson correction can partly recover the lost part of static correlation energy due to the incompleteness in the truncated reference space.

4 Conclusion

In this work, we propose a new implementation of externally contracted MRCISD method for large systems based on the most important part of configurations in a DMRG multi-configurational wave function as the reference state. The important configurations in a DMRG wave function can be selected using EDGA scheme. The number of these important configurations is significantly smaller than the number of all possible configurations in a large active space, which makes it possible to use externally-contracted schemes in the calculation of large systems. Examples have been given to demonstrate the effectiveness of this method. The calculations of the potential energy curve of Cr$_2$, the singlet-triplet energy gap of polyacenes and the energy of Eu-BTBP(NO$_3$)$_3$ complex show that our DMRG-ec-MRCISD+Q implementation is appropriate for evaluating dynamic correlations for systems with large active space containing more than 30 orbitals.
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