Multi-Reference Epstein-Nesbet Perturbation Theory with Density Matrix Renormalization Group Reference Wavefunction

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Abstract. The accurate electronic structure calculation for strongly correlated chemical systems requires an adequate description for both static and dynamic electron correlation, and is a persistent challenge for quantum chemistry. In order to account for static and dynamic electron correlations accurately and efficiently, in this work we propose a new method by integrating the density matrix renormalization group (DMRG) method and multi-reference second-order Epstein-Nesbet perturbation theory (ENPT2) with a selected configuration interaction (SCI) approximation. Compared to previous DMRG-based dynamic correlation methods, the DMRG-ENPT2 method extends the range of applicability, allowing us to efficiently calculate systems with very large active spaces beyond 30 orbitals. We demonstrate this by performing calculations on H₂S with an active space of (16e, 15o), hexacene with an active space of (26e, 26o) and trinuclear Manganese cluster with an active space of (47e, 43o).

1. Introduction

In recent years, the density matrix renormalization group (DMRG) method [1][2][3][4][5][6][7][8][9][10][11][12][13][14][15][16][17][18][19][20][21] has been shown to be a prominent new quantum chemical approach to approximate the full configuration interaction (FCI) solution within a large active space with only polynomial computational costs. However, electron correlation in realistic chemical systems is far more complicated than a restricted active space calculation can handle, and dynamic correlation outside the active space needs to be considered in order to get quantitative results. Over the last few years, a number of methods have been proposed to achieve this goal, including
DMRG-canonical transformation (CT) [22], DMRG-complete active space second-order perturbation theory (CASPT2) [23, 24], DMRG-\( N \)-electron valence perturbation theory (NEVPT2) [25, 26, 27], DMRG-multi-reference configuration interaction (MRCI) [28, 29, 30], and DMRG-tailored coupled cluster (TCC) [31, 32], matrix product state perturbation theory (MPSPT) [33, 34]. Because of the too huge number of the reference configurations within a very large active space in DMRG calculation, usually internally contraction (ic) [35, 36] or external contraction (ec) [37] approximations and/or a truncation for reference configurations have to be adopted in these post-DMRG dynamic correlation calculations. Alternatively, hybridizations with density functional theory (DFT) [38] or pair density functional theory (PDFT) [39] were also implemented as post-DMRG treatments. Recently, we have shown that DMRG-ec-MRCI is capable of adequately describing the static and dynamic electron correlation in systems with large active spaces beyond 30 orbitals, e.g. chromium dimer (\( \text{Cr}_2 \)) with an active space of \((12e, 42o)\), oligocenes with active spaces up to \((38e, 38o)\) and Eu-BTBP(NO\(_3\))\(_3\) complex with an active space of \((38e, 36o)\). [30] However, for the purpose of dealing with even larger active spaces, the development of economic treatments for dynamic electron correlations on top of DMRG calculations is still highly necessary.

Perturbation theory (PT) offers a simple and efficient way among various dynamic correlation treatments. This type of approximation goes as a power series of the perturbation parameter \( \epsilon \) defined by \( \hat{H} = \hat{H}_0 + \epsilon \hat{V} \), where \( \hat{H}_0 \) is the zeroth-order Hamiltonian operator while \( \hat{V} \) is the perturbation. In the domain of multi-reference PT (MRPT), CASPT2 [40, 41] and NEVPT2 [42] are widely used, with a difference in defining \( \hat{H}_0 \). In CASPT2 [40, 41], the zeroth-order Hamiltonian is defined in terms of a Fock-type one-electron operator (the generalized Fock operator), however it is well-known that CASPT2 suffers from a few defects: the energy of systems with open shells will be too low, and it faces intruder states due to too small denominators. [43] In order to address the two-electron interaction effect in the zeroth-order wavefunction, Dyall [44] suggested an auxiliary two-electron zeroth-order Hamiltonian, which is equivalent to the full Hamiltonian within the complete active space (CAS). Based on Dyall’s Hamiltonian, Malrieu et al. [42] proposed NEVPT2 as an alternative MRPT method, which is strictly additive and free of intruder states. Besides CASPT2 and NEVPT2, Epstein-Nesbet PT (ENPT) [45, 46] can provide a computationally simpler MRPT solution by partitioning the the full configurational space into a variational space and an outer space. The simplicity of only diagonal elements in the outer space for the zeroth-order Hamiltonian in ENPT makes it an attractive alternative to other MRPT methods, since no diagonalization or solving linear equations is required. [47] Such kind of ENPT2 treatment has been successfully adopted for a quick estimation of the perturbative energy correction in CI by perturbation with multi-configurational zeroth-order wavefunction selected by iterative process (CIPSI) [48], heat-bath CI (SHCI) [49] and quantum Monte Carlo (QMC) [50, 51] etc.

Sharma [52] and also Chan and co-workers [53, 54] recently applied ENPT2 corrections for DMRG calculations with a small bond dimension \( M \) in the context
of matrix-product states (MPS) to approach the DMRG calculations with a large bond
dimension \( M \) within a given active space. Their works showed that the selected CI-then-
perturbation strategy has the capacity to describe the transition metal complex up to
tens of active electrons/orbitals. When combining with a good choice of zeroth-order
Hamiltonian, the selected CI-then-perturbation strategy can provide highly accurate
total energies for challenging systems with significantly reduced computational resources
when comparing with the deterministic Epstein-Nesbet perturbed DMRG, and both of
stochastic and deterministic algorithms are much cheaper than the original variational
DMRG, in large orbital spaces with a mix of correlation strengths.

In this work, we integrate DMRG and ENPT2 based on our entanglement-
driving genetic algorithm (EDGA) scheme, to describe the static and dynamic electron
correlation within and outside the given active space adequately. It demonstrates that
the EDGA-based DMRG-ENPT2 approach provides an efficient tool for describing the
complex electronic structure of strongly correlated chemical molecules with very large
active spaces beyond 30-40 orbitals.

2. Methodology

As details of quantum-chemical DMRG have been discussed elsewhere [4, 5, 14, 15, 16,
55, 56, 57, 58, 59, 60], herein we only briefly introduce ENPT2 and selected CI (SCI)
as well as how they are employed in the context of DMRG-ENPT2.

In MR-ENPT, the full configurational space is partitioned into a variational space,
\( \Pi \), spanned by determinants labeled \( |D_i \rangle \) and \( |D_j \rangle \), and the rest of the space, spanned
by determinants labeled \( |D_a \rangle \). The zeroth-order Hamiltonian consists of the full
Hamiltonian block within \( \Pi \) and only the diagonal elements of \( \hat{H} \) outside \( \Pi \), by defining
\[
\hat{H}_0 = \sum_{ij \in \Pi} \langle D_i | \hat{H} | D_j \rangle |D_i\rangle\langle D_j| + \sum_{a \in \Pi} \langle D_a | \hat{H} | D_a \rangle |D_a\rangle\langle D_a|.
\] (1)
The zeroth-order wave function \( |\Psi_0\rangle = \sum_{i \in \Pi} c_i |D_i\rangle \) and the zeroth-order energy \( E_0 \) are
the eigenvector and eigenvalue of \( \hat{H}_0 \). By virtue of using standard perturbation theory,
the second-order energy correction can be calculated by
\[
\Delta E_{\text{ENPT2}} = \sum_{a \in \Pi} \frac{(\sum_{i \in \Pi} \langle D_a | \hat{H} | D_i \rangle c_i)^2}{E_0 - \langle D_a | \hat{H} | D_a \rangle}.
\] (2)

Next we show how DMRG provide \( |\Psi_0\rangle \) for ENPT2 calculation. DMRG wave function (spanned by \( L \) orbitals) is usually represented in MPS formulation by
\[
|\Psi\rangle = \sum_{\sigma_1, \ldots, \sigma_L, M_1, \ldots, M_{L-1}} A_{M_1, M_{L-1}}^{\sigma_1} \cdots A_{M_1, M_{L-1}}^{\sigma_L} |\sigma_1 \ldots \sigma_L\rangle,
\] (3)
where the basis states \( |\sigma_l\rangle \) for the \( l \)-th orbital has four possible occupation status as
\( |\uparrow \downarrow\rangle, |\uparrow\rangle, |\downarrow\rangle \) and \( |0\rangle \), \( M_{L-1} \times M_l \)-dimensional matrices \( A_{M_l}^{\sigma_l} = \{ A_{M_{L-1}, M_l}^{\sigma_l} \} \) are obtained by
successive singular value decomposition (SVD) procedures in DMRG sweeps by ignoring
the configurations with very small singular values. Collapsing the summation over the
\( a_l \) indices as matrix-matrix multiplications results in the last equality. Notice that
$m_{l-1} \times m_l$-dimensional matrices with 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.

The MPS representation for the wave function of Eq. (3) can be equivalent to a FCI or CASCI expansion with a Slater determinant (SD) configurational basis ($|\Psi\rangle = \sum_{\sigma_1,..,\sigma_L} c_{\sigma_1...\sigma_L} |\sigma_1...\sigma_L\rangle$) by calculating the CI coefficient $c_{\sigma_1...\sigma_L}$ by

$$c_{\sigma_1...\sigma_L} = A^{\sigma_1}A^{\sigma_2}...A^{\sigma_L}.$$ \hspace{1cm} (4)

where $A$ matrices for basis transformations can be obtained and kept in DMRG sweeps. This was first rationalized by Moritz et al. and can be used in wave function analysis [61]. However, the FCI expansion for a DMRG wave function in the large active space with more than 20 active orbitals would be prohibitive due to the number of SDs would be easily larger than $10^{10}$. [61] Two different schemes for efficiently sampling the most important configurations are recently proposed, Monte Carlo based sampling-reconstructed CAS (SR-CAS) algorithm by Boguslawski et al. [62] and the EDGA proposed by some of us [63]. Our recent work [30] illustrated that it is possible to use a limited number (e.g. thousands, or tens of thousands) of most important configurations that obtained by EDGA to achieve a wave function completeness of 0.99 for large active spaces. The solution of a SCI calculation with the sampled important configurations will be then used for the zeroth-order wave function $|\Psi_0\rangle$ and the zeroth-order energy $E_0$ in ENPT2 calculation.

All DMRG-CASCI calculations in this work are implemented using the QCMAQUIS DMRG software package [61, 65, 60]. The EDGA, SCI and subsequent ENPT2, ec-MRCI calculations are performed with our in-house code.

3. Results and discussion

3.1. $H_2S$

$H_2S$ is a medium sized molecular system that allows us to use DMRG-FCI method as a benchmark reference. First, we adopt DFT to optimize the ground state structure of $H_2S$ with $C_{2v}$ symmetry at the B3LYP/6-31G level by using GAUSSIAN09 [66] package. The equilibrium H-S-H angle $\theta = 94.06^\circ$ and S-H bond length $r = 1.379\text{Å}$, respectively, then we set $r = 1.7\text{Å}$ to get a stretched structure while keeping $\theta$ unchanged. In the following Multi-Configuration (MC)/MR electron correlation calculations, a large atomic natural orbitals basis sets that contracted to quadruple-zeta (ANO-L-VQZP) is used. We froze the 1s atomic orbital of S and defined a (16e, 15o) active space, which contains 2s, 2p, 3s, 3p, 3d atomic orbitals of S and 1s atomic orbitals of H. The DMRG-FCI (16e, 95o) and DMRG-CASCI (16e, 15o) calculations with $M = 2000$ and $M = 1000$ respectively are performed. The SCI, ec-MRCISD+Q, and ENPT2 calculations are performed using truncated reference wavefunctions constructed via EDGA framework with CI completeness of 0.9999.

The calculated results are listed in Table 1. It can be found that the results of SCI differs from CASCI by less than 1 mHartree. However, the number of reference
configurations for SCI is no more than 1000, among the full reference configurations of $10^{10}$ for the CASCI wavefunction. It means that we only need a limited number of reference states to get results close to CASCI. Compared with that of DMRG-FCI, all of the CASPT2, ec-MRCISD+Q, and ENPT2 can achieve semi-quantitatively satisfactory results and retrieve at least 88.0%, 92.2%, and 98.6% of the total dynamic correlation energies (-268 mHartree for equilibrium H$_2$S and -256 mHartree for the stretched one), respectively, shown in Figure 1. Because ENPT2 is not variational, the dynamic correlation retrieved by ENPT2 for equilibrium H$_2$S can be more than 100%. One may also notice that the dynamic correlation contribute to a significant increase of 12 mHartree from DMRG-CASCI(16e, 15o) to DMRG-FCI(16e, 95o) for the energy gap between the energies of the equilibrium and stretched structures. Both DMRG-ec-MRCISD+Q and DMRG-ENPT2 can reproduce this increase caused by dynamic correlation, and their results are close to each other. It demonstrates that, with a much cheaper computational cost than the variational DMRG and DMRG-MRCI, our DMRG-ENPT2 can still efficiently count the dynamic correlation.

Figure 1. Dynamic correlation retrieved by different MR methods with a (16e, 15o) active space for H$_2$S.
Table 1. Ground state energies of H\textsubscript{2}S and hexacene using different MC/MR methods

|          | \(E_{\text{equilibrium}}/\text{Hartree}\) | \(E_{\text{stretched}}/\text{Hartree}\) | \(\Delta/\text{mHartree}\) |
|----------|-------------------------------------------|----------------------------------------|-----------------------------|
| DMRG-FCI(16e, 95o) | -398.99268 | -398.91913 | 73.55 |
| DMRG-CASCI  | -398.72456 | -398.66271 | 61.85 |
| DMRG-SCI    | -398.72431 | -398.66241 | 61.91 |
| DMRG-ec-MRCISD+Q | -398.97456 | -398.89892 | 75.65 |
| DMRG-ENPT2  | -398.99665 | -398.91530 | 81.34 |

|          | \(E_{S_0}/\text{Hartree}\) | \(E_{T_1}/\text{Hartree}\) | \(\Delta/\text{mHartree}\) |
|----------|----------------------------|--------------------------|-----------------------------|
| hexacene (26e, 26o) | -994.34670 | -994.30763 | 39.07 |
| DMRG-CASCI | -994.31681 | -994.27863 | 38.18 |
| DMRG-SCI  | -994.40069 | -994.37197 | 28.73 |
| DMRG-ec-MRCISD+Q | -994.39042 | -994.36003 | 30.39 |

3.2. Hexacene

The nature of the ground state of higher acenes is still controversial, so that the \(S_0-T_1\) energy gap is an important parameter in higher acenes \cite{67, 68}. In this work, we take hexacene as an example to calculate its \(S_0-T_1\) gap. We firstly optimize the \(S_0\) and \(T_1\) structures of hexacene in \(D_{2h}\) symmetry at the B3LYP/6-31G(d) level respectively by using the GAUSSIAN09 \cite{66} package. A (26e, 26o) active space, which contains all the valence \(\pi\) orbitals and electrons, is then used in our MC/MR calculations with the ANO-L-VTZP and the minimum small atomic natural orbitals basis sets (ANO-S-MB) for C and H respectively. The DMRG-CASCI calculations with \(M = 1000\) are performed. The SCI, ec-MRCISD+Q and ENPT2 calculations are performed using truncated reference wavefunctions constructed via EDGA framework with CI completeness of 0.97.

The calculated results are listed in Table 1 and the tendency are similar to that of H\textsubscript{2}S. The DMRG-SCI energy gap differs from DMRG-CASCI by less than 1 mHartree, while the number of reference states for SCI is much smaller than CASCI, no more than 10000. DMRG-ENPT2 and DMRG-ec-MRCISD+Q results are in good agreement with each other, and both of them can describe the gap reduction caused by the dynamic correlation effect. Their difference of absolute energy values and energy gap between ENPT2 and ec-MRCISD+Q are around 10 and 2 mHartree, respectively. However, we have to note that ENPT2 only uses about 10% computational time of ec-MRCISD+Q. So that one can expect that the EDGA-based DMRG-ENPT2 can be used as an cheap alternative for describing both static and dynamic correlations in large strongly correlated systems.

3.3. \([\text{Mn})_3\text{O}_4\text{L}_4(\text{H}_2\text{O})]\

High-valent multinuclear oxomanganese complexes play an important role in photosystem II \cite{69, 70}. It is well-known that accurate characterization of the energetics of the low-lying spin-electronic states of mixed-valent transition metal complexes is
Table 2. Calculated energy results for LS and HS states as well as their difference 
($\Delta = E_{LS} - E_{HS}$) of [(Mn)$_3$O$_4$L$_4$(H$_2$O)] (47e, 43o)

| Method      | $E_{LS}$/Hartree | $E_{HS}$/Hartree | $\Delta$/kcal·mol$^{-1}$ |
|-------------|------------------|------------------|--------------------------|
| DFT         | -4991.54576      | -4991.61759      | 45.07                    |
| DMRG-CASCI  | -4978.82241      | -4978.82272      | 0.19                     |
| DMRG-SCI    | -4978.60204      | -4978.60625      | 2.64                     |
| DMRG-ENPT2  | -4978.69697      | -4978.70352      | 4.11                     |

still a significant challenge for DFT [71], and it becomes highly necessary to re-examine the electronic structure of these systems with electron correlation wavefunction theories. In this work, we perform DMRG-CASCI and DMRG-ENPT2 calculations for [(Mn)$_3$O$_4$L$_4$(H$_2$O)], with L = N,N′-bis(methylene)-Z-1,2-ethenediamine as an example, which is shown in Figure 2.

The geometry structure of [(Mn)$_3$O$_4$L$_4$(H$_2$O)] is adopted from ref [72] and constrained in $C_2$ symmetry. This structure is used for both low spin (LS) state ($S = 1/2$) and high spin (HS) state ($S = 3/2$). For a comparison, we perform DFT calculation with M06-L functional using OPENMOLCAS [73] package. In all DFT and MC/MR calculations, the ANO-RCC-VDZP and ANO-RCC-MB basis sets are used for Mn and H, respectively, and ANO-RCC-VDZ basis set is used for C and N. A (47e, 43o) active space, which contains 3d atomic orbitals and electrons of Mn, 2p atomic orbitals and electrons of bridged O, two 2p atomic orbitals and lone pair electrons of N, is used in MC/MR calculation. The DMRG-CASCI calculations with $M = 1000$ are performed. The SCI and ENPT2 calculations are performed using truncated reference wavefunctions constructed via EDGA framework with the CI completeness of 0.75. In order to account for the relativistic effect in the calculations, we adopt the scalar relativistic X2C (eXact-two-Component) [74, 75] corrections to the one-electron Hamiltonian as well as the property integrals.

Our calculated energy results for LS and HS states as well as their difference ($\Delta = E_{LS} - E_{HS}$) are listed in Table 2. Earlier electron paramagnetic resonance (EPR) experiments by Sarneski et al. found there is an energy near-degeneracy for LS and HS states with a gap around 0.2 kcal·mol$^{-1}$ [76]. However, DFT calculations with M06L gives a much larger gap around 45 kcal·mol$^{-1}$, and similar DFT failure with B3LYP functional was also found by Batista et al. [71], who predicted an energy gap of 21 kcal·mol$^{-1}$. Encouragingly, it can be found that, with the more proper treatment of electron correlation and getting rid of spin contaminations, both DMRG-CASCI and DMRG-ENPT2 predict a small energy gap between LS and HS states, being 0.2 and 4.1 kcal·mol$^{-1}$ respectively. This is qualitatively in good agreements with the EPR experiments by Sarneski et al. [76]. Further quantitative improvements can be achieved by enlarging the DMRG bond dimension M, using optimized MOs as DMRG basis and increasing the CI completeness in EDGA.
Figure 2. Structure of \([(\text{Mn})_3\text{O}_4\text{L}_4(\text{H}_2\text{O})]\), with \(\text{L} = \text{N,N'}\text{-bis(methylene)-Z-1,2-ethenediamine} \). Color key: purple = Mn, red = O, blue = N, grey = C and white = H.

4. Conclusion

In order to account for post-DMRG dynamic electron correlations efficiently, in this work we propose a new method (DMRG-ENPT2) by combining DMRG-SCI with and ENPT2. Test calculations on \(\text{H}_2\text{S} \) with an active space of (16e, 15o), hexacene with an active space of (26e, 26o) and trinuclear Manganese cluster with an active space of (47e, 43o) with comparisons to higher level calculations or experimental results show that DMRG-ENPT2 can effectively describe various low-lying spin states in complicated strongly correlated systems. Considering the computational time of DMRG-ENPT2 is only about one tenth of that of DMRG-ec-MRCISD+Q, this provides a cheaper but reliable post-DMRG option for large active spaces beyond 30-40 active orbitals.

5. Conflicts of interest

There are no conflicts of interest to declare.

6. Acknowledgments

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