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Quasi-degenerate perturbation theory using matrix product states

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In this work, we generalize the recently proposed matrix product state perturbation theory (MPSPT) for calculating energies of excited states using quasi-degenerate (QD) perturbation theory. Our formulation uses the Kirtman-Certain-Hirschfelder canonical Van Vleck perturbation theory, which gives Hermitian effective Hamiltonians at each order, and also allows one to make use of Wigner's $2n + 1$ rule. Further, our formulation satisfies Granovsky's requirement of model space invariance which is important for obtaining smooth potential energy curves. Thus, when we use MPSPT with the Dyll Hamiltonian, we obtain a model space invariant version of quasi-degenerate n -electron valence state perturbation theory (NEVPT), a property that the usual formulation of QD-NEVPT2 based on a multipartitioning technique lacked. We use our method on the benchmark problems of bond breaking of LiF which shows ionic to covalent curve crossing and the twist around the double bond of ethylene where significant valence-Rydberg mixing occurs in the excited states. In accordance with our previous work, we find that multi-reference linearized coupled cluster theory is more accurate than other multi-reference theories of similar cost. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4939752>]

INTRODUCTION

Perturbation theory (PT) has been one of the most successful theories in all of quantum chemistry as it provides accurate size-extensive energies at polynomial cost. But one of the major shortcomings of the usual single-reference perturbation theory is its instability in the presence of orbital degeneracies between occupied and virtual orbitals: for example, Möller-Plesset perturbation theory diverges when the target wavefunction is not dominated by a single determinant. To overcome this problem, several multi-reference perturbation theories have been proposed. These theories work within the “diagonalise-then-perturb” philosophy, where first the active space Hamiltonian is diagonalized and then perturbative correction is calculated by exciting up to two holes into the doubly occupied core and two particles into the empty virtual orbitals. Usually, a further approximation known as internal contraction (IC)^{1,2} is made to make the equations computationally tractable. Even with the IC approximation, these calculations can be expensive because they require three and four body reduced density matrices (RDMs) of the active space. This framework is widely used and works quite well as long as the number of active space orbitals is restricted to between ten and twenty.

With the invention of the density matrix renormalization group (DMRG)^{3–10} and full configuration interaction Monte Carlo methods^{11–14} calculations with up to 40–50 active orbitals have now become routine. With such large active spaces, calculating and storing high body reduced density matrices becomes a severe bottle neck. In this context, it should be

noted that Kurashige and Yanai¹⁵ have implemented DMRG-complete active space second-order perturbation theory (CASPT2) by using pseudo-canonical molecular orbitals which resulted in great simplification in constructing the four-body reduced density matrix. The full three body reduced density matrix was nevertheless required and problems with up to 28 active space orbitals have been tackled with this approach. But in general, to treat semi-internal excitations, at least the fourth order reduced density matrix is required¹⁶ which becomes prohibitively expensive for all but very small active spaces. For this reason, 4-RDMs are usually calculated using the approximate cumulant reconstruction^{17–19} in methods such as canonical transformation (CT),^{20,21} approximate multi-reference configuration interaction (MRCI),^{22,23} and approximate n -electron valence state perturbation theory (NEVPT2).²⁴

To overcome the need for calculating reduced density matrices, we have recently proposed a method called matrix product state perturbation theory (MPSPT)²⁵ that expresses the first order correction to the wavefunction as a MPS. This wavefunction is optimized by minimizing the Hylleraas functional of the appropriate perturbation theory. The advantage of this approach is that it completely bypasses the need for calculating reduced density matrices altogether, further it is highly flexible and essentially any zeroth order Hamiltonian (\hat{H}_0) can be used and finally, in the limit of large virtual bond dimension (M) of the MPS, we recover the fully uncontracted results. So far, we have used MPSPT to perform NEVPT2 and multi-reference linearised coupled cluster (MRLCC)²⁶ theory calculations on a large set of strongly correlated benchmark systems. In general, we have found that MRLCC theory, in particular the one formulated by Fink,^{27,28} is extremely accurate and outperformed other

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methods of similar cost by sometimes over an order of magnitude.

In the current publication, we extend the MPSPT to address the well known shortcoming of the usual multi-reference perturbation theories when the ground state is nearly degenerate with one or more other states, for example, in avoided crossings. In such cases, the “diagonalise-and-perturb” philosophy is insufficient because the zeroth order state calculated by diagonalizing the active space Hamiltonian can be quite inaccurate and one needs to allow it to relax in the presence of the perturbation, in absence of which spurious curve crossings can occur.^{29,30} This is accomplished by using the quasi-degenerate perturbation theory (QDPT)^{31–36} where an effective Hamiltonian is constructed in which both the diagonal and off-diagonal elements are perturbatively corrected. This Hamiltonian is then diagonalized which allows the desired reorganization of the structure of the zeroth order wavefunction.

The rest of the paper is organized as follows: in the section titled MPSPT, we outline the salient features of the MPSPT; after this, we show how MPSPT can be extended using the quasi-degenerate perturbation theory to calculate the energies of the excited state. Finally, we show some benchmark calculations on LiF and ethylene to access the accuracy of the ground and excited states calculated using this theory.

MPSPT

As noted in the Introduction, the novel aspect of MPSPT is that the first order correction to the wavefunction in the perturbation theory is written as a MPS, which is the wavefunction ansatz used in the DMRG algorithm. A MPS parametrizes a wavefunction by expressing it as a product of three-dimensional tensors,^{37,38} one tensor per orbital which is shown graphically in Figure 1. The dimension of the virtual indices (M) determines how accurately the MPS represents a wavefunction of interest. Although an exponentially large M is necessary to faithfully represent the ground state wavefunction in the absence of linear topology; in practice, it is often observed that a much smaller M is sufficient to obtain chemically accurate ground state energies.

The truly remarkable property of MPS is that operations of linear algebra, such as calculating the overlap ($\langle\Psi_1|\Psi_2\rangle$) and matrix element of an operator ($\langle\Psi_1|\hat{O}|\Psi_2\rangle$), can be performed with a cost that scales polynomially with M and the number of orbitals k . It is worth pointing out that many of the commonly used wavefunction ansatz in quantum chemistry do not have

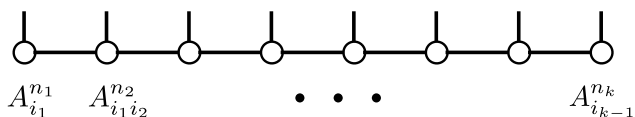


FIG. 1. A matrix product state (MPS) can be represented graphically using a series of three-dimensional tensors $A_{i_l-i_{l-1}}^{n_l}$ in which the physical index n_l (pointing upwards) denotes the occupation of the orbital and the other two indices i_l, i_{l-1} (pointing horizontally), known as virtual indices, are sequentially contracted.

TABLE I. The cost of performing various linear algebra operations with two MPSs $|\Psi_1\rangle$ and $|\Psi_2\rangle$. Here, k , M_1 , and M_2 are the number of orbitals and the virtual bond dimensions of $|\Psi_1\rangle$ and $|\Psi_2\rangle$, respectively. \hat{O}_1 and \hat{O}_2 are general one and two body operators, respectively.

Operation	cpu
$\langle\Psi_1 \Psi_2\rangle$	$kM_1^2M_2 + kM_1M_2^2$
$\langle\Psi_1 \hat{O}_1 \Psi_2\rangle$	$k^2M_1^2M_2 + k^2M_1M_2^2$
$\langle\Psi_1 \hat{O}_2 \Psi_2\rangle$	$k^3M_1^2M_2 + k^3M_1M_2^2$

this property; for example, calculating the expectation value of energy of a coupled cluster wavefunction is exponentially hard. Table I summarizes the cost of calculating overlaps and transition matrix elements between different MPSs. Finally, without getting bogged down in details, we would like to point out that the DMRG method consists of an ingenious algorithm called the “sweep algorithm” which uses all these properties of MPS to optimize the ground state $|\Psi_g\rangle$ by minimizing the energy functional shown in Equation (1) under the constraint that $\langle\Psi_g|\Psi_g\rangle = 1$,

$$\langle\Psi_g|\hat{H}|\Psi_g\rangle. \quad (1)$$

With this background about MPS, we show how they can be used to perform perturbation theory. Let us assume that the full Hamiltonian of the problem (\hat{H}) is partitioned into the zeroth order Hamiltonian (\hat{H}_0) with the m th eigenfunction $|\Psi_m^0\rangle$ with an eigenvalue E_m^0 and the rest which is treated as perturbation (\hat{V}). The first order correction to the ground state wavefunction ($|\Psi_g^1\rangle$) is calculated by solving Equation (2), where \hat{Q}_g is the orthogonal complement of $\hat{P}_g = |\Psi_g^0\rangle\langle\Psi_g^0|$, the projector onto the zeroth order approximation of the ground state,

$$(\hat{H}_0 - E_g^0)|\Psi_g^1\rangle = -\hat{Q}_g\hat{V}|\Psi_g^0\rangle. \quad (2)$$

This equation can alternatively be formulated as a variational problem, where the Hylleraas functional \hat{L} shown in Equation (3) is minimized with respect to $|\Psi_g^1\rangle$,

$$\hat{L}[|\Psi_g^1\rangle] = \langle\Psi_g^1|(\hat{H}_0 - E_g^0)|\Psi_g^1\rangle + 2\langle\Psi_g^1|\hat{Q}_g\hat{V}|\Psi_g^0\rangle. \quad (3)$$

Note that both the Hylleraas functional in Equation (3) and energy functional in Equation (1) are quadratic in their respective unknowns $|\Psi_g^1\rangle$ and $|\Psi_g\rangle$. Thus, by using essentially the same sweep algorithm as in DMRG, one can optimize $|\Psi_g^1\rangle$ by minimizing the Hylleraas functional with a cpu cost that scales as $k^3M_1^3$ for the first term and $k^3M_0^2M_1 + k^3M_0M_1^2$ for the second term assuming both \hat{H}_0 and \hat{V} are two body operators and M_0 and M_1 are the virtual bond dimension of states $|\Psi_g^0\rangle$ and $|\Psi_g^1\rangle$, respectively.

In this work, we will mainly focus on uncontracted NEVPT^{39,40} and MRLCC^{26–28} theories, in which the zeroth order Hamiltonian \hat{H}_0 are, respectively, the Dyll Hamiltonian, \hat{H}_D , and excitation conserving Hamiltonian of Fink, \hat{H}_{REPT} , specified in Equation (4), where i, j, k, l refer to core orbitals, a, b, c, d refer to virtual orbitals, r, s, t, u refer to active orbitals, and m, n, o, p refer to any orbital; $\Delta n_{ex} = 0$ signifies that all terms that change the number of electrons in the active, core, and virtual states are removed,

$$\begin{aligned}\hat{H}_D &= \sum_{ij} f_{ij} a_i^\dagger a_j + \sum_{ab} f_{ab} a_a^\dagger a_b \\ &+ \sum_{rs} t_{rs}^{eff} a_r^\dagger a_s + \frac{1}{2} \sum_{rstu} \langle rs|tu \rangle a_r^\dagger a_s^\dagger a_u a_t, \\ \hat{H}_{REPT} &= \sum_{\substack{mn: \\ \Delta n_{ex}=0}} t_{mn} a_m^\dagger a_n + \sum_{\substack{mnop: \\ \Delta n_{ex}=0}} \langle mn|op \rangle a_m^\dagger a_n^\dagger a_p a_o.\end{aligned}\quad (4)$$

QDPT

MPSPT like all other multi-reference perturbation theories becomes inaccurate near conical intersection or when describing excited states with significant Rydberg character. This is because the zeroth order states calculated by diagonalizing the active space Hamiltonian can be quite inaccurate and they need to be allowed to relax in the presence of the perturbation. This relaxation is allowed when one works within the QDPT framework which uses the “diagonalize-perturb-diagonalize” philosophy. There are several versions of QDPT the most common of which uses intermediate normalization⁴¹ and results in non-Hermitian effective Hamiltonians. In this work, instead, we use the Kirtman-Certain-Hirschfelder (KCH) form of the canonical Van Vleck perturbation theory (VVPT)^{33–36} which gives Hermitian effective Hamiltonians and in addition obeys Wigner’s $2n + 1$ rule, thus allowing us to calculate third order correction in energy with just the first order correction in the wavefunction. The disadvantage of KCH-VVPT is that it does not give size extensive energies beyond the fourth order. This is not a problem because most practical applications are restricted to orders no greater than three.

Let us assume that we will include m low lying states in our model space. The zeroth order approximation of these states is given by the m lowest eigenvectors of the zeroth order Hamiltonian $|\Psi_1^0\rangle, |\Psi_2^0\rangle, \dots, |\Psi_m^0\rangle$, with eigenenergies $E_1^0, E_2^0, \dots, E_m^0$, respectively. To the best of our knowledge, a simple order-independent expression for the effective Hamiltonian is not available,³⁶ but here we use the explicit expressions up to third order of perturbation theory given by Nakano.^{42,43} The effective Hamiltonian projected in the model space $P\mathcal{H}^{eff}P$ is an $m \times m$ matrix and the elements of this matrix up to third order are explicitly given by Equations (5), where $|\Psi_j^1\rangle$ is the first order correction to the j th model state,

$$\begin{aligned}\mathcal{H}_{ij}^0 &= E_i^0 \delta_{ij}, \\ \mathcal{H}_{ij}^1 &= \langle \Psi_i^0 | \hat{V} | \Psi_j^0 \rangle, \\ \mathcal{H}_{ij}^2 &= \frac{1}{2} \left(\langle \Psi_i^0 | \hat{V} | \Psi_j^1 \rangle + \langle \Psi_j^0 | \hat{V} | \Psi_i^1 \rangle \right), \\ \mathcal{H}_{ij}^3 &= \langle \Psi_i^1 | \hat{V} - E_{ij}^1 | \Psi_j^1 \rangle.\end{aligned}\quad (5)$$

The first order correction to the j th state can be calculated by solving Equation (6), where \hat{Q} is the orthogonal complement of the model space, or alternatively by minimizing the functional displayed in Equation (7),

$$(\hat{H}_0 - E_j^0) |\Psi_j^1\rangle = -\hat{Q} \hat{V} |\Psi_j^0\rangle, \quad (6)$$

$$\hat{L}[\Psi_j^1] = \langle \Psi_j^1 | (\hat{H}_0 - E_j^0) | \Psi_j^1 \rangle + 2 \langle \Psi_j^1 | \hat{Q} \hat{V} | \Psi_j^0 \rangle. \quad (7)$$

According to the above expression, one minimizes the Hylleraas functional in Equation (7) for different states to obtain the first order corrections; the first order states of all m states can be calculated in parallel independently of each other. These can then be used in the expression in Equation (5) to calculate an $m \times m$ effective Hamiltonian which is then diagonalized to calculate the QDPT energies. Note that in usual cases, one can ignore the off-diagonal elements of the effective Hamiltonian and this makes little difference; but in cases of near degeneracy, the off-diagonal elements are crucial to allow relaxation of the zeroth order wavefunctions and avoid spurious curve crossing as we will see in the following examples.

Before we move to the examples, it is appropriate to discuss the invariance of the QD-MPSPT energies with respect to rotations within the model states. Granovsky⁴⁴ has recently published his extended multi-configuration quasi-degenerate perturbation theory which lists the criterion for QDPT to have the desirable property of being invariant under rotations within the model space. The traditional QD versions of CASPT2⁴⁵ and multipartitioning⁴⁷ based QD-NEVPT2⁴⁶ do not satisfy this criterion; the former because the Fock operator is not invariant under rotations of model states (this shortcoming has been addressed to some extent with the implementation of extended multi-state CASPT2⁴⁸) and the latter because in QDNEVPT2, non-universal perturber functions are used for each model state. Both these problems are absent from our formulation because both in the MPSPT implementation of NEVPT and MRLCC, the zeroth order states are exact eigenfunctions of the unprojected zeroth order Hamiltonian \hat{H}_0 , i.e., the definition of the zeroth order Hamiltonian does not involve the zeroth order wavefunction. This is, for example, not true in the case of CASPT2 where the zeroth order Hamiltonian is defined as the projection of the Fock operator onto the zeroth order state. Further, we work with matrix product states that in the limit of large M span the same \hat{Q} space for each model state. Model-space invariance is lost when a small M calculation is performed, but nevertheless smooth potential energy curves can still be generated when

TABLE II. The table shows the energies of the ground and first excited states of LiF molecule at various internuclear distances. The second and third columns show the full configuration interaction (FCI) energy in Hartrees (E_h) calculated using DMRG and the rest of the columns show the error in energies of various methods in mE_h relative to the FCI energies for the two states. Both the MRLCC and NEVPT3 are calculated using MPSPT presented in the current publication. Extended multi-state CASPT2 (XMS-CASPT2) and MRCI are calculated using the Molpro package.

r/a_0	FCI		QD-MRLCC		QD-NEVPT3		XMS-CASPT2		MRCI	
	I	II	I	II	I	II	I	II	I	II
3	-107.2912	-107.0383	7.8	5.7	11.7	10.2	16.1	12.2	11.3	8.0
4	-107.2522	-107.0600	7.9	5.9	12.9	10.8	17.0	11.5	12.5	8.4
5	-107.2016	-107.0652	6.8	5.5	13.0	10.6	17.9	10.7	13.2	8.4
6	-107.1603	-107.0689	5.7	5.0	12.9	10.4	17.9	10.6	13.2	8.4
7	-107.1284	-107.0715	4.9	4.6	12.6	10.1	17.0	10.9	12.7	8.3
8	-107.1040	-107.0728	4.3	4.2	12.1	10.1	15.6	11.6	11.6	8.5
9	-107.0867	-107.0714	3.8	3.4	10.9	10.7	13.3	13.4	9.3	9.7
10	-107.0801	-107.0640	3.9	0.5	9.7	11.8	11.8	14.6	7.4	11.1

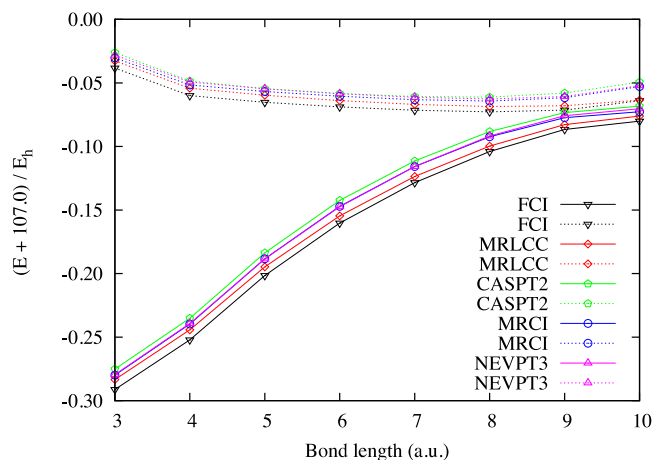


FIG. 2. The graph shows the first two excited states of LiF molecule with various internuclear distances using different methods. MRLCC appears to be the most accurate of all the methods presented here with NEVPT2 close behind.

calculations are restarted from the solution at a nearby geometry as the initial guess.

BENCHMARKS

Here, we test the effectiveness of the proposed theory by performing calculations on the lowest two states along the bond stretching of LiF molecule and the lowest three states of an ethylene molecule as it is twisted along the double bond.

LiF

LiF is the quintessential benchmark used to test QDPTs because of the presence of an avoided crossing between the ionic and covalent curves.^{43,45,46,49} At short internuclear distances, the ionic configuration dominates the ground state wavefunction and at large bond distances, the molecule dissociates with separation of neutral Li and F atoms. Thus, along the curve, the nature of the wavefunction changes drastically from ionic to covalent, but the two potential energy surfaces (PESs) never cross each other because both these

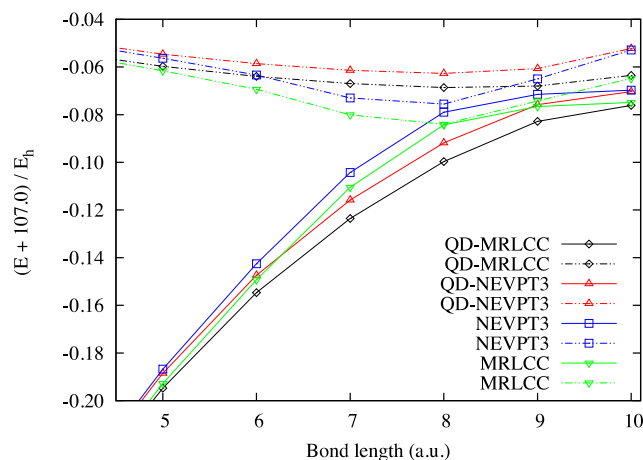


FIG. 3. The ground and first excited states of LiF calculated using quasi-degenerate NEVPT3 and MRLCC (solid lines). For comparison, we have also plotted simple NEVPT3 and MRLCC energies (dotted lines), which show spurious curve crossing and larger errors.

wavefunctions belong to the same irreducible representation $^1\Sigma_g^+$ and thus obey the non-crossing rule of diatoms.

Here, we first calculate nearly exact all electron full configuration interaction energies with a cc-pVTZ basis set^{50,51} using DMRG as implemented in the Block code.⁵² These energies are then compared to those calculated using MRCI,⁵³ CASPT2,^{48,54} NEVPT3, and MRLCC which are tabulated in Table II; MRCI and CASPT2 energies are calculated using Molpro quantum chemistry package.⁵⁵ The zeroth order wavefunction for these calculations is obtained by performing a two state-average complete active space self consistent field (CASSCF) calculations with an active space containing 6 electrons in 6 orbitals.

From Table II, it can be seen that the errors in MRLCC are the lowest, while CASPT2 shows the largest errors. The energies of all the methods including the FCI energies are also plotted in Figure 2. It should be noted that near avoided crossing at around 8 bohrs, it is essential to perform quasi-degenerate perturbation theory. For example, we have also plotted the energies obtained with simple multi-state perturbation theory of MRLCC and NEVPT3 in Figure 3; and

TABLE III. This table shows the energy of the ground state and of the two first excited states of the ethene molecule at different values of the dihedral angle. Second, third, and fourth columns are the near-exact FCI energies, in Hartree, obtained using the DMRG algorithm. The remaining columns show the error in energies of various methods in mE_h relative to the FCI energies for the three states.

ang	FCI			QD-MRLCC			QD-NEVPT3			MRCI			CASPT2		
	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
00	-78.3242	-77.8928	-77.8318	2.7	3.4	3.7	8.7	10.5	11.1	7.3	10.3	10.2	16.2	11.5	16.7
10	-78.3223	-77.8955	-77.8345	2.7	3.6	3.6	8.8	10.6	11.1	7.3	10.1	9.9	15.9	11.4	14.9
20	-78.3165	-77.9056	-77.8441	2.7	4.2	8.1	8.7	11.4	16.6	6.4	9.3	13.7	13.3	11.4	12.1
30	-78.3070	-77.9267	-77.8558	2.8	4.1	5.7	8.8	11.3	13.7	6.6	9.2	11.2	13.4	10.8	11.0
40	-78.2936	-77.9578	-77.8626	2.9	3.8	5.0	8.8	10.8	12.7	6.6	8.8	10.5	13.4	10.3	11.0
50	-78.2769	-77.9939	-77.8650	3.0	3.6	4.8	8.9	10.4	12.4	6.7	8.5	10.4	13.3	10.2	11.1
60	-78.2573	-78.0309	-77.8643	3.0	3.4	4.9	8.9	10.1	12.4	6.7	8.3	10.5	13.3	10.3	11.4
70	-78.2362	-78.0654	-77.8612	3.1	3.3	5.3	9.0	9.9	12.8	6.7	8.2	10.7	13.3	10.4	11.8
80	-78.2168	-78.0929	-77.8559	3.0	3.1	6.2	8.9	9.7	13.7	6.5	8.0	11.4	13.0	10.5	12.7
90	-78.2074	-78.1041	-77.8501	2.6	2.5	6.9	8.6	9.2	14.2	6.0	7.4	11.7	12.4	10.3	13.0

these energies show a much higher level of degeneracy with NEVPT3 showing a spurious curve crossing near 8 bohrs. In these cases, the off-diagonal term of the effective Hamiltonian \mathcal{H}^{eff} which is ignored in simple perturbation theory becomes absolutely essential and is responsible for relaxation of the zeroth order states.

C₂H₄

We now turn our attention to the evaluation of the three lowest electronic states of the totally symmetric representation of the ethylene molecule with different values of the dihedral angle. The PESs of the ground and excited states of ethylene have been extensively studied both experimentally and theoretically because it is the simplest model of the photo-induced *cis-trans* isomerization. During the isomerization, an initial photoexcitation of the molecule from the ground state N (π^2) to the excited valence state V ($\pi\pi^*$) is followed by torsional motion around the C=C double bond where the V state crosses the Z state (π^*2) and remains approximately degenerate with it. The V, Z, and N states are thought to play an important role in the isomerization.

The accurate characterization of the ground and excited state PESs is complicated by the fact that in addition to being strongly correlated, these states show several avoided crossings.^{45,56-58} Here, we calculate the first three states of ethylene involved in *cis-trans* isomerization using various multi-reference methods. Even though the point group symmetry of the molecule changes from D_{2h} in the flat molecule to D_2 symmetry at intermediate geometries and C_{2v} when the two CH₂ fragments are orthogonal, we use the D_2 point group for all the calculations to generate smooth curves. The geometry of the flat molecule is obtained from the G2-1 test set of Curtiss *et al.*;⁵⁹ the geometries at different torsional angles are obtained by keeping all the internuclear distances and angles fixed except the torsion angle. We use Pople's, i.e., 6-31G*⁶⁰ basis set for all the calculations.

Nearly exact FCI calculations have been performed using DMRG on these (36o, 16e) systems. These energies are

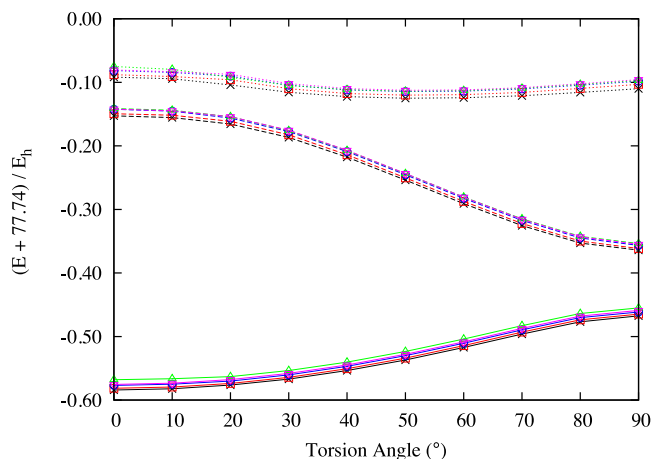


FIG. 4. Energies of the ground (straight line) and two first excited states (dashed and dotted lines) of ethylene at several C=C angles. The full CI results are indicated by crosses, MRLCC with squares, NEVPT2 with triangles down, CASPT2 with triangles up, and MRCI with circles.

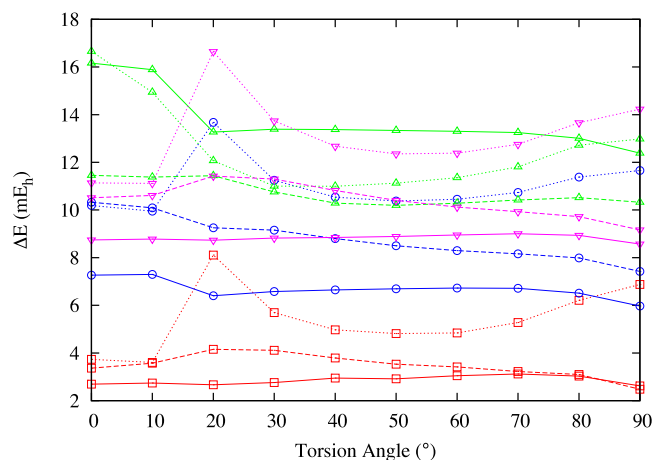


FIG. 5. The error, in mE_h , with respect to FCI calculations are displayed with the same legend as in Fig. 4.

then compared with MRLCC, NEVPT3, CASPT2, and MRCI results presented in Table III and are also plotted in Fig. 4. The zeroth order wavefunction has been obtained by CASSCF calculations on a (12o, 12e) active space.

The lowest errors are found with MRLCC and the largest errors with CASPT2; the same trends were observed with the LiF molecule. In Figure 5, it can be seen that the MRLCC errors are at least a factor of 2 smaller than the errors obtained by the other methods.

CONCLUSION AND OUTLOOK

In this article, we have shown that quasi-degenerate version of MPSPT can be used to calculate highly accurate energies of ground and excited states when near degeneracies are present. The most accurate energies were obtained by using MPSPT with Fink's excitation retaining zeroth order Hamiltonian (MRLCC), in agreement with our previous findings. We have used Kirtman-Certain-Hirschfelder's canonical Van Vleck perturbation theory, which enables us to use Wigner's $2n + 1$ rule and thus all MPSPT energies in this paper are calculated up to third order with only the first order correction in the wavefunction. Finally, the presented theory satisfies Granovsky's requirement of being model space invariant which gives smooth potential energy surfaces.

In this article, we have performed calculations on small problems with modest basis sets; so we would like to end by describing the prospect of using the current approach with a large basis set. The strength of MPS based methods is their ability to treat static correlation with active spaces containing around 30-40 orbitals, but the usual DMRG algorithm is not a practical route for calculating dynamical correlation where one is often required to work with several hundred to a few thousand orbitals. The current approach can nevertheless be used for performing NEVPT2 calculation by using the fact that such calculations can be embarrassingly parallelized over pairs of virtual orbitals. The NEVPT2 energy can be written as a sum of pair energies which can be calculated independently of each other and in parallel. Such embarrassing parallelization

is not possible for performing canonical MRLCC calculations. For such calculations, we can truncate the external perturber space (states containing two virtual orbitals) by using internal-contraction, while the semi-internal and internal perturber states can be treated using the current approach. The advantage of such an approach is that one does not need four body RDM, which poses a severe bottleneck for large active spaces treatable by DMRG. We are working on a manuscript which will describe this approach in detail.

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