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Application of improved virtual orbital based multireference methods to N_2, LiF, and C_4H_6 systems

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The *improved virtual orbital (IVO) complete active space configuration interaction (CASCI)* based multiconfigurational quasidegenerate perturbation theory (MCQDPT) and its single-root version (termed as MRMPPT) are applied to assess the efficacy and the reliability of these two methods. Applications involve the ground and/or excited state potential energy curves (PECs) of N_2, LiF, and C_4H_6 (butadiene) molecules, systems that are sufficiently complex to assess the applicability of these methods. The ionic-neutral curve crossing involving the lowest two $^1\Sigma^+$ states of LiF molecule is studied using the IVO-MCQDPT method, while its single-root version (IVO-MRMPPT) is employed to study the ground state PEC for isomerization of butadiene and to model the bond dissociation of N_2 molecule. Comparisons with the standard methods (full CI, coupled cluster with singles and doubles, etc.) demonstrate that the IVO-based MRMPPT and MCQDPT approaches provide smooth and reliable PECs for all the systems studied. The IVO-CASCI method is explored to enable geometry optimization for ground state of C_4H_6 using numerical energy gradients. The ground spectroscopic constants of N_2 and LiF determined using the numerical gradient based IVO-CASCI method are in accord with experiment and with other correlated calculations. As an illustration, we may point out that the maximum deviation from the experiment in our estimated normal mode frequency of LiF is 34 cm^{-1}, whereas for the bond length, the maximum error is just 0.012 Å. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3046454]

I. INTRODUCTION

The study of chemical reactions occurring in the ground/excited state requires accurate knowledge of the potential energy curves (PECs) of the systems of interest. The generation of accurate and reliable PECs is one of the most nontrivial problem in quantum chemistry. Despite tremendous methodological advances, the development of computationally inexpensive schemes capable of providing global potential energy surfaces/curves with uniform accuracy still remains an active area of research in quantum chemistry. The great success of single reference (SR) formulations[1–4] in describing systems that are predominantly of single-determinantal character has motivated numerous attempts to extend the limit of its applicability to the bond making/breaking regions by treating the quasidegeneracy through the inclusion of the higher-body cluster operators. The low order perturbative approximations to SR approaches are incapable of providing a viable, accurate computational scheme in these quasidegenerate regions.[2,4] On the other hand, the treatment of large systems with varying degree of quasidegeneracy and with actual or avoided curve crossings would greatly benefit from an accurate low order perturbation method.

Multireference (MR) generalizations of the SR theory describe the nondynamical electron correlation by using an *active* space containing reference functions that can adequately describe the quasidegeneracy, while the dynamical electron correlation is introduced via MR-perturbation theory (MRPT) schemes. Some effective Hamiltonian based MRPT methods, however, are often plagued by ubiquitous intruder problems,[5] thereby seriously limiting their viability for global potential energy surfaces/curves. Among several recent attempts at devising a chemically accurate MRPT approach[6–11] for computing smooth potential surfaces, the most promising MRPT methods include those based on the use of a zeroth order multiconfigurational self-consistent field (MCSCF) or complete active space configuration interaction (CASCI) approximation, viz., the H^v,[6] MRMPPT,[7] MCQDPT,[8] CASPT2,[9] MRMPPT using APSG,[10] etc., methods. The state specific second-order MR PT (SS-MRPT) (Ref. 11) and the generalized van Vleck second-order PT (Ref. 12) (GVVPT2) have also promising applicability.

At this point it is pertinent to mention the fact that the MRMPPT method of Hirao[7] (MRPTMP) can be viewed as a single-root version of MCQDPT scheme. Hereafter, we will call these two methods as Hirao–Nakano perturbation theory (HNPT) for convenience. In the HNPT method, the reference(s) wave function is (are) first determined from the complete active space self-consistent field (CASSCF) method and then the perturbation calculation is done with those wave functions used as reference based on Rayleigh–Schrödinger

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(RS) PT in MRMPPT and van Vleck PT in MCQDPT. It is important to mention that the CASSCF is an iterative method and involves transformations of two-electron molecular integrals and subsequent matrix diagonalization in each iteration and, hence, becomes time consuming which is primarily responsible for the increasing computational cost of HNPT method. This can seriously limit the wide applicability of the HNPT method. To overcome these difficulties associated with the CASSCF calculation, one can focus on the improved virtual orbital (IVO)-CASCI scheme[13–15] which avoids the convergence problems without sacrificing accuracy at considerably reduced computational labor. The computationally efficient IVO-CASCI scheme can thus be used to remove the problem of convergence and to reduce the computational cost of the HNPT (MRMPPT/MCQDPT) method[7,8] without undue sacrifice in accuracy.

Recently, Chaudhuri *et al.*[16,17] proposed a computationally inexpensive version of HNPT in which the first order reference functions are generated from the IVO-CASCI method[15,18–21] and are then used in subsequent MRPT calculations. The IVO-CASCI scheme is computationally simpler than CI singles (CISs) and CASSCF methods. The latter arises because the IVO-CASCI calculations do not involve iterations beyond those in the initial SCF calculation, nor do they possess features that create convergence difficulties with increasing size of the CAS in CASCI calculations. Since the IVO-CASCI approach contains both singly and doubly excited configurations in the CAS (in addition to higher order excitations), it provides descriptions of both singly and doubly excited states with comparable accuracy to CASSCF results. The CIS method, on the other hand, cannot treat doubly excited states. Thus, the main computational advantages of our newly proposed IVO-HNPT approach over the traditional HNPT method are (i) the absence of iterations beyond those in the initial SCF calculation and (ii) the lack of convergence difficulties due to the intruder states[5] that plague CASSCF calculations with increasing size of the CAS. Consequently, the IVO-CASCI based MR strategy is attractive in terms of the applicability to bigger systems. Thus, for a potential utility for treating large systems with varying degree of quasidegeneracy and real or avoided curve crossings, IVO-HNPT theory would be of enormous utility.

To assess and demonstrate the applicability of the IVO-HNPT method (which is now in the GAMESS package[22]), a few test case calculations have already been presented in our previous papers dedicated to the IVO-HNPT.[16,17] The IVO-HNPT method has already been applied successfully to calculate the state energies and various chemical properties of different chemically interesting systems[16,17] such as *cis* effect in 1,2-dihaloethenes, PEC of isomerization of N_2H_2 and C_2H_4, and so on. A particularly severe test, involving vinyl cation PEC has been reported by Chaudhuri and Freed.[17] Prompted by encouraging results of Chaudhuri *et al.*,[16,17] we have attempted to use the IVO-NHPT method to investigate the systems for which both nondynamical and dynamical correlations have to be considered at a sufficiently high level in a balanced manner. This paper presents the difficulties met by the MRPT method during the computation of PEC of LiF neutral/ionic avoided crossing and the N_2 ground state wave function despite the tremendous methodological developments of MRPT approaches. In this paper, we also provide the calculation of the *cis-trans* reaction path of C_4H_6 through C–C single bond rotation. The systems considered here are sufficiently complex for demonstrating the potentiality and generality of the IVO-HNPT method.

The accuracy of the MRPT theory decreases significantly in the presence of avoided crossing in a PEC. The case of weakly avoided crossings is especially difficult to handle. Around the crossing region, the exact extent of splitting of the two states as well as the barrier height generated due to the weakly avoided crossing becomes very sensitive to the accuracy of the formalism used. Of course, the most stringent tests for the generality of IVO-HNPT formalism (or of any MRPT) would be in situations where the orbitals change very rapidly as a function of minor geometrical distortions, as happens in weakly avoided crossings. We have shown the effectiveness of IVO-HNPT formalism in one such difficult system, namely, LiF. Nakano[8] and Spiegelmann and Malrieu[23] showed that in the case of a second-order MR-perturbation approach, a spurious double crossing is found instead of weakly neutral/ionic avoided crossing in the case of LiF. For this reason, the LiF system has often been used to establish the applicability and generality of new methods developed with the aim to demonstrate the efficacy of the methods to compute the PECs consisting of ionic-covalent curve crossing. We also consider the torsional barrier in the C_4H_6 molecule. This example, although simple, represents a wide class of chemically important problems such as transition states and diradicals. Another important advantage of our study is that we can describe with reasonable accuracy C–C single bond rotation in C_4H_6 without altering the active space throughout the PEC. This advantage is of tremendous importance where chemistry in polyatomic molecules is concerned: very often several reaction channels can be opened for the same molecule, and it is impossible to calculate reliable relevant energetics for them when the active space is different for each channel. To establish the efficacy of a MR-based method, the results generated via triple bond breaking (such as of N_2 molecule) are more instructive than those for single bond as the matter becomes more complex around the dissociative region for triple bond systems. It is worth mentioning that the problem of SR-based method to compute highly accurate PECs manifests itself most emphatically when the computations of the multiple bond breaking and avoided curve crossing phenomena are considered. It is nevertheless interesting to compare the potentiality of the traditional MRMPPT/MCQDPT and IVO-HNPT methods to compute the dynamical and nondynamical correlations in a balanced manner in such systems as studied by us in this paper. We will discuss this issue in Sec. IV.

The organization of the article is as follows. We begin with a brief description of the IVO scheme (Sec. II) followed by the theoretical background of IVO-HNPT method (Sec. III). Numerical results are presented and compared in Sec. IV.

II. GENERATION OF IMPROVED VIRTUAL ORBITALS

Because the basic philosophy of generating the IVOs applies equally for restricted and unrestricted Hartree–Fock (HF) orbitals, the approach is illustrated for a closed shell restricted HF reference function as used in the present calculations.

When the ground state of the system is a closed shell, the HF approximation to the ground state wave function is expressed in terms of HF molecular orbitals (MOs) as $\Phi_0 = \mathcal{A}[\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\cdots\phi_n\bar{\phi}_n]$, where $\mathcal{A}$ is the antisymmetrizer. Let the indices $i,j,k,\ldots$ refer to the HF MOs $\{\phi_i\}$ that are occupied in the ground state and $u,v,w,\ldots$ to the remaining unoccupied HF MOs. All the HF MOs are eigenfunctions of the one-electron HF operator ${}^1F$,

$$ {}^1F_{lm} = \langle\phi_l|H_1 + \sum_{k=1}^{\mathrm{occ}} (2J_k - K_k)|\phi_m\rangle = \delta_{lm}\epsilon_l, \tag{1}$$

where l and m designate any (occupied or unoccupied) HF MO and ϵ_l is the HF orbital energy. The operator H_1 is the one-electron portion of the Hamiltonian, and J_k and K_k are Coulomb and exchange operators, respectively, for the occupied orbital ϕ_k.

An excited state HF computation would provide a new set $\{\chi\}$ of MOs that produce the lowest possible energies for the low lying singly excited $\Psi_{\alpha\to\mu}$ state,

$$\Psi(\alpha\to\mu) = \mathcal{A}[\chi_1\bar{\chi}_1\chi_2\bar{\chi}_2\cdots(\chi_\alpha\bar{\chi}_\mu \pm \chi_\mu\bar{\chi}_\alpha)\cdots\chi_n\bar{\chi}_n], \tag{2}$$

corresponding to the excitation of an electron from the orbital χ_α to χ_μ, where the + and − signs correspond to triplet and singlet states, respectively. The new MOs $\{\chi_\alpha\}$ and $\{\chi_\mu\}$ may be expressed as a linear combination of the ground state MOs $\{\phi_i,\phi_u\}$. If, however, the orbitals are further restricted such that the $\{\chi_\alpha\}$ are linear combinations of only the occupied ground state MOs $\{\phi_\alpha\}$ and the $\{\chi_\mu\}$ are expanded only in terms of the unoccupied $\{\phi_u\}$,

$$\chi_\alpha = \sum_{i=1}^{\mathrm{occ}} a_{\alpha i}\phi_i, \quad \chi_\mu = \sum_{u=1}^{\mathrm{unocc}} c_{\mu u}\phi_u, \tag{3}$$

then the new orbital set $\{\chi_\alpha,\chi_\mu\}$ not only leaves the ground state wave function unchanged but also ensures the orthogonality and applicability of Brillouin's theorem between the HF ground state and the $\Psi_{\alpha\to\mu}$ excited states. In addition, this choice also benefits from using a common set of MOs for the ground and excited states, a choice that simplifies the computation of oscillator strengths, etc. However, we avoid the computationally laborious reoptimization of the occupied orbitals by setting $\{\chi_\alpha\}\equiv\{\phi_\alpha\}$, i.e., by choosing $a_{\alpha j}=\delta_{\alpha j}$, thereby simplifying enormously the procedure for generating the IVOs. Hence, the coupled equations determining the coefficients $a_{\alpha j}$ and $c_{\mu\nu}$ reduce to a single eigenvalue equation of the form $F'C=C\Gamma$, where the one-electron operator F' is given by

$$F'_{vw} = {}^1F_{vw} + A^{\alpha}_{vw}, \tag{4}$$

${}^1F$ is the ground state Fock operator and the additional term A^{α}_{vw} accounts for excitation of an electron out of orbital ϕ_α,

$$A^{\alpha}_{vw} = \langle\chi_v| - J_\alpha + K_\alpha \pm K_\alpha|\chi_w\rangle. \tag{5}$$

The minus sign in Eq. (5) applies when ${}^3\Psi_{\alpha\to\mu}$ is a triplet state, while the plus sign is for the singlet ${}^1\Psi_{\alpha\to\mu}$ state.[24,25] The corresponding transition energy is

$$ {}^{1,3}\Delta E(\alpha\to\mu) = E_0 + \gamma_\mu - {}^1F_{\alpha\alpha}, \tag{6}$$

where E_0 is the HF ground state energy and γ_μ is the eigenvalue of $F'C=C\Gamma$ for the μth orbital.

III. THEORETICAL BACKGROUND FOR IVO-HNPT METHOD

The following is a succinct recapitulation of the essential issues of HNPT method pertaining to our recent development.

The HNPT is based on the RS perturbation theory (RSPT) where CI coefficients as well as MOs are computed first through IVO-CASCI and then RSPT is applied using the IVO-CASCI wave function as reference. As in conventional many-body perturbation theory, the IVO-HNPT method begins with the decomposition of the total Hamiltonian H as

$$H = H_0 + V, \tag{7}$$

where H_0 is the unperturbed Hamiltonian and V is the perturbation. In this method, the zeroth order Hamiltonian is defined as

$$H_0 = |\alpha\rangle E^0_\alpha\langle\alpha| + \sum_k |k\rangle E^0_k\langle k| + \sum_q |q\rangle E^0_q\langle q|, \tag{8}$$

where q is the qth determinantal state, or configuration state function (CSF), outside the CAS and k is the kth multideterminantal state from the CAS that is orthogonal to α.

The zeroth order Hamiltonian H_0 can be defined more conveniently using the following expression:

$$H_0 = \sum_{pq} f_{pq} a^\dagger_p a_q, \tag{9}$$

to obtain the zeroth order energies as a sum of orbital energies ϵ_p. The matrix f_{pq} in Eq. (9) is defined as

$$f_{pq} = h_{pq} + \frac{1}{2}\sum_{rs} D^{\alpha}_{rs}\left[\langle pr||qs\rangle - \frac{1}{2}\langle pr||sq\rangle\right], \tag{10}$$

where h_{pq} and $\langle pr||qs\rangle$ (or $\langle pr||sq\rangle$) represent one- and two-electron integrals and D^{α}_{pq} denotes the average of the one-particle density matrix over all the IVO-CASCI states in the CAS. The one- and two-electron integrals appearing in f_{pq} (and in subsequent HNPT calculations) are computed using the IVOs. (Hunt and Goddard[13] and Bair and Goddard[14] also used a similar approach in their IVO based CI calculations.)

The effective Hamiltonian within the IVO-CAS reference space through first order is the diagonal matrix

$$\langle\alpha|\mathcal{H}^{0-1}|\beta\rangle = E^{\mathrm{IVO\text{-}CASCI}}_\alpha\delta_{\alpha\beta}, \tag{11}$$

where $E^{\mathrm{IVO\text{-}CASCI}}_\alpha$ denotes the CASCI/MCSCF energy.

The second-order energy for the target state is

$$E_{\alpha}^{(2)} = \sum_{q} E_{\alpha q}^{(2)},$$

where

$$E_{\alpha q}^{(2)} = \frac{\langle \alpha | V | q \rangle \langle q | V | \alpha \rangle}{\Delta E_{\alpha q}^{(0)}},$$

with

$$\Delta E_{\alpha q}^{(0)} = E_{\alpha}^{(0)} - E_{q}^{(0)}, \tag{12}$$

α is a IVO-CASCI wave function and is defined as $\langle \alpha | = \Sigma_p c_p \langle p |$, where $\langle p |$ is the pth single-determinantal state from the CAS. In this case, a single wave function that is multiconfigurational is used as reference and hence the name *multiconfiguration basis single state PT*.

In the IVO-HNPT, the reference function is constructed via IVO-CASCI scheme, then the energies of interest are obtained via diagonalization of the effective Hamiltonian. The effective Hamiltonian to the second order is given by

$$(H_{\text{eff}}^{(0-2)})_{\alpha\beta} = \langle \alpha | H | \beta \rangle + \frac{1}{2} \sum_{q} \left\{ \frac{\langle \alpha | V | q \rangle \langle q | V | \beta \rangle}{E_{\beta}^{(0)} - E_{q}^{(0)}} + \frac{\langle \beta | V | q \rangle \langle q | V | \alpha \rangle}{E_{\alpha}^{(0)} - E_{q}^{(0)}} \right\}, \tag{13}$$

where the reference functions α and β are multiconfigurational in nature. The specification of an active space, the choice of active orbitals, and the definition of H_0 determine the potentiality of the perturbation approximation.

We are now in a position to mention the fact that the one particle density matrix is the CASSCF density matrix in the case of CASSCF scheme, but in the case of IVO-CASCI scheme it is not the HF density matrix as the active space includes some HF virtual orbitals. The IVO modification of the HNPT scheme retains all the advantages of the traditional HNPT theory without sacrificing its accuracy. In addition, as we have already mentioned in Sec. I, the IVO-HNPT method does not require tedious and costly CASSCF iterations beyond those in an initial SCF calculation.

IV. NUMERICAL APPLICATION

In this section, we consider the numerical application of IVO-HNPT method to various chemically interesting situations (such as PEC of N_2 and LiF and C_4H_6), where the dynamical and nondynamical electron correlations play a crucial role. A balanced description of both dynamical and nondynamical correlations over the entire range of internuclear distance is a challenging problem for all MRPT methods.

A. The ground state PEC of N_2 molecule

The reliable description of the dissociation profile of the ground state of the N_2 molecule is a very difficult problem for any *ab initio* method due to the presence of strong dynamical and nondynamical correlation effects. This system possesses very significant quasidegeneracy not only at the region of large internuclear separations but also at equilibrium region. Hence this system provides a critical test case for any MR-based methods.[26–28]

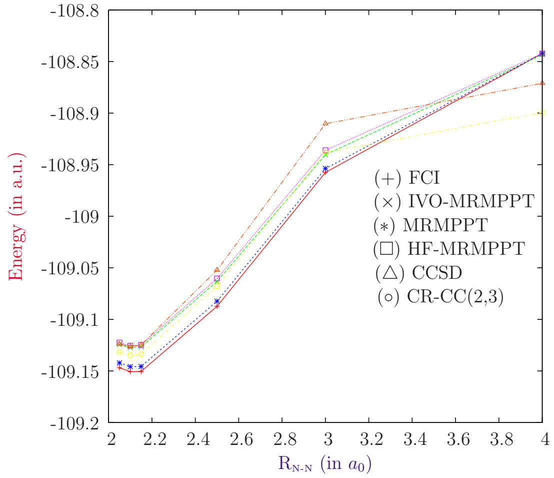

FIG. 1. (Color online) The ground $^1\Sigma_g^+$ state PEC of N_2 obtained using the FCI, CCSD, CR-CC(2,3), IVO-MRMPPT, MRMPPT, and HF-MRMPPT (MRMPPT using the HF orbitals) methods with DZP basis set.

In the present communication, we consider the bond breaking of N_2 molecule using a DZP basis,[28] for which an exact treatment of electron correlation [full CI (FCI)] is available.[28] The active space used in our calculations comprises three bonding MOs (σ, π_x, π_y) and three antibonding MOs $(\sigma^*, \pi_x^*, \pi_y^*)$. This is the minimal set of active orbitals and active electrons $(6e, 6v)$ that is required to study the PEC of triply bonded systems such as N_2.[29]

Figure 1 compares the ground $X\ ^1\Sigma_g^+$ state potential curve of N_2 as computed using the IVO-HNPT (such as IVO-MRMPPT) method as well as MRMPPT method with MCSCF orbital (termed as MRMPPT) and HF orbital (termed as HF-MRMPPT) with the FCI and with SR based coupled cluster singles and doubles (CCSD) and its variants. The errors in all these approximate methods may be examined more critically in Fig. 2 which presents the deviation $[E(\text{FCI}) - E(\text{theory}) \equiv \Delta E]$ of the computed ground state energies from the FCI as a function of internuclear distance.

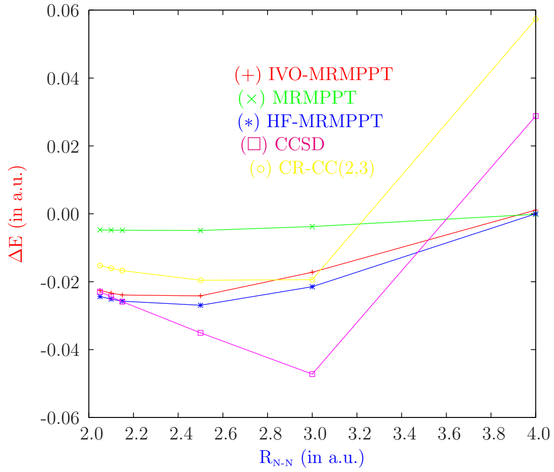

FIG. 2. (Color online) Plot of $E(\text{FCI}) - E(\text{theory})$ $(\equiv \Delta E)$ (in a.u.) for the ground state of N_2 molecule as a function of N–N internuclear distance with DZP basis set.

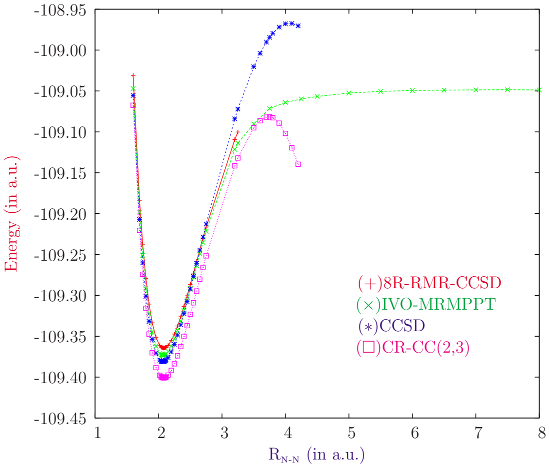

FIG. 3. (Color online) The IVO-MRMPPT, CCSD, CR-CC(2,3), and 8R-RMR-CCSD ground state energies (a.u.) of N_2 as a function of the N–N bond length with cc-pVTZ basis set.

Figure 3 effectively displays the nonparallelity errors (NPEs) of these approximate methods. The parameter NPE is a measure of *global accuracy* of these methods and is defined as the difference between the maximum deviation and the minimum deviation from the FCI estimate over the entire PEC/surface. It is evident from Figs. 3 and 4 that the quality of the IVO-HNPT results is quite encouraging. The errors (ΔE) for IVO-HNPT method are generally small at large bond distances, but become larger at shorter distances. The PEC for IVO-HNPT is very close to the FCI beyond 3.8 a.u., and hence the corresponding error curve (ΔE) (see Fig. 5) is nearly flat. Although the performance of the completely renormalized CC theory[30,31] [CR-CC(2,3)] and IVO-HNPT is very close in proximity at shorter bond distances, the quality of CR-CC(2,3) method goes down with increase in bond length (after 3.4 a.u.). The NPEs for CCSD, CR-CC(2,3), and IVO-MRMPPT are 47.70, 48.29 and 15.85 kcal/mol, respectively. Thus the quality of PEC computed via IVO-HNPT method is better than that of the CCSD and CR-CC(2,3) methods. From the given figures and NPEs we may conclude that the overall performance of the IVO-HNPT method is consistent and promising to compute the total energy of the ground state of such a challenging system as N_2.

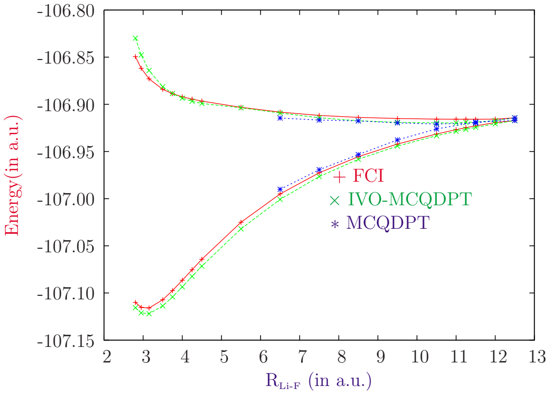

FIG. 4. (Color online) PECs with respect to Li–F bond length generated via IVO-MCQDPT, MCQDPT, and FCI methods for the ground X $^1\Sigma^+$ and first excited singlet B $^1\Sigma^+$ state of LiF molecule.

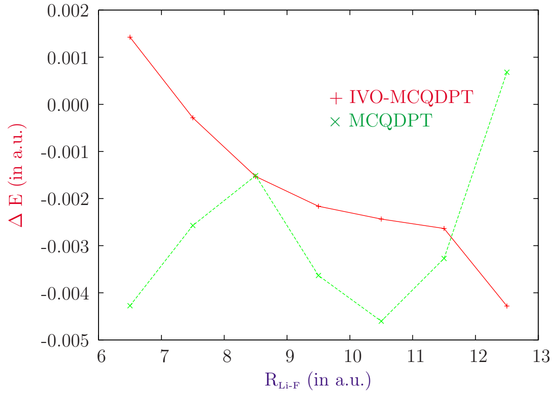

FIG. 5. (Color online) Plot of $E(\mathrm{FCI})-E(\mathrm{theory})$ ($\equiv\Delta E$) (in a.u.) for the ground state of LiF molecule as a function of Li–F internuclear distance.

In passing, we note that the performance of IVO MRMPPT is better than HF orbital based MRMPPT but slightly poorer than the traditional MRMPPT. It is worth mentioning that the traditional MRMPPT is computationally more expensive than the IVO-HNPT.

We also compare our calculations with the MR based CCSD method to assess the performance of the IVO-HNPT against the state-of-the-art MR approach. The cc-pVTZ basis set is used[32] to generate the ground $^1\Sigma_g^+$ state PEC of N_2. The same basis set was also used by Li and Paldus[29] in their 8R-RMR-CCSD calculations for the ground state PEC of N_2. Figure 6 plots the IVO-HNPT, CCSD, CR-CC(2,3), and 8R-RMR-CCSD (Ref. 29) ground state energies of N_2 as a function of N–N internuclear distance. For clarity of comparison between these methods, the IVO-HNPT, CCSD, and CR-CC(2,3) ground state energies are shifted so that they all become equal to 8R-RMR-CCSD at $R(\mathrm{N-N})=1.30$ a.u. Figure 7 clearly exhibits that the CCSD and CR-CC(2,3) methods fail badly upon dissociation. Moreover, the CR-CC(2,3) produces an artificial hump in the PEC around $R(\mathrm{N-N})=3.7a_0$. However, this type of behavior of the CC PECs near the bond breaking region is quite common and appears even in other diatomic systems.[33]

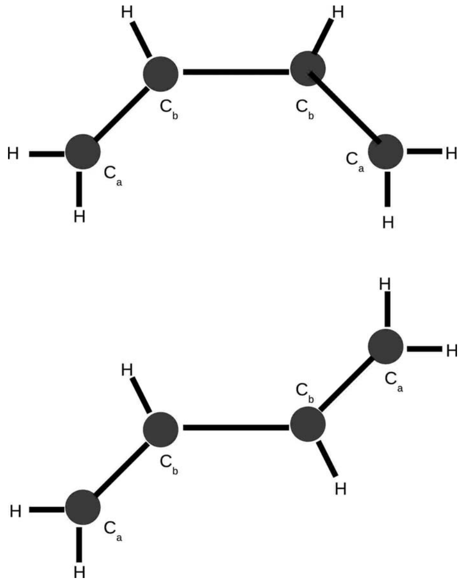

FIG. 6. Geometrical structure of *cis*- and *trans*-butadiene molecules.

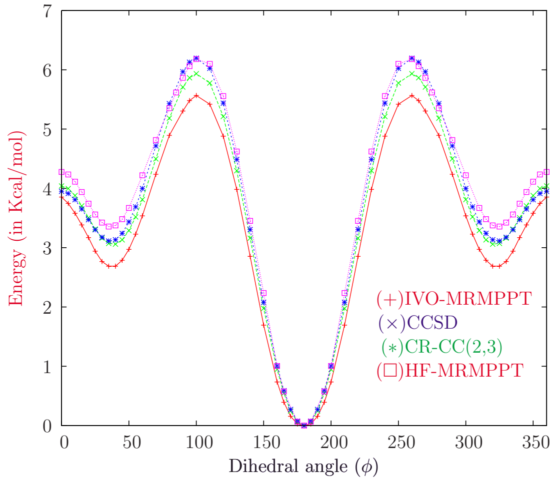

FIG. 7. (Color online) PECs (kcal/mol) with respect to the $C_a-C_b-C_b-C_a$ torsional angle generated via IVO-MCQDPT, CCSD, and CR-CC(2,3) methods for the ground state of butadiene molecule.

It is pertinent to remark that the CCSD calculations (and hence CR-CC) do not converge at all beyond R(N–N) $>4.5a_0$. Thus, the SR based CC methods fail in the ultimate challenging case of N_2. The difficulties faced by the SR based CCSD and MBPT methods to generate the total PEC of N_2 molecule were first pointed out by Laidig *et al.*[27] Our study clearly shows that in order to compute energy of a state with pronounced degeneracy or quasidegeneracy (usually present with stretching and/or breaking of chemical bonds), one has to use a MR-type formalism. Figure 3 makes clear that the IVO-MRMPPT scheme yields a smooth curve even at highly stretched geometry and the maximum deviation from the full-blown 8R-RMR-CCSD energy[29] is 16 mH. In passing, we want to say that the 8R-RMR-CCSD is computationally more expensive than the IVO-MRMPPT method.

B. Ionic-covalent avoided curve crossing between singlet PECs in LiF

In our next application, for a different type of dissociation phenomena, we have calculated the total energies of the two lowest singlet states ($^1\Sigma^+$) of LiF molecule[34–36] as a function internuclear distance via IVO-HNPT method, which, in fact, provides a smooth and continuous curve even close to the avoided crossing. The accurate calculation of the ionic/covalent curve crossing of this molecule has been the subject of various studies. It has been observed that the relaxation of the orbitals in ionic/covalent structure plays a crucial role in the accurate calculation of the curve crossing zone. The avoided crossing is also found in other alkali halides, but the LiF molecule is particularly interesting due to its small size and availability of the FCI results.[34] The ionic-neutral curve crossing phenomena involving the two lowest $^1\Sigma^+$ states of LiF have been extensively studied to model various chemi-ionization processes ($M+X\rightarrow M^++X^-$). Needless to say, the interest in the ionic-neutral curve crossing in LiF goes well beyond the methodological point of view. The real-time dynamics experiments have been reported for NaI, NaBr, and LiI.[37] In fact, these experiments can be used to locate the crossing point and the coupling of electronic states. In passing, it is worth mentioning that it is difficult to obtain a good approximation to FCI energy values at the point of the avoided crossing of LiF molecule using general quantum chemical methods.

The computational study of the avoided curve crossing problem of LiF is a critical test case for MR-based methods as it involves a narrow avoided crossing between two lowest $^1\Sigma^+$ states which have a very different orbital character. In the equilibrium region, the ionic state $[(Li^+F^-)]$ is lower in energy, whereas the neutral $[(Li\cdots F)]$ state is lower at the dissociation region. In avoided crossing zone, the relative contribution of the two-state functions tends to change very rapidly and strongly with slight variations in nuclear distances. Thus, internally contracted MR-based methods may not be suitable to study such curve crossing phenomena. The principal problem with this approach is the lack of relaxation of the zero-order function. The effect of correlations is strong for the ionic form than that for the neutral one. An unbalanced treatment of the correlation effects changes the relative energy of these two states with respect to each other, and thus the crossing zone changes from its appropriate position. Thus, this system has often been used to assess and calibrate the performance and reliability of multiroot MRPT methods. The single-root MRPT methods are known to fail in this situation, and hence, the multistate version of IVO-HNPT (IVO-MCQDPT) method is employed instead of IVO-MRMPPT method (the single-root formalism) to describe the PECs of LiF system. In this paper, our aim is to assess the stability of the IVO-HNPT method in the avoided crossing region as well as to show the accuracy of the results provided by the IVO-HNPT method with respect to the FCI energy.

Bauschlicher and Langhoff[34] studied this system at the FCI level to delineate the performance of the truncated CASSCF/MRCI method. In this paper, the ground and the first excited $^1\Sigma^+$ state energies of LiF are calculated using the IVO-MCQDPT method with the same basis set and active space.[8] Results are displayed in Fig. 4. For comparative purposes, the IVO-HNPT and MCQDPT (reported in Ref. 8) state energies are shifted so that they are all equal to the FCI energy at $R=12.5$ a.u. As can be seen from Fig. 4, the IVO-MCQDPT calculation yields smooth PECs for both the adiabatic states. The figure makes clear that the IVO-HNPT method provides very close results to the FCI results. The errors (ΔE) of the IVO-HNPT and MCQDPT are plotted in Fig. 4. The overall error for IVO-HNPT is smaller than that of the parent MCQDPT method. It is worth noting that the NPEs of IVO-HNPT for the ionic and neutral states are 3.6 and 2.0 kcal/mol, respectively. It is thus evident that the IVO-HNPT results of the two lowest $^1\Sigma^+$ (adiabatic) states are overall consistent, and the method is capable of providing results which are reasonably close to FCI.

C. Study of internal rotations of butadiene

In our last example, we consider the computation of the torsional potential of butadiene due to the rotation about the C–C bond in order to demonstrate the efficiency of the IVO-HNPT method. Butadiene, the simplest conjugated hydrocarbon molecule, exists as a mixture of *cis* and *trans* conformers

TABLE I. The ground state spectroscopic constants for N_2 and LiF using cc-pVTZ basis. Bond lengths and frequencies are given in Å and cm^{-1}, respectively.

	Parameters	CASSCF	IVO-CASCI[a]	CCSD	RMR-CCSD	Expt.
N_2	R_e	1.104	1.097	1.098	1.101	1.0977[a]
	ω_e	2352	2336	2426	2365	2359[a]
LiF	R_e	1.578	1.555	1.580		1.564[b]
	ω_e	904	944	900		910[b]

[a] Reference 42.

[b] Reference 43.

(see Fig. 7). At room temperature, 96% of butadiene exists as *trans* conformer which is energetically more stable (less strained) than the *cis* structure. The first *ab initio* calculation of butadiene was performed by Skaarup *et al.*,[38] and since then, many theoretical investigations have been carried out on butadiene and its derivatives. Recent theoretical investigations predict the *gauche* conformer (twisted by ~40° around the central carbon bond) to be energetically more (less) stable than the *cis*(*trans*) structure.

The ground state geometrical parameters and the energy of butadiene are calculated using the 6-311G** and cc-pVDZ basis sets,[32] respectively. The basis set used for the geometry optimization in these calculations is same as that used by Gong and Xiao[39] in their MP2 level calculations for this system. The IVO-CASCI and CASSCF geometry optimizations are carried out with $(8e,12v)$ CAS, whereas a $(4e,4v)$ CAS is used for generating the ground state torsional PEC via IVO-HNPT procedure. Figure 7 compares the torsional PECs of butadiene obtained at IVO-MRMPPT, HF-MRMPPT, CCSD, and CR-CC(2,3) levels of theories. It is pertinent to note that the MCSCF-based MRMPPT calculations suffer from convergence difficulties near the *cis-trans* geometry. Moreover, the PEC generated from MCSCF-based MRMPPT is not smooth over the entire torsional PEC. Our calculations show that the MRMPPT method with HF orbitals yields smooth PEC but overestimates the barrier height. Inspection of the results depicted in Fig. 6 leads to the following conclusions: (a) there is a substantial energy difference (~4 kcal/mol) between the *cis* and the *trans* conformers, (b) the conformer (*gauche*) having a dihedral angle of approximately 40° is ~2.7 kcal/mol above the *most* stable *trans*-isomer, (c) the shape of internal rotational PEC of butadiene generated via IVO-HNPT method is almost identical to those obtained from CCSD and CR-CC(2,3) methods. The present calculation further shows that the rotational barrier height (5.6 kcal/mol) between the *trans*- and *gauche*-conformers predicted from IVO-HNPT is in good agreement with experiment (5.7 kcal/mol).[40]

D. Spectroscopic constants

The ground state spectroscopic constants of N_2, LiF, and C_4H_6 determined from the gradient based IVO-CASCI method[41] are compared with experiment and with other cor-

TABLE II. Comparison of selective ground state geometrical parameters of butadiene obtained from CASSCF, MP2, IVO-CASCI, and CCSD methods with 6-311G** basis. Bond lengths (R), bond angles (∠), and relative energies (E_{rel}) are given in Å, degrees, and kcal/mol, respectively. Entrees within parentheses are energy differences calculated via IVO-MRMPPT procedure.

Parameters	CASSCF	MP2	IVO-CASCI	CCSD	Expt.
		trans			
$R(C_b{-}C_b)$	1.463	1.460	1.464	1.469	1.476
$R(C_a{=}C_b)$	1.356	1.345	1.344	1.344	1.337
$\angle C_a{-}C_b{-}C_b$	124.0	123.6	124.3	123.7	122.9
$\angle C_a{-}C_b{-}C_b{-}C_a$	180.0	180.0	180.0	180.0	180.0
E_{rel}	0.0	0.0	0.0	0.0	0.0
		cis			
$R(C_b{-}C_b)$	1.476	1.474	1.479	1.483	1.472
$R(C_a{=}C_b)$	1.356	1.345	1.342	1.343	1.349
$\angle C_a{-}C_b{-}C_b$	126.9	126.3	126.6	126.4	124.4
$\angle C_a{-}C_b{-}C_b{-}C_a$	0.0	0.0	0.0	0.0	0.0
E_{rel}	3.56	3.67	2.82(3.81)	3.49	3.45
		gauche			
$R(C_b{-}C_b)$	1.476	1.472	1.474	1.481	
$R(C_a{=}C_b)$	1.357	1.344	1.341	1.342	
$\angle C_a{-}C_b{-}C_b$	125.3	123.8	125.2	124.2	
$\angle C_a{-}C_b{-}C_b{-}C_a$	35.2	39.9	34.5	39.7	
E_{rel}		4.57	2.74(2.80)	2.57	2.86

related calculations in Tables I and II. The basis sets used in these calculations are same as those used for the state energy calculations (see Secs. IV A–IV C). The IVO-CASCI predicted geometries agree well with experiment and with other theoretical calculations. The average discrepancy in our estimated equilibrium bond length is 0.006 Å, while the corresponding CASSCF and CCSD deviations are 0.01 and 0.007 Å, respectively. The maximum deviations in the bond lengths and bond angles obtained using IVO-CASCI method are 0.012 Å and 2°, respectively (see Table II). The IVO-CASCI estimated vibrational frequencies (computed only for N_2 and LiF) are also in good agreement with experiment.[42,43] The maximum error in our estimated harmonic vibrational frequency (ω_e) is only 34 cm^{-1} for LiF molecule.

V. CONCLUDING REMARKS

In this work, we have presented the numerical applications of the IVO-HNPT method which is computationally cost effective and designed to capture the essential strength of the parent MRMPPT/MCQDPT method without significantly sacrificing its accuracy. The present communication demonstrates that the IVO-HNPT method is capable of providing reliable PECs of N_2, LiF, and C_4H_6 systems over a wide range of geometries (in the presence of near degeneracy) for which a proper and balanced treatment of both dynamical and nondynamical correlations over the entire internuclear separations is very essential. Summarizing our feeling from the results using the IVO-CASCI based HNPT (IVO-HNPT) approach, we may say that the IVO-HNPT method can be viewed as a reliable and computationally inexpensive method to compute continuous PECs of N_2 as well as C_4H_6 and smooth LIF ionic/covalent curve crossing. We have also performed calculations for spectroscopic properties using numerical gradient technique. The spectroscopic constants presented here show that the numerical gradient based IVO-CASCI works very well despite our use of the conceptually minimal choice of the reference space.

The IVO-HNPT has more room for further development and wide chemical applications. More extensive applications of the method are underway and be reported in our forthcoming publications.

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