

Balancing Static and Dynamic Correlation in Diradicals: A Low-Cost Multireference Perturbative Strategy

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Abstract

Radical systems remain difficult for electronic structure theory arising from their dominant multiconfigurational nature and the presence of near-degenerate electronic states. In such situations, a single reference description is generally insufficient, and even higher single-reference correlation methods can fail to provide a consistent ordering of low-lying states, especially when the single-triplet gap is small. These difficulties generally arise from an inadequate zeroth-order treatment of static correlation. Multireference perturbation theory offers an alternative that is more balanced by incorporating static correlation within a multiconfigurational framework, while dynamic correlation is recovered perturbatively. In a state-specific form, each electronic state is corrected independently, which tends to be more stable in situations where states are near-degenerate. This theory also mitigates some of the compromises that arise in the treatment of state-averaged approaches, although it comes at the cost of treating each state separately. The integration of improved virtual orbitals (IVO) into a specific framework gives additional advantages. By organizing the virtual space according to the desired electric character, the IVO strategy enhances stability and physical consistency in perturbative expansions without any enlargement of the active space. The IVO-enabled SSMRPT (state-specific multireference perturbation theory) method achieves an effective balance between precision and computational expense, making it suitable for the *ab initio* treatment of radiocolloid and open systems prototypes.

Keywords: *Diradicals; Improved Virtual Orbitals; Multireference Perturbation Theories; Open Shell Systems*

Introduction

Diradical and Radicaloids species hold a distinctive position in chemical theory because they contain two weakly interacting electrons that lie in nearly degenerate MOs (Williams *et al.*, 2013). These electronic states are either closely or openly spaced, having different spin multiplicities and imparting different levels of chemical reactivity, producing chemical systems that are prominent in different mechanistic pathways in organic, inorganic, and biological chemistry. Starting from pericyclic reactions and bond rearrangement to photochemical reactions, diradical character is the basis of striking chemical phenomena. Many diradicals having low lifetimes restrict them to being detected directly in experimental arrest, thereby elevating the role of theoretical methods in clarifying their structural and electronic properties. The main theoretical difficulty arises from the multiconfigurational electronic character of these systems (Borden *et al.*, 1982; Ramos-Cordoba *et al.*, 2014). When the FMO (Frontier Molecular Orbitals) become nearly degenerate, the wave function of molecular systems cannot be well captured by a sole Slater-type determinant. In such a context, static (nondynamical) correlations showing the interplay among near-degenerate electrons—becomes dominant. On the same note, dynamical correlation, related to instantaneous electron-electron interactions, persists as essential for total correlation (Liu *et al.*, 2026; Zhao *et al.*, 2026). Single reference strategies, with even high-level correlation treatments, often struggle in the presence of quasi-degenerate cases. This shortcoming typically leads to the incorrect prediction of singlet-triplet energy gaps throughout the reaction coordinates.

These clearly indicate the necessity of applying a multireference (MR) scheme for systems demonstrating profound diradical character. Over the last few decades, a range of MR approaches has been introduced to incorporate dynamical correlation in different levels of theories on addition of a multiconfigurational space. Multireference configuration interaction (MRCI) (Szalay *et al.*, 2012), multireference perturbation theory (MRPT), and multireference coupled cluster (MRCC) methods represent few distinct strategies for achieving the said objective. While MRCC formulations (Čársky *et al.*, 2010) are competent for highly accurate descriptions of electronic states, their computational cost and complexity often restrict the wide usage. Truncated MRCI methods are widely employed, but it is not strictly size-extensive. So, on demand, MRPT approaches have emerged as very attractive and favorable computational methods (Otani *et al.*, 2025; Hubač *et al.*, 2010). But the formulation of wholly reliable MRPT schemes is not a trivial task (Chattopadhyay *et al.*, 2016). Early effective Hamiltonian formulations based on quasi-degenerate perturbation theory are prone to numerical breakdowns forming due to small denominators—termed as intruder-state problems (Sinha Ray, 2020). Several strategies have been proposed, comprising level-shift techniques and intermediate Hamiltonian strategies to isolate physically meaningful roots by limiting fake couplings. The state-specific methods provide a state-by-state basis result and become an important alternative boon. Other second-order MRPT methodologies like PASPT2 (Partitioned Active Space Second-Order Perturbation Theory) (Liu *et al.*, 2026), CASPT2 (Complete Active Space Second-Order Perturbation Theory) (Roos *et al.*, 1996), NEVPT2 (N-Electron Valence State Second-Order Perturbation Theory) and MRMP2 (Multi-Reference Møller–Plesset Second-Order Perturbation Theory) have shown their efficacy. These approaches have limitations due to intruder problems and empirical parameter dependence. Multistate (MS) versions increase vivid efficiency in describing the systems, but they are related to effective Hamiltonian formulation. Other complexities may arise. The CAS-based SSMRPT (*aka* Mk-MRPT) (Mahapatra *et al.*, 1999) provides a unique alternative. SSMRPT reduces chance to intruder problems without any dependence on arbitrary level shifts. The method can be designed with different partitioning schemes using Brillouin-Wigner (BW) or Rayleigh-Schrödinger (RS) expansions. Traditional SSMRPT calculations rely on CASSCF i.e. complete active space self-consistent field method. The said method presents a multiconfigurational base with nonlinear optimization of orbitals. It often leads to failures at convergence criteria. Also, multiple unphysical solutions may arise. To ameliorate these concerns, various alternative strategies have been proposed. One such approach involves the use of IVO with complete active space configuration interaction (CASCI). By improving virtual orbitals and also eliminating iterative orbital optimization beyond SCF, the IVO-CASCI framework increases numerical balance and reduces computational cost. The integration of IVO-CASCI reference orbitals with the SSMRPT formalism gives birth to IVO-SSMRPT (Sinha Ray, 2020) methodology. This method attains a favorable balance between accuracy and computational need, making it well suited for the systematic investigation of diradical and other higher-order radicaloid systems.

In the following section, the efficacy of the developed IVO-SSMRPT approach is compared and analyzed in the context of model quasi-degenerate molecular systems, including singlet *m*-benzyne and singlet 2,6-pyridyne (Sinha Ray *et al.*, 2016). These species offer strict benchmarks for assessing the robustness and predictive reliability of the method in capturing the characteristics of diradical chemistry.

Results and Discussion

Electronic Structure and Geometry of *m*-Benzyne:

m-Benzyne (1,3-didehydrobenzene) is one of the most important test scenarios for high-level electronic structure methods. The main issue lies in the essence of its single lowest energy state—whether it is attributed to a monocyclic or a bicyclic closed-shell configuration. The answer to this question depends on a comprehensive analysis of dynamic and non-dynamic electronic correlation. Multiconfigurational self-consistent field (MCSCF) optimizations have indicated that the monocyclic structure is more stable than the bicyclic alternative by the order of 12 to 13 kcal/mol. In contrast, Restricted Hartree-Fock (RHF) calculations

mistakenly favor the bicyclic form by nearly 18 kcal/mol due to the failure of single-reference mean-field approaches (Sinha Ray *et al.*, 2016). High-level correlated treatments provide a more consistent picture. The Monte Carlo approach based on CAS (8,8) references declare the single-ring structure as the lower in energy by about 2 kcal/mol. In a similar manner, coupled-cluster calculations including connected triple excitations like CCSD(T) and CCSDT methods recover the monocyclic structure to be the ground state, whereas lower-level CCSD calculations often predict the bicyclic geometry. This clearly indicates the importance of higher-order correlation inclusion.

Geometry optimizations were executed using the IVO-SSMRPT approach with a compact CAS (2,2) reference. For comparison, CASSCF based on (8,8) space and IVO-CASCI based on (8,8) space calculations were also examined prior to the perturbative approach. It was revealed that this broadening of the active space from (2,2) to (8,8) space did not yield considerable improvements in the structural parameters, indicating that the biradical electronic character is successfully captured within the smaller active space when combined with an appropriate level of dynamical correlation.

At the IVO-SSMRPT/cc-pVTZ level (Sinha Ray *et al.*, 2016) of theory, the optimized monocyclic structure indicates a C1-C3 separation of around 1.89 Å and a C1-C2-C3 bond angle of 90°. SSMRPT calculations, including conventional CAS SCF(2,2) level, predict a similar structural parameter, with a C1 to C3 bond distance close to 1.88 Å and that angle of roughly 87°. These values correspond well compared with Mk-MRPT2 and relaxed Mk-MRPT2 results, which yield the C1 and C3 atomic distances in the range of 1.87 to 2.00 Å according to the treatment of relaxation level. More intensive multireference coupled-cluster calculations (e.g., Mk-MRCCSD/pCVTZ) also tend to the monocyclic structure. Reported C1-C3 separations from CCSD(T) calculations with triple-zeta basis sets generally fall in the range of 2.02 to 2.10 Å, while CASPT2 calculations with high level CAS(12,12) reference space predict values around 2.07 Å and bond angles around 98-99°. Despite the fact that IVO-SSMRPT level predicted C1-C3 bond separation is slightly of smaller extent than some of the larger-active-space CASPT2 alternatives, the overall structural parameters are in close agreement. The small deviations are all within the expected range due to the differences in basis set and active space prototypes.

The comparative data of geometric parameters clearly indicates that the IVO-SSMRPT reproduces the features obtained from the methods which are considerably more costly. It achieves this performance with a compact active space and a state-specific perturbative level. This analysis clearly confirms that the IVO-SSMRPT provides a trustworthy and computationally cost-effective description of the diradicals plagued by static and dynamic correlation effects.

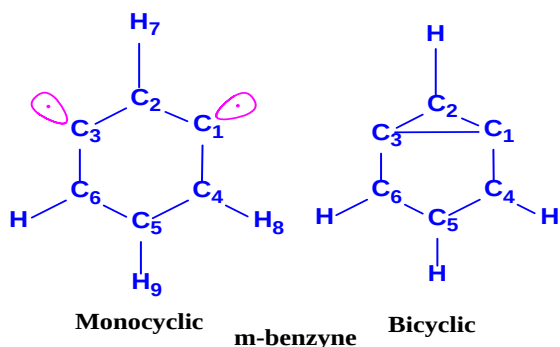


Figure 1: Geometrical Arrangement of m-benzyne (Sinha Ray *et al.*, 2016)

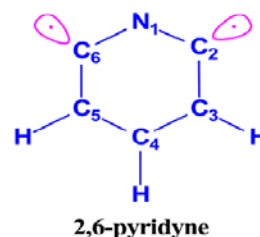


Figure 2: Geometrical Arrangement of 2,6-pyridyne (Sinha Ray *et al.*, 2016)

Electronic Structure and Geometry of 2,6-Pyridyne:

The isomer of di-dehydropyridine molecule i.e. 2,6-pyridyne presents a challenge for high-level electronic structure approaches because of its strong biradical nature and the susceptibility of its ground-state nature to electronic correlation effects. Heterocyclic substitution of a nitrogen atom into the *m*-benzyne framework modifies both the electronic distribution and the geometric parameters of the system, thus influencing the balance between monocyclic and bicyclic structures. Here, the structural assignment may be analyzed either through the C2-C6 internuclear distance or the C2-N1-C6 bond angle.

The energy ordering of the two forms is highly method dependent. At the CCSD level, bicyclic nature is predicted to be energetically lower by approximately 2 kcal/mol. Multireference coupled-cluster treatments, such as Mk-MRCCSD, reverse this energy ordering and stabilize the single-ring form by approximately 4 kcal per mole. Inclusion of triple excitations at the CCSD(T) or CCSDT level further increases the stability of the monocyclic configuration by about 4-6 kcal/mol lower than its bicyclic alternative. These observations clearly indicate that the double excitations alone are insufficient to describe the electronic structure and thus higher-order correlation inclusion is needed. Similarly, Mk-MRCCSD(T) calculations also favor the monocyclic geometry by around 5 kcal/mol. By contrast, Hartree-Fock and other common density functional treatments (e.g., BPW91/cc-pVDZ) lead to a bicyclic minimum level, thereby indicating their inability to capture both types of electronic correlation effects.

Geometry optimization performed at SSMRPT or IVO-SSMRPT/cc-pCVTZ methodology consistently gives a monocyclic ground state. The calculated C2-C6 distances are 2.0434 Å and 2.0421 Å for SSMRPT and IVO-SSMRPT, respectively. These values closely align with those found from the “gold standard” CCSD(T) method and also the Mk-MRCCSD calculations by approximately 2.01 to 2.02 Å. Whereas CCSD predicts a shorter C2 & C6 separation of 1.9140 Å, showing its preference for the bicyclic arrangement.

Table 1: Structural Values of the Lowest-Energy State of m-Benzyne.

Geometrical Parameters	CCSD(T)/ cc-pVTZ	CASPT2/ ANO-L	Mk-MRCCSD/ cc-pCVTZ	SS-MRPT/ cc-pVTZ	IVO-SSMRPT/ cc-pVTZ
R C1-C2	1.3717	1.367	1.3586 (1.3594)	1.3611	1.3429
R C1-C4	1.3785	1.368	1.3697 (1.3696)	1.3681	1.3690
R C4-C5	1.4031	1.397	1.3945 (1.3954)	1.4082	1.4007
R C1-C3	2.0581	2.074	2.5506 (2.5459)	1.8823	1.8932
R C2-H7	1.0775		1.0745 (1.0748)	1.0768	1.0745
R C4-H8	1.0821		1.0789 (1.0788)	1.0817	1.0801
R C5-H9	1.0862		1.0825 (1.0827)	1.0831	1.0811
∠ C1-C2-C3	97.2	98.7	94.65 (95.60)	87.00	89.60
∠ C2-C3-C6	137.49	136.3	139.66 (138.91)	145.70	144.64
∠ C3-C6-C5	117.00	117.4	116.32 (116.49)	117.07	117.10
∠ C6-C5-C4	113.8	113.9	113.39 (113.61)	113.40	112.82

Source: Sinha Ray et al., 2016

Note: Bond Separations Are in Å and Angles are in Degree (°). Values in Bracket are of Mk-MRCCSD-TCSCF Method

CCSD also yields a relatively shorter angle of 86.15°, whereas SSMRPT and IVO-SSMRPT predict values near 99.8°. These predictions are in well agreement with CCSD(T) (~96.8°) and Mk-MRCCSD (~98°) results. Larger active space-based CASSCF calculations report an even wider angle of ~106°, stating the biradical character of the monocyclic form. In contrast, the BPW91/cc-pVDZ level produces a C2-C6 distance of 1.561 Å and an angle of 69°, indicative of a fully bicyclic structure minimum. Notably, spin-flip EOM-CCSD calculations also provide C2-C6 separations on the order of 2.08 Å, with the same structural finding by the IVO-SSMRPT treatment.

It can be stated safely that the close agreement between SSMRPT/IVO-SSMRPT and high-level triples-inclusive CC or MRCC methods demonstrates that the intrinsic static-dynamic correlation in 2,6-pyridyne is essentially captured within the current framework. At the same time, the IVO-SSMRPT approach avoids

the wrong stabilization of the bicyclic character as suggested in lower-order single-reference wave function-based and DFT treatments. These results clearly predict that an SSMRPT strategy, when combined with an IVO reference space, creates a robust method, namely, IVO-SSMRPT. It can provide a very reliable description of heterocyclic biradical systems at significantly reduced computational cost.

Table 2: Structural Variables of the Global Minimum of 2,6-pyridyne. Bond Distances are in Å and Angles are in Degree (°)

Geometrical Parameters	CCSD(T)	Mk-MRCCSD	B3LYP	CASSCF-SSMRPT	IVO-SSMRPT
N1–C2	1.3470	1.3361	1.337	1.3355	1.3349
C2–C3	1.3801	1.3735	1.380	1.3783	1.3772
C3–C4	1.3964	1.3908	1.411	1.3929	1.4010
C2–C6	2.0146	2.0169		2.0434	2.0421
C3–H	1.0800	1.0777		1.0772	1.0767
C4–H	1.0855	1.0825		1.0808	1.0810
∠C2–N1–C6	96.80	98.01	69	99.82	99.80
∠N1–C2–C3	138.12	137.45		136.99	136.83
∠C2–C3–C4	117.01	116.80		116.07	116.00
∠C3–C4–C5	112.93	113.49	111	113.30	113.22
∠C2–C3–H	119.51	119.78		119.34	119.30

Source: Sinha Ray et al., 2016

By depicting the refined balance between electron pairing during bond formation and biradical delocalization with low computational resources, the IVO-SSMRPT technique offers a realistic alternative to both the CAS-based PT methods and highly iterative MRCC approaches for these representative quasi-degenerate systems.

Conclusion

The present study reflects that an accurate yet computationally efficient multireference framework can be constructed by coupling state-specific perturbation theory with IVO-CASCI reference. Incorporation of a multipartition Møller-Plesset level of Hamiltonian (zeroth level) within the Jeziorski-Monkhorst (JM) ansatz yields the IVO-SSMRPT formulation, which achieves a balanced and theoretically coherent approach of quasi-degenerate electronic systems. It is observed that the IVO-SSMRPT can consider the intricate interplay between static and dynamic correlations of systems with radical characters. The numerical results clearly prove that the IVO-SSMRPT provides geometrical and energy data comparable to those obtained from highly demanding MRCC treatments.

The intrinsic extensive size nature, computational affordability and improved reference space bring the newly developed IVO-SSMRPT method a vital role among other *state of the art* methods related to many-body systems. It highlights its potential for wide usage in chemically and biologically relevant pathways involving radicals of arbitrary levels of electronic correlation effects.

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