

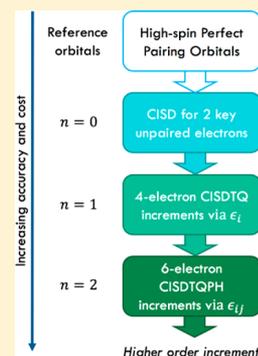
Singlet–Triplet Gaps through Incremental Full Configuration Interaction

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S Supporting Information

ABSTRACT: The method of increments is herein applied to produce accurate singlet–triplet gaps in a variety of challenging polyatomic systems involving main group elements. This strategy computes incremental Full Configuration Interaction (iFCI) energies for the two spin states in a size-extensive n -body expansion. iFCI avoids exponential costs when n is small and thus is dependent on choice of reference function to maintain good accuracy at polynomial cost. The new algorithm presented in this article therefore employs a high-spin perfect pairing reference to capture the major qualities of the singlet and triplet wave functions at $n = 0$. Systematic studies will show that singlet–triplet gap predictions approach 1 kcal/mol accuracy at small n ($n \leq 3$) compared with available experimental and high-level theoretical values.



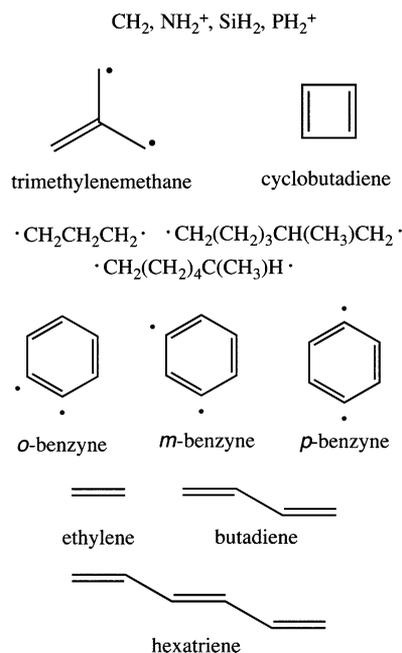
INTRODUCTION

Diradicals have distinct chemical characteristics compared with common closed-shell electronic states.^{1–3} While many electronic structure methods treat the latter effectively, diradicals (and more broadly, diradicaloids) pose greater difficulties for simulation.^{4,5} To correctly simulate these states, nontrivial treatments of static and dynamic correlation are needed to reach quantitative accuracy. These challenges are manifest in the computation of singlet–triplet energy gaps, where singlets and triplets of widely varying character must be correctly described for consistently accurate results.

Numerous methods are capable of computing singlet–triplet gaps when the singlet is closed shell and the triplet can be represented by a single determinant with two unpaired alpha (or beta) electrons (Scheme 1, bottom). In contrast, singlet diradicals occur when high-lying valence orbitals are close to degenerate, and these cannot be treated with a single-electron configuration (Scheme 1, top). It is these cases that make popular single-reference mean-field methods qualitatively fail and apply the most stress to wave function theories. In the general case, multireference techniques are often assumed necessary to treat these strongly correlated wave functions. Accurate total energies, however, are not totally necessary for obtaining quality singlet–triplet gaps because the difference in energies is most important. Relative energies can thus be computed at relatively lower cost by specifically targeting the gap between states.^{6,7}

The spin-flip class of methods is designed to reduce costs by computing accurate gaps between electronic states rather than accurate total energies.^{8–10} Instead of computing the singlet and triplet states independently and to high accuracy, spin flip starts from a high-spin reference (e.g., a triplet, restricted open-shell Hartree–Fock (ROHF) determinant) and flips spins to

Scheme 1. Representative Challenging Cases for Singlet–Triplet Gap Computations



the $m_s = 0$ manifold where the singlet and triplet coexist. This strategy leads to a relatively balanced description of high- and low-spin states and therefore captures gaps between states to good accuracy. Variations on the spin-flip approach have harnessed time-dependent density functional theory,^{11–17}

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coupled-cluster,^{18–22} algebraic diagrammatic construction,^{23,24} and restricted active-space^{25–27} ansatzes to compute such gaps. While spin flip is a largely successful theory, it cannot reach quantitative accuracy in all cases, leaving room for new methods to simulate open-shell species with increased reliability.

To reach higher accuracy, multireference approaches are the standard tools. For example, methods such as CASSCF^{28–31} and its dynamically correlated variants^{32–40} are commonly used, despite the fact that they suffer from strong dependencies on active-space choice. Full valence active spaces are needed to avoid arbitrary active-space selections, but these are computationally intractable for most chemical systems due to their associated exponential cost. Alternatives such as projected Hartree–Fock^{41,42} and random-phase approximations^{43–45} have therefore been recently investigated, yielding interesting lower cost methods with reasonable accuracy. Considering these factors, no one electronic structure theory has demonstrated polynomial cost, relative freedom from active-space choice, and high-accuracy treatment of correlations in diradicals. Indeed, diradicals and diradicaloids greatly stress quantum-chemical methods in general.^{46–51}

Near-exact solutions to the electronic Schrödinger equation offer alternatives that are free from active-space choices but limited primarily by computational cost. These strategies estimate the full configuration interaction^{52–58} (FCI) energy by correlating all electrons on equal terms. Recently the author introduced an incremental solution to FCI, denoted iFCI,^{59,60} which can begin from Hartree–Fock (HF) or Perfect Pairing (PP)^{61–64} reference wave functions. By recovering correlation energy in small, incremental units, close approximations to the FCI energy are found at much lower cost compared with conventional FCI solvers. The iFCI computational cost scales as a polynomial with system size,⁵⁹ giving it an advantage over powerful prefactor-reduction strategies such as quantum Monte Carlo FCI,^{65–69} density matrix renormalization group,^{70,71} and select-CI^{72–76} approaches, all of which have exponential scaling. iFCI's polynomial cost is achieved by treating correlations between localized orbitals, thus avoiding many-body effects among numerous spatially overlapping delocalized orbitals. When the localized orbitals are formed via PP, substantial amounts of correlation can also be captured at zero-order, leading to fast, systematic convergence. Motivated by these promising results,^{59,60} this article studies the applicability of PP-iFCI for computing singlet–triplet gaps.

To obtain such gaps, the lowest energy state of each spin multiplicity is required, preferably from a single simulation. A potential problem, however, is that the incremental expansion uses localized orbitals as the basic unit of correlation, and no one localized orbital pair will necessarily represent the triplet for many chemical systems. To remedy this issue, concepts from spin flip will be invoked to produce a starting point for iFCI. Specifically, orbitals from high-spin PP will form the first approximation to the wave function. This choice bypasses an active-space selection, making it more black-box than most multireference methods. Using this overall strategy, benchmarks will show that iFCI yields quantitative results (1 kcal/mol accuracy) for the variety of polyatomic molecules shown in Scheme 1.

THEORY

Incremental Full Configuration Interaction. The iFCI method using a PP reference function has been shown to reach high-accuracy singlet ground-state energies.⁶⁰ The basic idea

will be summarized here to lay foundations for the proposed method for computing singlet–triplet gaps. The reader is referred to prior publications for detailed descriptions of iFCI.^{59,60}

iFCI uses the many-body expansion^{77–84} to recover correlation energy in a collection of small units, the sum of which asymptotically approaches FCI. Specifically, the correlation energy is expressed as

$$E_c = E - E_{\text{ref}} = \sum_i \epsilon_i + \sum_{j < i} \epsilon_{ij} + \sum_{k < j < i} \epsilon_{ijk} + \dots \quad (1)$$

with

$$\epsilon_i = E_c(i)$$

$$\epsilon_{ij} = E_c(ij) - \epsilon_i - \epsilon_j$$

$$\epsilon_{ijk} = E_c(ijk) - \epsilon_{ij} - \epsilon_{ik} - \epsilon_{jk} - \epsilon_i - \epsilon_j - \epsilon_k$$

The terms of this expansion, ϵ_X , quantify correlations in n -body units of interaction. For singlet ground-state iFCI, the $n = 1$ terms, ϵ_i , are the correlation energies (beyond the reference) for each pair of electrons, i , treated independently. At $n = 2$, ϵ_{ij} are the residual correlation energies when two pairs of electrons (i, j) are correlated in the mean field of the remaining electrons and so on for higher n -body increments. The correlation increments, ϵ_X , are evaluated in a virtual natural orbital basis that is specific to its n occupied orbitals.⁵⁹ Each term is converged to within a threshold, ζ , which limits the number of correlating virtual orbitals in the increment.

For N electron pairs (and $n \ll N$), there are $O(N^n)$ incremental units, ϵ_X , such that iFCI requires polynomial effort for finite n . Fortunately, eq 1 produces size-extensive energies when the correlation energies, $E_c(X)$, come from a theory that is also extensive. FCI is one such theory, and therefore any value of n provides an intrinsically size extensive method. This property has been suggested by numerous benchmark cases in prior work, including systems with up to 10 carbon atoms being treated to high accuracy at $n = 3$.⁶⁰

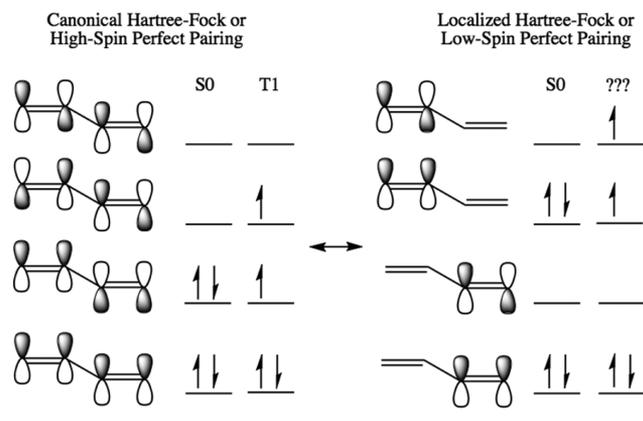
Converging iFCI up to $n = 3$ or 4 therefore requires solving a polynomial number of configuration interaction (CI) eigenvalue problems. This computational expense becomes quite high when using a conventional Davidson algorithm.⁵⁹ To alleviate this issue, the heat-bath CI (HBCI) solver⁷² is used to provide rapid, close estimates of CI energies. HBCI relies on two parameters that allow an asymptotic reproduction of the exact CI energy as they are decreased to zero. One parameter controls the selection of the CI space, which is exactly diagonalized, and the second controls the perturbation from this CI solution. By using small cutoffs, small errors are introduced into iFCI by HBCI, with the benefit of orders-of-magnitude reduction in computational time.

The success of iFCI also relies on the choice of reference function, which gives E_{ref} and defines the orbital bodies for the many-body expansion. In prior work, localized orbitals from a HF reference were shown to provide a good starting place for equilibrium geometries with closed-shell character,⁵⁹ while a singlet PP wave function was needed for rapid convergence of open-shell electronic states.⁶⁰ In the latter case, the bodies of expansion were localized bonding–antibonding orbital pairs, each containing two electrons. Neither of these choices is suitable for computing a variety of triplet states, which may be intrinsically delocalized beyond localized HF or low-spin PP

orbitals. To compute triplet states using iFCI, a different set of orbitals from a new reference will be required.

High-Spin Perfect Pairing Reference. PP uses a variational procedure to maximize correlation from double excitations within explicitly paired orbitals (but not between pairs of pairs). For example, the PP orbitals of butadiene (Scheme 2) show correlations via nodes in the center of each

Scheme 2. Comparison of Orbital Types and Electronic States in Butadiene



local π bond. While this is useful for recovering (some) correlation in the singlet ground state, the lowest energy triplet cannot be constructed from two unpaired electrons in any two PP orbitals. Indeed, a reconfiguration of all four localized π orbitals would be required to correctly represent the triplet. The assignment of the triplet state is therefore unnecessarily complex, and no single electron configuration can be used to describe it. Starting with singlet PP orbitals in eq 1 will only result in slow convergence of the triplet with respect to n .

While it is obvious that a better reference must be found for the triplet, this choice should take into consideration the singlet as well. Specifically, an optimal reference could specifically target the electronic configurations that best represent the singlet and triplet simultaneously. One excellent solution—inspired by spin flip methods—is to use high-spin PP as the reference. The π and π^* orbitals of high-spin, triplet PP for butadiene resemble their Hartree–Fock counterparts (left side of Scheme 2), and the σ orbitals retain the localized bonding–antibonding structure of low-spin PP. For high-lying valence π orbitals, this amounts to a good description of the triplet via two unpaired electrons in two orbitals. Effective descriptions of open- or closed-shell singlets are also available through CI in the same space, in close analogy to the spin flip procedure.⁴

Incremental Full Configuration Interaction for Spin Gaps. With a useful set of reference orbitals available through high-spin PP, iFCI can be redesigned with a focus on singlet–triplet gaps. To understand how this will work, consider that the ϵ_i terms from eq 1 for each electron pair are computed in the mean field of the remaining $2(N - 1)$ electrons. Terms with $i \neq a$, where a is the pair of singly occupied triplet orbitals, contribute to the total energy but do not affect the energy gap. Such terms can be avoided, and the focus can instead be on terms that do influence the gap.

CI singles and doubles (CISD) for the two active electrons (in the mean field of $2(N - 1)$ electrons) give a simple correlated wave function where the lowest singlet and triplet states can be computed. Correlation beyond this reference via

iFCI entails one-body correlations that involve one electron pair plus the two active electrons (CISDTQ), two-body terms that involve two electron pairs plus the active electrons (CISDTQPH), and so on. In each increment, the total energies for both spin states are computed. This strategy is diagrammed in Figure 1, where each CI computation is a complete-active-space CI (CAS-CI) involving all $2n + 2$ active electrons correlated in a natural orbital virtual space.

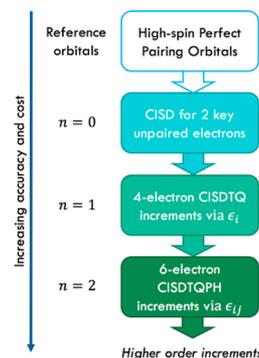


Figure 1. Singlet–triplet gap computations via iFCI.

The overall scheme deviates from the previous implementation of iFCI in that the two high-spin PP electrons, and corresponding orbitals are included in every incremental term (ϵ_x). Rather than computing the singlet or the triplet independently with different reference (pairing) orbitals, the two electronic states are computed in a single simulation. Their incremental differences in energy, $\epsilon_x(T) - \epsilon_x(S)$, and total energies are collected in the process. Because energy gaps should converge much more quickly than total energies, significant error cancellation is expected to be built into the method.

On the basis of the algorithm suggested by Figure 1, it becomes clear that the procedure is certainly dependent on the reference orbitals. At high n , this dependence will disappear because the incremental expansion guarantees such convergence, but low n solutions are of greatest interest. The examples below will serve to test the generality and reliability of high-spin PP orbitals for use in iFCI.

COMPUTATIONAL DETAILS

iFCI is implemented in C++ in a development version of the Q-Chem 5.0 software package.⁸⁵ The double- ζ polarized 6-31G* basis⁸⁶ and the polarized triple- ζ cc-pVTZ⁸⁷ basis were used as specified in the benchmark examples. Pipek–Mezey (PM) localization⁸⁸ was used to initiate the PP procedure of the coupled-cluster valence bond implementation in Q-Chem. Orbital pairs from the (orthogonal) natural orbital representation of PP were semicanonicalized before use in iFCI.

The HBCI solver⁷² was used to obtain full-valence benchmarks as well as eigenvalues of the incremental Hamiltonians. For iFCI, relatively small values of the heat-bath cutoff parameters were used, $\epsilon_1 = 200 \mu$ Ha and $\epsilon_2 = 0.5 \mu$ Ha, such that HBCI energies are precise. HBCI computations were initiated by diagonalizing CAS-CI Hamiltonians consisting of $2n + 2$ electrons in $2n + 2$ orbitals and targeting either the lowest singlet or triplet state. When used as a full valence benchmark, ϵ_1 was sequentially reduced until convergence to within 1 mHa (see the Supporting Information). Further details of this procedure are described in ref 72.

The summation natural orbital procedure of ref 59 generated the natural virtual orbitals for each increment. The convergence metric ζ was chosen to be $10^{-5.5}$ Ha, unless otherwise noted. These values provide good convergence of the total energies while minimizing expense for larger system sizes (see convergence test in the subsequent section).

Four-center, two-electron integrals were computed using the resolution of the identity (RI) approximation.^{89,90} All simulations used the RIMP2-cc-pVTZ auxiliary basis set for this purpose. Conventional Fock matrices account for frozen core contributions. Point-group symmetry is not invoked. Geometries for most molecules were obtained from ref 45, while ethylene, butadiene, and hexatriene geometries were optimized at the MP2/cc-pVQZ level.⁹¹

RESULTS

A variety of test cases were collected to evaluate iFCI for singlet–triplet gaps. The first several were diradicals and diradicaloids, including carbenes, trimethylenemethane, cyclobutadiene, and benzynes, which are commonly used to test ab initio methods.⁴⁵ Ethylene, butadiene, and hexatriene were added to this set to represent species with delocalized triplets in conjugated π systems.

Because the carbenes are small, HBCI⁷² can correlate all valence electrons at once and provide total energies within 1 mHa of FCI. This excellent level of convergence for HBCI is verified in the Supporting Information to show these numbers are quantitative benchmarks. HBCI is similarly applicable to C_3H_6 but cannot be easily applied to the larger systems due its exponential scaling.

Carbene Analogues. Four triatomic analogues of carbenes, CH_2 , NH_2^+ , SiH_2 , and PH_2^+ , were considered as the first benchmark set. Carbenes have strong correlations between the σ and π valence orbitals, providing electronic configurations of $\sigma^2\pi^0$, $\sigma^1\pi^1$, and $\sigma^0\pi^2$ as especially vital. The complexity of these configurations leads to qualitatively different ordering of spin states depending on the carbene, giving two singlet and two triplet ground states. On top of the strong correlation, dynamic correlation must be included to reach high accuracy gaps. For the carbenes—and all examples in this article—all valence electrons are correlated in iFCI. Having only six valence electrons, HBCI provides near-exact energies (within the basis set) for comparison. Similarly, $n = 2$ consists of just one incremental term that correlates all valence electrons, so $n = 2$ iFCI will closely replicate HBCI results.

Figure 2 shows the convergence progress for methylene as a function of the threshold, ζ , that controls the natural orbital cutoffs used in the increment computations. Using $\zeta = 10^{-7.5}$

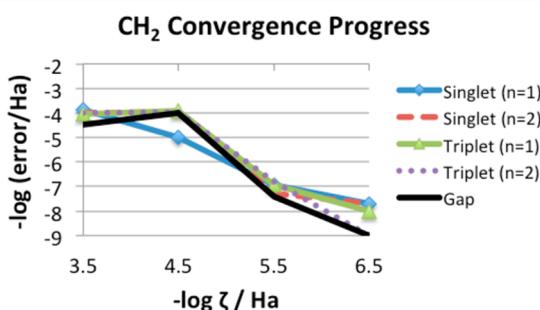


Figure 2. Convergence of iFCI total energies and singlet–triplet gap for methylene in the cc-pVTZ basis with respect to ζ .

Ha as the benchmark limit, errors in total energies are small at all chosen thresholds, although three of the four increase from $\zeta = 10^{-3.5}$ to $\zeta = 10^{-4.5}$. This effect is likely due to serendipitous error cancellation at loose convergence (the same property is not observed for the other three carbenes). Regardless, the total energies are converged to 0.1 mHa or better for $\zeta \leq 10^{-4.5}$. For all values of ζ , the gap is also converged to within 0.1 mHa and within 1 μ Ha for $\zeta \leq 10^{-5.5}$. While somewhat slower convergence is expected for larger polyatomics that follow, because they have more virtual orbitals, $\zeta = 10^{-5.5}$ Ha was chosen as a reasonable threshold for general use.

In Table 1, iFCI results for the carbenes at $\zeta = 10^{-5.5}$ are compared with HBCI and experiment. The HBCI and iFCI at $n = 1$ agree to within 2.0 kcal/mol, indicating that even the lowest level of iFCI expansion can produce usefully accurate gaps. iFCI at $n = 2$ and HBCI with the triple- ζ basis agree with experiment to within 1 kcal/mol in all four cases, with the double- ζ basis being substantially less accurate. Because these results are essentially exact within the basis, the cc-pVTZ basis set is therefore sufficient to reproduce accurate gaps. In the larger systems that follow, the 6-31G* and cc-pVTZ basis sets will continue to be used with these convergence metrics in mind.

Trimethylenemethane and Cyclobutadiene. Trimethylenemethane (TMM) and cyclobutadiene have four strongly correlated π electrons and significant dynamic correlations with the occupied σ orbitals. In TMM, the lowest energy singlet state (B_1) has four H in the plane of the carbon atoms, and the remaining two H are perpendicular to the plane. There also exists another singlet state (A_1), which like the lowest triplet (A_2), has all atoms within the plane. The resulting electronic structures are therefore considerably different due to one carbon p orbital that either aligns or is orthogonal to the other three. Cyclobutadiene provides a similarly difficult correlation structure, having two degenerate π orbitals that result in an open-shell singlet ground state, in violation of Hund's rules. In total, 22 valence electrons must be correlated for TMM and 20 for cyclobutadiene. With the 6-31G* basis, TMM has 68 valence basis functions and cyclobutadiene has 64, while cc-pVTZ provides 200 and 172, respectively.

Benchmark values for the vertical transition in cyclobutadiene are not available via experiment. Multireference simulations are therefore quoted from the literature for comparison to iFCI (Table 2), but because this reference used a double- ζ basis and a minimal active space (CAS(2,2)),⁹⁸ its quantitative accuracy is limited.

The planar and nonplanar adiabatic gaps of TMM and the vertical gap of D_{4h} symmetric cyclobutadiene are shown in Table 2. The iFCI gap at $n = 2$ in TMM compares favorably to the reference energies for both basis sets. At $n = 1$ for the cc-pVTZ basis, iFCI gives a B_1 – A_2 gap that is 0.6 kcal/mol away from the $n = 2$ gap, while the $n = 1$ value is less converged for the A_1 – A_2 gap, being 2.2 kcal/mol away. Nonetheless, the $n = 2$ values are within 1 kcal/mol of the $n = 3$ values, indicating rapid convergence with respect to n . In cyclobutadiene, the correct ground state is recovered at all $n > 1$, even though the reference energy (i.e., $n = 0$) predicts a triplet ground state favored by 6.3 kcal/mol. This result suggests that a large amount of correlation must be recovered to treat cyclobutadiene with good accuracy. Furthermore, this suggests that even when the starting guess has poor quantitative accuracy, iFCI does recover the correct solution with increasing n , which is a useful property. This property is confirmed by $n = 3$ computations in the 6-31G*

Table 1. Carbene Analogue Adiabatic Singlet–Triplet Gaps in kcal/mol^a

	6-31G*			cc-pVTZ			experiment ^b
	<i>n</i> = 1	<i>n</i> = 2	HBCI	<i>n</i> = 1	<i>n</i> = 2	HBCI	
CH ₂	16.1	15.1	15.0	11.7	10.0	9.9	9.0
NH ₂ ⁺	34.6	32.9	32.8	31.3	29.3	29.3	29.0
SiH ₂	−16.9	−16.7	−16.8	−20.2	−20.1	−20.3	−21.0
PH ₂ ⁺	−14.3	−13.6	−13.8	−17.6	−17.1	−17.4	−17.0

^aGeometries from ref 45. ^bExperimental gaps for CH₂,^{92,93} NH₂⁺,⁹⁴ SiH₂,^{95,96} and PH₂⁺.⁹⁷

Table 2. Singlet–Triplet Gaps for Trimethylenemethane (Adiabatic) and Cyclobutadiene (Vertical) in kcal/mol

	6-31G*			cc-pVTZ		best other ^a	experiment ^b
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 1	<i>n</i> = 2		
TMM							
B ₁	14.7	16.0	15.5	16.9	16.3	16.4	
A ₁	17.1	20.1	19.5	17.0	19.2	19.1	18.2
cyclobutadiene	−9.7	−5.9	−5.0	−7.1	−4.2	−8.1	

^aTMM results at the MCQDPT2(10,10)/cc-pVTZ level from ref 4. Cyclobutadiene results at the CASSCF-MkCCSD/cc-pVDZ level from ref 98.

^bExperiment from ref 99 with zero-point energy removed based on ref 4.

Table 3. Benzyne Adiabatic Singlet–Triplet Gaps in kcal/mol

	6-31G*			cc-pVTZ			experiment ^a
	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2	
ortho	−21.6	−41.1	−31.5	−23.0	−42.6	−38.6	−37.5
meta	−4.2	−15.9	−19.0	−5.6	−21.1	−21.1	−21.0
para	0.2	−1.0	−4.1	0.0	−0.8	−4.1	−3.8

^aExperimental results from ref 101.

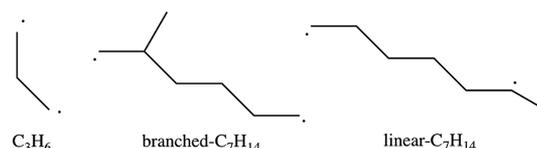
basis, where the corrections from *n* = 2 to *n* = 3 are <1 kcal/mol.

***o*-, *m*-, and *p*-Benzynes.** When two hydrogen atoms are removed from benzene, benzyne is formed.¹⁰⁰ These species have distinct structures in their singlet and triplet states, changing degrees of radical σ overlap depending on the isomer, and enough electrons (28 valence) to challenge highly correlated multireference theories. Because geometries for the singlet and triplet state differ substantially from one another,⁴⁴ computation of accurate adiabatic gaps is additionally difficult.

Table 3 compares iFCI singlet–triplet gaps in *ortho*-, *meta*-, and *para*-benzyne to experiment. All iFCI simulations at *n* > 0 predict the correct ground state, and the cc-pVTZ results at *n* = 2 agree closely with experiment. This occurs even though the *n* = 0 reference values are poor quality and only capture the qualitative trends in singlet–triplet gap for the three isomers. In addition, the *n* = 1 and 2 values differ significantly from one another, suggesting that many-body correlations substantially affect the radical pair. In summary, the benzyne is found to be substantially difficult problems for a correlated method: The active-space results (*n* = 0) are poor, including pairwise correlations (active-space plus all valence PP pairs at *n* = 1) substantially corrects this, and including up to hexuple excitations (i.e., CISDTQPH at *n* = 2) and a triple- ζ basis is required to reach quantitative accuracy. iFCI, however, naturally captures this correlation progression to accurately reproduce the experimental series of singlet–triplet gaps.

Isolated Diradicals. In the insulating analogue of the benzyne, weakly coupled diradicals emerge when two H atoms are abstracted from distant carbon atoms in alkanes. Three such diradicals are shown in Scheme 3, with varying electronic environments and degrees of separation between the radical

Scheme 3. Isolated Diradicals under Consideration



electrons. While such radicals appear somewhat trivial compared with other cases considered herein, these three molecules have a unique radical electronic structure—near degeneracy—that represents moieties vital to combustion chemistry.¹⁰²

Table 4 shows the results from iFCI for *n* = 1 and *n* = 2 in the 6-31G* and cc-pVTZ basis sets. Because of the insulating character of the alkanes, the gaps are small and not highly sensitive to basis set. For the same reason, *n* = 1 provides a close approximation to the *n* = 2 results, being within 0.5 kcal/mol for C₃H₆ and 0.1 kcal/mol for the C₇H₁₄ structures. For C₃H₆, *n* = 3 provided a correction of 0.04 kcal/mol (to give 1.93 kcal/mol) compared with *n* = 2, suggesting *n* = 2 is well converged. Because C₃H₆ has only 18 valence electrons, HBCI results in the double- ζ basis are available to substantiate this convergence, and HBCI closely agrees (within 0.1 kcal/mol) with *n* \geq 2 iFCI. For the larger C₇H₁₄ diradicals, *n* = 2 computations were not performed at the cc-pVTZ level due to their large size (42 valence electrons in 399 orbitals) and sub-0.1 kcal/mol convergence with respect to *n* in the 6-31G* basis. The iFCI results at *n* = 1, however, agree well with the best available electronic structure benchmarks, which also were performed in polarized triple- ζ basis sets.

Shorter Polyenes. The polyene series, C_{2*n*}H_{2*n*+2}, is a prototypical set of conjugated molecules with delocalized π

Table 4. Vertical Singlet–Triplet Gaps for Isolated Diradicals in kcal/mol

	6-31G*			cc-pVTZ		best other ^a
	<i>n</i> = 1	<i>n</i> = 2	HBCI	<i>n</i> = 1	<i>n</i> = 2	
C ₃ H ₆	1.48	1.97	1.88	1.39	1.88	1.8
branched C ₇ H ₁₄	−0.01	0.07		0.02		0.0
linear C ₇ H ₁₄	−0.20	−0.22		−0.21		−0.2

^aCASMP2(8,8)/6-311++G(2d,2p) results for C₃H₆ from ref 103 EOM-SF-CCSD(dT)/6-311G(d) results from ref 16.

networks.^{104,105} The first three species in this series, ethylene, *trans*-butadiene, and *all-trans*-hexatriene, have closed-shell singlet ground states, and the triplet can be considered an excited state. These states have dominated by single-reference character,^{106–109} so coupled-cluster singles and doubles with perturbative triples (CCSD(T))¹¹⁰ is an accurate theory for computing the gap. For benchmarking iFCI, the canonical CCSD(T) method is therefore available along with experimental results. Because the latter are experimental band maxima, comparisons with vertical excitation energies should not be quantitative.¹¹¹

Table 5 shows iFCI gaps for the three polyenes compared with CCSD(T) and experiment. For all three species and all

Table 5. Polyene Vertical Triplet–Singlet Gaps in eV

	6-31G*				CCSD(T)
	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	
ethylene	4.51	4.67	4.67	4.66	4.65
butadiene	2.23	3.53	3.46	3.45	3.46
hexatriene	1.36	2.43	2.86	2.81	2.80
	cc-pVTZ			CCSD(T)	experiment ^a
	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2		
ethylene	4.51	4.66	4.64	4.63	4.3 to 4.6
butadiene	2.31	3.52	3.44	3.45	3.22
hexatriene	1.46	2.49	2.84	2.80	2.61

^aExperimental band maxima for ethylene,^{112–116} butadiene,¹¹⁷ and hexatriene.¹¹⁸

basis sets, *n* = 2 iFCI agrees with CCSD(T) to within 0.1 eV. iFCI at *n* = 1 is similarly accurate for ethylene and butadiene but drifts 0.3 to 0.4 eV for hexatriene. This error at low *n* can be understood by noting the *n* = 0 reference values deteriorate as the polyenes grow in size. Whereas ethylene has an excellent *n* = 0 gap that is within 0.2 eV of the benchmarks, hexatriene at *n* = 0 is off by 1.4 eV. This observation shows the quantitative accuracy of the reference is important at low *n*, as *n* = 1 cannot fully recover from this large error. Fortunately, the *n* = 2 corrections remedy the issue, and iFCI consistently returns high-quality spin gaps at this level. At *n* = 3 in the 6-31G* basis, smaller corrections of 0.1, 0.5, and 1.5 mHa for ethylene, butadiene, and hexatriene, respectively, indicate that *n* = 3 is only vital for high accuracy at hexatriene. Whether higher *n* will be required for conjugated networks with greater degrees of delocalization is unclear, as six carbon atoms is roughly the limit where *n* = 3 corrections can be readily applied.

DISCUSSION

PP-iFCI was previously shown⁶⁰ to be effective at recovering singlet ground-state energies for closed- and open-shell wave functions. PP-iFCI was successful due to PP's good behavior in bond-breaking situations and its smoothly varying orbitals, such that qualitatively correct reference energy profiles were

produced for multiple bond dissociation problems. This strategy worked well because broken bonds are localized, that is, between the two atoms involved in the bond, and PP readily captures this situation in its singlet ground state. By adding significant correlation via the *n*-body expansion to this PP reference, PP-iFCI consistently led to near-FCI-quality energies in several test examples.

In the present advance, a new set of orbitals was required to handle triplet states. Specifically, high-spin PP was converged to its lowest energy triplet, which creates the requisite high-spin orbitals to demarcate the gap. This adds black-box character to the method compared with most active-space methods, as HS-PP-iFCI does not require an active-space selection. Indeed, because all CAS-CI spaces involving $2n + 2$ electrons are involved in the *n*-body expansion of iFCI, all such active spaces contribute to the total correlation energies. Compared with standard multireference methods, this unusual property allows systematic convergence of iFCI with increasing *n* and relative freedom from active space bias. This property led to reproduction of experimental spin gaps and high-level theoretical results to within ~ 1 kcal/mol (0.04 eV) for all cases considered.

It should be noted, however, that PP does not trivially converge to the high-spin state of interest, as it is well-known that multiple solutions exist. This appears to be the primary limitation of HS-PP-iFCI, in that the reference pairing orbitals must be (at least) qualitatively correct. Despite this cautionary note, a correct restricted open-shell HF initial guess for PP remedied this dependence for all examples in this article. Therefore, at least for the species in Scheme 1, the PP reference appears sufficient for iFCI to quickly converge upon high-accuracy singlet–triplet gaps. Further study will be needed to determine the PP reference's applicability to molecules with long conjugation lengths.^{119–121}

Despite being a polynomial scaling method, iFCI relies on the greatly reduced costs of HBCI⁷² to determine the many incremental energies at *n* > 1. This advance has been key to the continued progress of the iFCI method,^{59,60} as future improvements in fast FCI solvers can further improve iFCI's efficiency.

CONCLUSIONS

The method of increments is herein shown to be useful for computing gaps between spin states to high accuracy by approaching FCI-level correlation energies. Whenever iFCI converges at low *n*, the method maintains tractable polynomial scaling with growing system size. Fortunately, the zero-order reference state constructed from PP allows rapid convergence with respect to *n* of the *n*-body expansion, making iFCI applicable to computing singlet–triplet gaps for polyatomics that are far from the reach of FCI. This advance therefore greatly expands the realm of systems where near-exact solutions of the electronic Schrödinger equation are available. Ongoing

studies will determine whether similar strategies are applicable to multistate solutions where the electronic states are not orthogonal due to spin or spatial symmetry.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.7b03998.

Table S1. HBCI Energies of Carbenes. Table S2. HBCI Energies for C₃H₆ ($\epsilon_2 = 0.5 \mu\text{Ha}$). (PDF)

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Notes

The author declares no competing financial interest.

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