iCISCF: An Iterative Configuration Interaction-based Multiconfigurational Self-consistent Field Theory for Large Active Spaces

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Abstract

An iterative configuration interaction (iCI)-based multiconfigurational self-consistent field (SCF) theory, iCISCF, is proposed to handle systems that require large complete active spaces (CAS). The success of iCISCF stems from three ingredients: (1) efficient selection of individual configuration state functions spanning the CAS, meanwhile maintaining full spin symmetry; (2) the use of Jacobi rotation for the optimization of active orbitals, in conjunction with a quasi-Newton algorithm for the core/active-virtual and core-active orbital rotations; (3) a second-order perturbative treatment of the residual space left over by the selection procedure (i.e., iCISCF(2)). Just like selected iCI being a very accurate approximation to CASCI, iCISCF(2) is a very accurate approximation to CASSCF. Several examples that go beyond the capability of CASSCF are taken as showcases to reveal the performances of iCISCF and iCISCF(2).
1 Introduction

It is well known that a multiconfigurational wave function is demanded even for a qualitative description of a chemical system with a dense set of energetically adjacent frontier molecular orbitals (MO). The complete active space self-consistent field (CASSCF) theory\textsuperscript{1–7} is usually taken as the first step towards an accurate description of such strongly correlated systems. The popularity of CASSCF stems from its operational simplicity: starting with the partition of the in total $M$ MOs into $M_c$ core (always doubly occupied), $M_a$ active (variably occupied) and $M_v = M - M_c - M_a$ virtual (always zero occupied) orbitals, all configurations are then generated by distributing the $N_a = N_e - 2M_c$ active electrons in the $M_a$ active orbitals in all possible ways, thereby leading to a subspace full configuration interaction (FCI) problem, usually denoted as CASCI. While the total energy cannot be altered by arbitrary rotations (unitary transformations) within each of the three subsets of orbitals, the rotations in between do lower the energy further. Therefore, a CASSCF calculation amounts to optimizing the CI and MO coefficients simultaneously to make the energy stationary. Yet, given so many years of algorithmic developments (see Refs.\textsuperscript{8–10} for the most recent ones), the largest CASSCF calculation performed so far involves only 22 active electrons in 22 active orbitals, which was made possible only by massive parallelization.\textsuperscript{11} The huge computational cost stems of course from the exponential growing of the size of CASCI. To break the record, some approximation must be introduced to simplify the CASCI calculation. As a matter of fact, as long as the approximation can be controlled so as to guarantee the quality of the orbitals, the approximation itself is not an issue at all, simply because CASSCF is not the end of the calculation but rather the preparation for subsequent treatment of dynamic correlation, which can fully recover the marginal loss due to the approximate treatment of the CI coefficients. A large number of approaches have been developed in the last decades to approximate FCI/CASCI (see Ref.\textsuperscript{12} for a complete collection and classification of such approaches). In particular, some of these\textsuperscript{13,28} have been adapted to CASSCF, enabling much larger
CASSCF calculations. The present work aims to combine the iterative configuration interaction (iCI) approach with CASSCF, leading to iCISCF as a new member of the static-dynamic-static (SDS) family of methods (SDSPT2, SDSCLI, iCI, iCIPT2, iVI (iterative vector interaction), iCAS (imposed automatic selection and localization of active orbitals), and iOI (iterative orbital interaction)). Among the various unique features of iCI, the following ones are particularly relevant to CASSCF:

1. Configuration state functions (CSF) instead of Slater determinants (SD) are taken as the many-electron basis so as to guarantee full spin symmetry, which is of vital importance for describing low-spin states of general open-shell systems.

2. Individual CSFs can be selected with a very efficient algorithm.

3. A particle-hole representation is employed to establish connections between randomly selected CSFs so as to construct the Hamiltonian matrix very efficiently in a compressed form. In particular, the connections between hole-strings and between particle-strings can be shared by CSF spaces of different spatial and/or spin symmetries, thereby facilitating the simultaneous calculation of several states of different spatial and/or spin symmetries with a common set of orthonormal orbitals.

4. The diagonalization of the Hamiltonian matrix is done by iVI, which is able to access directly the roots of a given energy window or specified characters, thereby guiding the SCF iterations to converge to excited states free of variational collapse (a point that is not pursued here though).

The iCISCF algorithm is described in Sec. 2, which is followed by pilot applications in Sec. 3. The following conventions are to be used throughout: (1) core, active, virtual, and arbitrary MOs are designated by \{i,j,k,l, \cdots \}, \{t,u,v,w, \cdots \}, \{a,b,c,d, \cdots \}, and \{o,p,q,r,s, \cdots \}, respectively; (2) repeated indices are always summed up.

4
2 iCISCF

Given a set of MOs that are partitioned into core, active and virtual ones, the selection of individual CSFs in the CASCI space \( P \) is performed iteratively until convergence, with a single parameter \( C_{\text{min}} \) for controlling the size of the final, selected space \( P_m \). Specifically, starting with a guess space \( P_0 \), only those CSFs \( \{ |I\rangle \in P - P_0 \} \) satisfying the ranking criterion \( \max_{J \in P_0} | \frac{H_{IJ}C_J}{E^{(0)} - H_{II}} | \geq C_{\text{min}} \) are put into \( P_0 \), so as to extend \( P_0 \) to \( P_1 \); the Hamiltonian matrix in \( P_1 \) is then diagonalized\(^{33,34}\) to prune away those CSFs of coefficients smaller in magnitude than \( C_{\text{min}} \), so as to reduce \( P_1 \) to \( P_m \) upon convergence (for more details, see Ref. \(^{12}\)). Finally, the Hamiltonian matrix \( H^{(0)} \) in \( P_m \), viz.

\[
H_{IJ}^{(0)} = \langle I|\hat{H}|J\rangle, \quad \forall I, J \in P_m, \\
\hat{H} = h_{pq}\hat{E}_{pq} + \frac{1}{2}g_{pq,rs}\hat{e}_{pq,rs}, \\
\hat{E}_{pq} = a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}, \\
\hat{e}_{pq,rs} = \{ \hat{E}_{pq}\hat{E}_{rs} \} = \{ \hat{E}_{rs}\hat{E}_{pq} \} = \hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps},
\]

is diagonalized to yield the normalized iCI wave function

\[
|0\rangle = \sum_{|I\rangle \in P_m} |I\rangle C_I^{(0)}, \quad \langle I|J \rangle = \delta_{IJ}, \quad \sum_I C_I^2 = 1,
\]

with energy

\[
E^{(0)} = \text{tr}(hD) + \frac{1}{2} \sum_{rs} \text{tr}(J^{rs}P^{sr}), \\
D_{pq} = \langle 0|\hat{E}_{pq}|0\rangle = D_{qp}, \quad \Gamma_{pq,rs} = \langle 0|\hat{e}_{pq,rs}|0\rangle = \Gamma_{qp,rs}, \\
J^{rs}_{pq} = g_{pq,rs}, \quad P^{rs}_{pq} = \frac{1}{2}(\Gamma_{pq,rs} + \Gamma_{qp,rs}) = P^{sr}_{pq} = P^{pq}_{rs}.
\]

Note in passing that the basic coupling coefficients \( \langle I|\hat{E}_{pq}|J\rangle \) and \( \langle I|\hat{e}_{pq,rs}|J\rangle \) in the Hamiltonian matrix \( \{1\} \) depend only on the relative occupations of the MOs in the CSF pairs.
\{ |I\rangle, |J\rangle \} but not on the individual MOs. As such, they can be evaluated and reused very efficiently with the tabulated unitary group approach.\cite{32} For later use, we here define \( P_s = P - P_m \) as the residual of \( P \) left over by the selection, whereas \( Q = 1 - P \) as the complementary space for dynamic correlation.

To further optimize the orbitals, we parameterize the iCISCF wave function as\cite{33}

\[
|\tilde{0}\rangle = \sum_{I \in P_m} \exp(-\hat{\kappa}) |I\rangle \xi_I, \quad (9)
\]

\[
\hat{\kappa} = \sum_{pq} \kappa_{pq} \hat{E}_{pq} = \sum_{p>q} \kappa_{pq} \hat{E}_{pq} = \frac{1}{2} \sum_{p,q} \kappa_{pq} \hat{E}_{pq}, \quad (10)
\]

\[
\kappa = -\kappa^\dagger, \quad \hat{E}_{pq} = \hat{E}_{pq} - \hat{E}_{qp}, \quad \frac{\partial \hat{\kappa}}{\partial \kappa_{rs}} = \hat{E}_{rs}. \quad (11)
\]

The skew symmetry of \( \kappa \) implies that only \( \kappa_{pq} (p > q) \) are independent parameters. Moreover, rotations within the core and within the virtual orbitals are also redundant. Therefore, the \( \hat{\kappa} \) operator actually reads

\[
\hat{\kappa} = \sum_{ai} \kappa_{ai} \hat{E}_{ai} - \sum_{ti} \kappa_{ti} \hat{E}_{ti} + \sum_{at} \kappa_{at} \hat{E}_{at} - \sum_{tu} \kappa_{tu} \hat{E}_{tu}. \quad (12)
\]

The last term in Eq. (12) vanishes in CASSCF but has to be included in iCISCF due to the truncation of CASCI. It is precisely this term that renders the orbital optimization of iCISCF more difficult than that of CASSCF. Minimizing the Lagrangian

\[
L[\kappa, \xi] = \langle \tilde{0} | \hat{H} | \tilde{0} \rangle - E(\xi^\dagger \xi - \mathbf{I}) \quad (13)
\]
leads to the stationary conditions

\begin{align*}
G^c_i &= 2\langle i | \hat{H} - E^{(0)} | 0 \rangle = 0, \quad (14) \\
G^o_{pq} &= \langle 0 | [\hat{E}_{pq}, \hat{H}] | 0 \rangle = 2\langle 0 | [\hat{E}_{pq}, \hat{H}] | 0 \rangle = 2(F - F^\dagger)_{pq} = 0, \quad (15) \\
F &= Dh + \sum_{rs} P^{rs} J^{sr}, \quad (17)
\end{align*}

where the partial derivatives are evaluated at the expansion point \( \xi^{(0)} = (C^{(0)}, 0)^T \). Eq. \( (16) \) can be recast\textsuperscript{38} into a Hartree-Fock-like equation, such that it can be solved by diagonalization, just like Eq. \( (14) \). However, such first-order orbital optimization method is hardly useful due to very slow convergence. A more robust method is the second-order Newton-Raphson (QR) scheme, which amounts to expanding the Lagrangian \( L \) \( (13) \) to second order at the expansion point \( \xi^{(0)} \),

\begin{align*}
L^{(2)}[\kappa, C] = E^{(0)} + \xi^{(1)^T} G + \frac{1}{2}\xi^{(1)^T} E\xi^{(1)}, \quad (18)
\end{align*}

the stationary condition of which is

\begin{align*}
E\xi^{(1)} &= -G \quad (19)
\end{align*}

or in block form

\begin{align*}
\begin{pmatrix}
E^{cc} & E^{co} \\
E^{oc} & E^{oo}
\end{pmatrix}
\begin{pmatrix}
C^{(1)} \\
\kappa^{(1)}
\end{pmatrix}
= -
\begin{pmatrix}
G^c \\
G^o
\end{pmatrix}, \quad (20)
\end{align*}
where the second-order partial derivatives (at the expansion point $\xi^{(0)}$) read

$$E_{IJ}^{cc} = \frac{\partial^2 L}{\partial C_I \partial C_J} = 2 \langle I | \hat{H} - E^{(0)} | J \rangle, \quad (21)$$

$$E_{pq,I}^{co} = \frac{\partial^2 L}{\partial \kappa_{pq} \partial C_I} = 2 \langle 0 | [\hat{E}_{pq}^{-}, \hat{H}] | I \rangle = E_{I,pq}^{co}, \quad (22)$$

$$E_{pq,rs}^{oo} = \frac{\partial^2 L}{\partial \kappa_{pq} \partial \kappa_{rs}} = \frac{1}{2} \{ \langle 0 | [\hat{E}_{pq}^{-}, [\hat{E}_{rs}^{-}, \hat{H}]] | 0 \rangle + \frac{1}{2} \langle 0 | [\hat{E}_{rs}^{-}, [\hat{E}_{pq}^{-}, \hat{H}]] | 0 \rangle \} \quad (23)$$

$$= \langle 0 | [\hat{E}_{pq}^{-}, [\hat{E}_{rs}^{-}, \hat{H}]] | 0 \rangle + \frac{1}{2} \langle 0 | [\hat{E}_{rs}^{-}, \hat{H}] | 0 \rangle. \quad (24)$$

The first row of Eq. (20) can be rearranged to

$$2(H^{(0)} - E^{(0)} I) C^{(1)} = -G^{c} - 2H^{(1)} C^{(0)}, \quad (25)$$

where

$$H_{IJ}^{(1)} = \langle I | \hat{H}_K | J \rangle, \quad (26)$$

$$\hat{H}_K = \frac{1}{2} \kappa^{(1)}_{pq} [\hat{E}_{pq}^{-}, \hat{H}] = \hat{H}_K^{+} \quad (27)$$

$$= [\kappa^{(1)}_{pq}, \hat{E}_{pq}^{-}, \hat{H}] + \frac{1}{2} [\kappa^{(1)}_{pq}, \hat{E}_{pq}^{-}, \hat{I}]_{pq} \hat{E}_{pq,rs} + \frac{1}{2} [\kappa^{(1)}_{pq}, \hat{I}_{pq}]_{rs} \hat{E}_{pq,rs} \quad (28)$$

$$= [\kappa^{(1)}_{pq}, \hat{E}_{pq}^{-}, \hat{I}]_{pq} + [\kappa^{(1)}_{pq}, \hat{I}_{pq}]_{rs} \hat{E}_{pq,rs} \quad (29)$$

in which $\hat{H}_K$ is a bona fide Hamiltonian operator. Likewise, the second row of Eq. (20) can be rearranged to

$$\langle 0 | [\hat{E}_{pq}^{-}, \hat{H}] C^{(1)}_f = 2 \langle 0 | (D^{(1)}_f)_{pq} \rangle + 2 \sum_{rs} (P^{(1)}_{rs})_{pq} (J^{sr})_{pq} \quad (30)$$

$$= \frac{1}{2} \langle 0 | \hat{E}_{pq}^{-} + \hat{E}_{pq}^{+} | J \rangle C^{(1)}_f \quad (31)$$

$$= \frac{1}{2} \langle 0 | \hat{E}_{pq}^{-} + \hat{E}_{pq}^{+} | J \rangle C^{(1)}_f \quad (32)$$

$$D^{(1)}_{pq} = \frac{1}{2} \langle 0 | \hat{E}_{pq}^{-} + \hat{E}_{pq}^{+} | J \rangle C^{(1)}_f \quad (33)$$

$$P^{(1)}_{pq} = \frac{1}{2} \langle 0 | \hat{E}_{pq}^{-} + \hat{E}_{pq}^{+} | J \rangle C^{(1)}_f \quad (34)$$
Eqs. (25) and (30) can be viewed as response equations for the CI displacements \( C^{(1)} \) and orbital Newton steps \( \kappa^{(1)} \), respectively. The former involves the first-order active space Hamiltonian (26) due to \( \kappa^{(1)} \), whereas the latter involves the first-order reduced density matrices (RDM) (33)/(34) due to \( C^{(1)} \). This particular reformulation is advantageous in that it decouples the orbital optimization from the CI solver implementation in each Newton step, such that any CI solver can readily be used. An even more sophisticated formulation is the Werner-Meyer-Knowles (WMK) approach, where the Lagrangian is expanded to second order in \( T = e^{-\kappa} - I \), thereby containing terms infinite order in \( \kappa \). However, considering that the simultaneous optimization of the CI coefficients and the orbitals suffers from severe linear dependence due to the presence of active-active orbital rotations and that the CI step is rate determining for a large CAS, the second term on the right-hand side of both Eqs. (25) and (30) can be ignored, thereby leading to

\[
(H^{(0)} - E^{(0)} I) C^{(1)} = -G^c, \quad (35)
\]

\[
E^{oo} \kappa^{(1)} = -G^o. \quad (36)
\]

Eq. (35) is the usual iterative partial diagonalization of the CI matrix \( H^{(0)} \). For the given RDMs, Eq. (36) can, in the spirit of quasi-Newton (QR) methods, be solved iteratively with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm, which amounts to updating iteratively the inverse of the orbital Hessian \( E^{oo} \) with the diagonal elements (see Appendix A) as the initial guess. While such QN-based CASSCF has been in use for a long time, preliminary experimentations showed that the QN-based iCISCF often does not converge. To handle the troublesome active-active orbital rotations, we adopt the Jacobi rotation (JR) algorithm, which is the most robust first-order optimization method. In particular, it has been shown that the convergence pattern of JR-based MCSCF is not much affected when a not fully converged CI vector is used. In the actual running of iCISCF, the JR algorithm is first employed to optimize the active orbitals until a con-
vergence threshold is fulfilled. Then, the QN algorithm is invoked to determine the remaining core/active-virtual and core-active rotation parameters. This hybrid algorithm is to be denoted as JR+QN, to distinguish from the pure QN algorithm. The flowchart of iCISCF is depicted in Fig. [1]. If a state-specific Epstein-Nesbet type of second-order perturbation theory (ENPT2) is carried out in $P_s$, the method will be denoted as iCISCF(2). Likewise, if the ENPT2 is carried out in the joint space $P_s + Q = 1 - P_{tt}$, the method will be the original iCIPT2. Just like that iCIPT2 is very close to FCI, iCISCF(2) is very close to CASSCF. In principle, the iCISCF(2) energy functional can be minimized for orbital optimization. However, it has been shown that this does not change the orbitals discernibly.

Figure 1: Flowchart of iCISCF using two different active-active rotation schemes.
3 Results and discussion

All calculations were performed with the BDF program package\cite{15,19} on a computer node equipped with Intel(R) Xeon(R) Gold 6240 CPUs (in total 36 physical cores) and 128 GB memory. The convergence threshold for the energy is $10^{-10} E_h$. All extrapolations were based on a four-point linear fit of $E_{i\text{CISCF}(2)}$ versus $E^{(2)}$ calculated with different $C_{\text{min}}$, which is possible because the orbitals with different $C_{\text{min}}$ are virtually identical.

3.1 Optimization of active orbitals

Compared with CASSCF, the additional couplings between the active-active orbital rotations and the CI displacements render iCISCF (and other approximate CASSCF approaches as well) more difficult to converge, especially when they are optimized simultaneously. To overcome such difficulties, the two sets of parameters have to be decoupled. Even in this case, special care has to be taken of. For instance, in the adaptive sampling configuration interaction-based CASSCF approach (ASCISCF)\cite{27,28} a sequence of supermacro-, macro-, and micro-iterations is invoked: the selection of a fixed number of SDs is performed in each supermacroiteration, which consists of a fixed number of macroiterations, where the list of SDs is kept fixed, such that only the CI coefficients are allowed to respond to changes in the orbitals resulting from the microiterations. As such, the macro- and micro-iterations together mimic CASSCF (where the list of SDs is fixed by construction). In contrast, in iCISCF, the selection of individual CSFs is performed in each macroiteration. Since the selection is controlled by a single parameter $C_{\text{min}}$, both the size and members of the resulting $P_m$ space may change along macroiterations. Therefore, it is of first interest to see how the optimization of the active orbitals behaves. To this end, the lowest adiabatic singlet and triplet states of hexacene (six linearly fused benzene rings) are studied with CAS(26,26)/cc-pVDZ\cite{50} and $D_{2h}$ symmetry. As a matter of fact, identifying the restricted (open-shell) Hartree-Fock (R(O)HF) orbitals as initial guesses for iCISCF
is nontrivial for calculations with large active space. However, the pre-CMOs obtained by diagonalizing the molecular Fock matrix projected on the prechosen valence atomic orbitals or the localized pre-CMOs (pre-LMOs)\textsuperscript{35} can be employed to construct initial guess CMOs or LMOs for iCISCF calculations. Thus, in the calculations of hexacene, two different set of initial guess MOs, CMOs and LMOs, constructed by the iCAS method are used as initial guesses.

In both QN and JR+QN algorithms, the optimization of the active orbitals is turned off when the energy difference between two adjacent macroiterations is below the threshold $A_{\text{min}}$. The results with different $A_{\text{min}}$ setting are plotted in Fig. 2 where the energies without optimizing the active orbitals are taken as the zero points. It can be seen that both algorithms converge to essentially the same results for the same $A_{\text{min}}$, and a value of $1.0 \times 10^{-6} \, E_h$ is required for $A_{\text{min}}$ to get fully converged results. It is also seen from the Fig. 2 that the initial guess has a great effect on the convergence of iCISCF results. By using LMOs as initial guess, internal active space optimization is not as important as in the calculations with CMOs. Moreover, the calculations, with different initial MOs, do not always converge to the same results. For example, by setting $C_{\text{min}} = 5.0 \times 10^{-5}$ and $A_{\text{min}} = 1.0 \times 10^{-8}$, the triplet calculations with LMOs guesses deliver lower absolute iCISCF energies than those with CMOs do, which is as large as $6.8 \, mE_h$, although the final iCISCF(2) results are close to each other.

The numbers of macro- and microiterations in these calculations are further summarized in Table 1. The results show that JR+QN does outperform QN in general: QN requires somewhat more microiterations than JR+QN and even fails to converge within 200 macroiterations in two cases. When using a tight $A_{\text{min}}$ threshold, the JR+QN algorithm needs fewer macroiterations to converge for most cases. It can also be seen that using LMOs as initial guesses, the number of macroiterations reduces substantially, especially for calculations with the $C_{\text{min}} = 5.0 \times 10^{-4}$ setting. The triplet state calculations converge faster than that of singlet states. However, the calculations for singlet states
with \( C_{\text{min}} = 5.0 \times 10^{-5} \) and \( A_{\text{min}} = 1.0 \times 10^{-8} \) settings still need more than one hundred iterations. The convergence trends of the calculations with these settings optimized by QN and JR+QN algorithms are given in Fig. [3]. Within the region from \( 1.0 \times 10^{-3} \) to \( 1.0 \times 10^{-6} E_h \), all calculations converge slowly. This could be attributed to the coupling between active-active rotation and the CI coefficients.

In the present work, the JR+QN algorithm is used as the default algorithms for the iCISCF wave function optimization. The LMOs constructed by iCAS from the pre-LMOs are used as initial guesses for all calculations, if not otherwise specified. By default, \( A_{\text{min}} \) is chosen to be 100 times the energy convergence threshold, such that iCISCF has only one parameter, \( C_{\text{min}} \), to play.

![Convergence patterns of the iCISCF calculations of hexacene. The energies without active-active rotations are taken as zero points. For calculations not converged within 200 macroiterations, the iCISCF energies of the 201st cycle are used.](image)

(a) \( C_{\text{min}} = 5.0 \times 10^{-4} \)  
(b) \( C_{\text{min}} = 5.0 \times 10^{-5} \)
Table 1: Number of macroiterations (MA) of the iCISCF calculations of hexacene using the quasi-Newton (QN) and hybrid Jacobi rotation and QN algorithms (JR+QN) with CMOs and LMOs as initial guess, respectively. Averaged number of microiterations (MI) per macroiteration are given as well.

|                | C_{\text{min}} = 5.0 \times 10^{-4}^a | C_{\text{min}} = 5.0 \times 10^{-5}^a |
|----------------|--------------------------------------|--------------------------------------|
|                | Singlet MI | Triplet MI | Singlet MI | Triplet MI |
| w/o active-active rotations |                 |                   |             |             |
| CMOs           | 6 3.7 6 3.8 | 7 3.3 8 3.0      |             |             |
| QN             | 1.0 \times 10^{-2} | n.c.\(^c\) 7 5.0 6 6.2 8 5.1 | 1.0 \times 10^{-4} | 8 6.8 7 6.0 7 7.5 51 14.8 |
|                | 1.0 \times 10^{-6} | 128 11.1 133 12.0 174 12.4 78 14.5 |
|                | 1.0 \times 10^{-8} | 168 11.1 147 12.0 n.c.\(^c\) 12.3 80 14.6 |
| JR+QN          | 1.0 \times 10^{-2} | 8 3.6 6 4.0 7 3.6 7 3.7 | 1.0 \times 10^{-4} | 9 3.6 8 3.5 8 3.4 51 3.0 |
|                | 1.0 \times 10^{-6} | 125 3.4 123 3.1 173 2.3 72 2.7 |
|                | 1.0 \times 10^{-8} | 147 3.4 128 3.1 n.c.\(^c\) 2.3 78 2.7 |
| LMOs           | 6 5.3 6 5.5 6 6.0 12 3.3 |
| w/o active-active rotations |                 |                   |             |             |
| QN             | 1.0 \times 10^{-2} | 5 8.2 6 7.5 11 4.3 7 6.1 | 1.0 \times 10^{-4} | 9 12.0 11 10.1 11 7.5 14 9.0 |
|                | 1.0 \times 10^{-6} | 22 10.2 25 11.4 87 8.2 50 8.2 |
|                | 1.0 \times 10^{-8} | 28 8.8 34 10.4 154 5.7 82 5.5 |
| JR+QN          | 1.0 \times 10^{-2} | 6 6.2 6 6.0 8 5.0 7 5.3 | 1.0 \times 10^{-4} | 11 4.9 11 5.3 13 4.1 14 4.1 |
|                | 1.0 \times 10^{-6} | 19 3.9 13 5.2 89 1.9 46 2.5 |
|                | 1.0 \times 10^{-8} | 21 3.6 36 3.8 112 1.7 46 2.5 |

\(^a\) C_{\text{min}}: threshold for terminating the selection of individual configuration state functions.

\(^b\) A_{\text{min}}: threshold for terminating the active-active orbital rotations.

\(^c\) n.c.: not converged within 200 macroiterations.
Figure 3: The convergence trends of hexacene calculations using QN and JR+QN algorithms, with $C_{\text{min}} = 5.0 \times 10^{-5}$ and $A_{\text{min}} = 1.0 \times 10^{-8}$ settings, using LMOs as initial guesses.
3.2 Adiabatic singlet-triplet gaps of Polyacenes

The singlet-triplet (S-T) gaps of polyacenes have been studied by several groups using various methods tailored for large active spaces. To compare with such calculations, the adiabatic S-T gaps are recalculated with iCISCF and iCISCF(2) using the cc-pVDZ basis. The geometries of naphthalene and C$_{4n+2}$H$_{2n+4}$ ($n$=3-10) are taken from Refs. 52 and 28 respectively. The distributions of the orbitals in the irreducible representations (irrep) of $D_{2h}$ are given in Table 2. Interestingly, the increments of inactive orbitals in $B_{1g}$ and $B_{2u}$ are different for even and odd n-acenes. As a result, the HOMO and LUMO of even and odd n-acenes have different symmetries. The calculated energies of hexacene are given in Table 3. To make a close comparison with ASCISCF running with $10^6$ SDs, we also report the interpolated iCISCF and iCISCF(2) energies. It can be seen that iCISCF produces slightly lower absolute energies than ASCISCF does for both singlet and triplet state employing the same $P_m$ size. The deviation between the two methods at the variational level is about 3.4 kcal/mol for $^1A_g$ state and 1.74 kcal/mol for $^3B_u$ state. Presumably, this small discrepancy stems from spin contamination in ASCISCF, which is partly removed by the PT2 correction, thereby leading to a closer agreement between ASCISCF(2) and iCISCF(2) for the S-T gap, within 1.0 kcal/mol. The extrapolated S-T gaps by iCISCF(2) and ASCISCF(2) agree within 1.0 kcal/mol as well.

Table 2: Distributions of core and active orbitals of n-acenes in irreducible representations of $D_{2h}$

| n | active space | $A_g$ | $B_{3g}$ | $B_{2g}$ | $B_{1g}$ | $A_u$ | $B_{3u}$ | $B_{2u}$ | $B_{1u}$ |
|---|-------------|------|--------|--------|--------|------|--------|--------|--------|
| 5 | (22, 22)    |      |        |        |        |      |        |        |        |
|   | core active | 18   | 0      | 0      | 13     | 0    | 15     | 16     | 0      |
| 6 | (26, 26)    |      |        |        |        |      |        |        |        |
|   | core active | 21   | 0      | 5      | 0      | 5    | 0      | 0      | 6      |
|   | core active | 0    | 6      | 7      | 0      | 6    | 0      | 0      | 7      |
| 7 | (30, 30)    |      |        |        |        |      |        |        |        |
|   | core active | 24   | 0      | 0      | 18     | 0    | 20     | 22     | 0      |
|   | core active | 0    | 7      | 8      | 0      | 7    | 0      | 0      | 8      |

The absolute energies of n-acenes computed at iCISCF and iCISCF(2) level have been provided in the Supporting information (SI). The extrapolated iCISCF(2) S-T splittings
Table 3: iCISCF and iCISCF(2) energies (+994.0 \( E_h \)) of hexacene with CAS(26, 26)/cc-pVDZ

| \( C_{\min} \)     | \( N_{\text{CSF}}^a \) | \( N_{\text{SD}}^b \) | \( E_{\text{iCISCF}}^1 \) | \( A_g^1 \) | \( E_{\text{iCISCF(2)}} \) | \( N_{\text{CSF}}^a \) | \( N_{\text{SD}}^b \) | \( E_{\text{iCISCF}}^3 \) | \( B_{3u}^3 \) | Gap (kcal/mol) |
|---------------------|------------------------|------------------------|-------------------|--------|--------------------|------------------------|------------------------|-------------------|-------------|----------------|
| 1.0 \( \times 10^{-4} \) | 80618                  | 305351                 | -0.29320          | -0.30699 | 46057          | 200173              | -0.25549             | -0.27317         | 23.66        | 21.22         |
| 7.5 \( \times 10^{-5} \) | 128424                 | 495560                 | -0.29675          | -0.30901 | 197610         | 343609              | -0.26043             | -0.27586         | 22.79        | 20.80         |
| 5.0 \( \times 10^{-5} \) | 227406                 | 900944                 | -0.30084          | -0.31119 | 346020         | 612068              | -0.26517             | -0.27837         | 22.38        | 20.59         |
| 2.5 \( \times 10^{-5} \) | 577599                 | 2405533                | -0.30641          | -0.31407 | 875294         | 1593875             | -0.27174             | -0.28185         | 21.76        | 20.22         |
| Estimated \( ^c \)   |                        |                        | -0.31126          |         |                 | 1000000             | -0.26847             | -0.28012         | 20.46        | 19.54         |
| Extrapolated \( ^d \) | 3.7 \( \times 10^{12} \) | 2.7 \( \times 10^{13} \) | -0.32300          | 8.4 \( \times 10^{12} \) | 2.3 \( \times 10^{13} \) | -0.29345             |                        |                   | 18.53        |                |
| ASCISCF(2) \( ^e \) |                        |                        | -0.29562          | -0.30753 | -                 | 1000000             | -0.26570             | -0.27771         | 18.78        | 18.72         |
| Extrapolated          |                        |                        | -                 | -        | -                 | -                   |                        |                   | -              |                |

\( ^a \) Number of selected configuration state functions.

\( ^b \) Number of Slater determinants corresponding to \( N_{\text{CSF}} \).

\( ^c \) Estimated by linear fit of \( E_{\text{iCISCF}} \) or \( E_{\text{iCISCF(2)}} \) as function of \( \log_{10} N_{\text{SD}} \).

\( ^d \) \( N_{\text{CSF}}/N_{\text{SD}} \): total number of CSFs/SDs in the symmetry adapted CAS.

\( ^e \) Ref.\[28\]

The obvious deviations of iCISCF(2) from ASCISCF(2) should then be ascribed to dynamic correlation from the Q space that is accounted for by DSRG-MRPT2. For more details, the differences \( \Delta E_{\text{ST}} \) between the actually calculated and the extrapolated S-T gaps are further plotted in Fig. [5], which shows that \( \Delta E_{\text{ST}} \) becomes larger as the system size increases but can be reduced by decreasing \( C_{\min} \). However, even for the smallest \( C_{\min} \) (i.e., 2.5 \( \times 10^{-5} \)) used here, \( \Delta E_{\text{ST}} \) for decacene is still as large as 3.0 kcal/mol, which is to be compared with the extrapolated value of S-T gap, 5.2 kcal/mol. Therefore, predicting accurately the S-T gaps of decacene and beyond remains a challenge if the extrapolation step is not taken.
Figure 4: Extrapolated iCISCF(2) adiabatic S-T gaps of polyacenes with cc-pVDZ and cc-pVTZ, to compare with those by ASCI-CF(2)/cc-pVDZ and ACI(2)-DSRG-MRPT2/cc-pVTZ.\textsuperscript{52}
Figure 5: Differences ($\Delta E_{ST}$) between the calculated and extrapolated adiabatic S-T gaps of polyacenes by iCISCF(2)/cc-pVDZ.
3.3 Fe-porphyrin complex

Fe(II) porphyrin (FeP) complexes are another set of classic test systems for strongly correlated methods, due to both large active spaces and small energy gaps between different spin states. The free-base porphyrin already has 24 valence π orbitals. Therefore, considering the eight electrons and five 3d orbitals of Fe, a minimal active space of FeP would be as large as CAS(32, 29). Even so, the correct spin ordering still cannot be reproduced.

That $^3B_{1g}$ is lower than $^5A_g$ was only found by going to CAS(44, 44), which consists of additional Fe 4d4p4d and 4 × N 2p x 2p y. Realizing that CAS(44, 44) is not really rational, Levine et al. proposed to use CAS(40, 42), which includes Fe 4s4p4d and four σ lone pair orbitals of N coordinated to Fe on top of CAS(32, 29). To compare directly with these results, the iCISCF/cc-pVDZ calculations were performed with the $^3B_{1g}$ geometry for both $^3B_{1g}$ and $^5A_g$. The distributions of the orbitals of FeP in the irreps of $D_{2h}$ are given in Table 4. Upon convergence after 140 macroiterations of iCISCF-CAS(32, 29) with $C_{min} = 1.0 \times 10^{-4}$, close inspections reveal that 24 of the 29 active orbitals are indeed the valence π orbitals of porphyrin, but the remaining 5 are not all the expected Fe 3d. It can be seen clearly from Fig. 6 that in the case of $^5A_g$, the nearly doubly occupied 3d z2 orbital is pushed out of the active space, whereas a doubly occupied ligand orbital is rotated into the active space to correlate the singly occupied 3d x2−y2 orbital. For the $^3B_{1g}$ state, the converged active space does not contain the 3d x2−y2 orbital, which is pushed to the virtual space. Instead, the 4d z2 orbital enters the active space to incorporate the 3d z2 orbital. The five 3d orbitals can be kept inside the active space only by freezing the 3d z2 (3d x2−y2) orbital in the calculations of $^5A_g$ ($^3B_{1g}$).

The iCISCF-CAS(32, 29) energies are documented in Table 5. As the previous studies, the $^5A_g$ state is predicted to be the ground state. The extrapolated iCISCF(2) results are in good agreement with those from HCISCF(2) for both the total and relative energies. In contrast, the extrapolated energy gap by ASCISCF(2) is just half that by iCISCF(2) or HCISCF(2). This is mainly because the ASCISCF(2) energy for $^3B_{1g}$ is too
Table 4: Distributions of orbitals of FeP in irreducible representations of $D_{2h}$

| active space | core | active | \( A_g \) | \( B_{3g} \) | \( B_{2g} \) | \( B_{1g} \) | \( A_u \) | \( B_{3u} \) | \( B_{2u} \) | \( B_{1u} \) |
|-------------|------|--------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| (32, 29) | 23   | 0      | 0         | 14        | 0         | 19        | 19        | 2         |
| (40, 42) | 21   | 0      | 0         | 14        | 0         | 18        | 18        | 2         |
| (44, 44) | 21   | 0      | 0         | 14        | 0         | 17        | 17        | 2         |

Figure 6: The CAS(32, 29) active orbitals of (a) initial guess, (b) converged $^5A_g$, and (c) converged $^3B_{1g}$. The 24 valence $\pi$ orbitals of porphyrin are not shown.
low as compared with the iCISCF(2) one. Freezing the \(3d_{x^2-y^2}\) (\(3d_z^2\)) orbital inside the active space increases the energy of \(3B_{1g}\) (\(5A_g\)) by 3.6 (0.3) kcal/mol, thereby increasing the gap by 3.3 kcal/mol.

Table 5: iCISCF-CAS(32, 29) energies (+2245.0 \(E_h\)) of FeP \(^{a}\)

| \(C_{\text{min}}\) | \(N_{\text{CSF}}\) | \(N_{\text{SD}}\) | \(E_{\text{iCISCF}}\) | \(E_{\text{iCISCF}}\) | \(E_{\text{iCISCF}}\) | \(E_{\text{iCISCF}}\) | \(E_{\text{iCISCF}}\) | \(\text{Gap (kcal/mol)}\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.0 \(\times\) 10\(^{-4}\) | 103238 | 186387 | 0.02457 | 0.00983 | 108153 | 161556 | -0.00508 | -0.02113 | -18.61 | -19.43 |
| 7.5 \(\times\) 10\(^{-5}\) | 154932 | 284279 | 0.02144 | 0.00850 | 165285 | 249441 | -0.00860 | -0.02283 | -18.85 | -19.66 |
| 5.0 \(\times\) 10\(^{-5}\) | 271010 | 507312 | 0.01768 | 0.01709 | 296625 | 454698 | -0.01231 | -0.02413 | -18.82 | -19.48 |
| 2.5 \(\times\) 10\(^{-5}\) | 691268 | 1331168 | 0.01258 | 0.00474 | 774101 | 1211597 | -0.01777 | -0.02639 | -19.04 | -19.53 |
| Extrapolated | 1.7 \(\times\) 10\(^{14}\) | 5.0 \(\times\) 10\(^{14}\) | - | -0.0010 | 1.7 \(\times\) 10\(^{14}\) | 3.4 \(\times\) 10\(^{14}\) | - | -0.0323 | -19.64 |

| Extrapolated | 1.0 \(\times\) 10\(^{-4}\) | 106323 | 193856 | 0.02069 | 0.00467 | 109165 | 162983 | -0.00533 | -0.02149 | -16.33 | -16.41 |
| 7.5 \(\times\) 10\(^{-5}\) | 165932 | 307657 | 0.01723 | 0.00323 | 165971 | 250522 | -0.00858 | -0.02284 | -16.19 | -16.36 |
| 5.0 \(\times\) 10\(^{-5}\) | 296081 | 558728 | 0.01314 | 0.00152 | 302190 | 463045 | -0.01273 | -0.02455 | -16.23 | -16.36 |
| 2.5 \(\times\) 10\(^{-5}\) | 758072 | 1469095 | 0.00763 | -0.00077 | 785566 | 1228691 | -0.01818 | -0.02680 | -16.19 | -16.33 |
| Extrapolated | 1.7 \(\times\) 10\(^{14}\) | 5.0 \(\times\) 10\(^{14}\) | - | -0.0068 | 1.7 \(\times\) 10\(^{14}\) | 3.4 \(\times\) 10\(^{14}\) | - | -0.0328 | -16.36 |

HCISCF(2) \(^{c}\) | - | 533623 | 0.0224 | - | - | - | - | - | -12.80 | - |
| Extrapolated | - | - | - | -0.0049 | - | - | - | -0.0314 | - | -16.63 |

ASCISCF(2) \(^{d}\) | - | 500000 | -0.0022 | - | - | 500000 | -0.0191 | - | -10.60 | - |
| Extrapolated | - | - | - | -0.0186 | - | - | - | -0.0324 | - | -8.63 |

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\(^{a}\) See Table [3] for additional explanations.

\(^{b}\) The \(3d_{x^2-y^2}\) and \(3d_{z^2}\) orbitals are kept frozen in the active space when calculating \(5A_g\) and \(3B_{1g}\), respectively.

\(^{c}\) Ref. \(^{24}\)

\(^{d}\) Ref. \(^{27}\)

To compare with the HCISCF-CAS(44, 44) results,\(^{24}\) the iCISCF-CAS(44, 44) calculations were also performed. Except for the \(24\) \(\pi\) orbitals of porphyrin, the remaining active orbitals are plotted in Fig. S1 in the SI. It turns out that the Fe \(4d_{x^2-y^2}\) orbital is pushed out of the active space (in line with the previous observation\(^{27}\)), while the \(27^{\text{th}} A_g\) orbital, consisting mainly of Fe \(4s\) and N \(3p\), is pulled into the active space. The former can be viewed as the “anti-bonding” orbital of \(3d_{x^2-y^2}\) whereas the latter can be viewed as the “anti-bonding” orbital of the \(22^{\text{th}} A_g\), a lone pair orbital of four N atoms coordinate to Fe. It is better to put both \(4d_{x^2-y^2}\) and \(4s\) into the active space as in the case of CAS(40, 42). If only one of them is to be included, the Fe \(4s\) instead of \(4d_{x^2-y^2}\) orbital is favored for lower
energies. Again, we performed calculations by freezing the $4d_{x^2-y^2}$ orbital in the active space, see Fig. S2 for the converged $4d_{x^2-y^2}$ and $4d_z^2$ orbitals. The latter is slightly mixed with the $4s$ orbitals after optimization.

Table 6: iCISCF-CAS(44, 44) energies (+2245.0 $E_h$) of FeP $^a$

| $C_{\text{min}}$ | $N_{\text{CSF}}$ | $N_{\text{SD}}$ | $E_{\text{iCISCF}}$ | $E_{\text{iCISCF(2)}}$ | $E_{\text{HCISCF}}$ | $E_{\text{ASCISCF}}$ | Gap (kcal/mol) |
|------------------|------------------|----------------|---------------------|---------------------|---------------------|---------------------|----------------|
| $1.0 \times 10^{-4}$ | 197817 | 366295 | -0.133538 | -0.169007 | 179562 | 264701 | -0.135383 | -0.167162 | -1.16 | 1.16 |
| $7.5 \times 10^{-5}$ | 309455 | 582411 | -0.139264 | -0.171517 | 280883 | 419065 | -0.140490 | -0.169338 | -0.77 | 1.37 |
| $5.0 \times 10^{-5}$ | 574704 | 1103405 | -0.146524 | -0.174667 | 527665 | 800161 | -0.147107 | -0.172201 | -0.37 | 1.55 |
| $2.5 \times 10^{-5}$ | 1629683 | 3222519 | -0.156921 | -0.179173 | 1510972 | 2345179 | -0.156565 | -0.176247 | 0.22 | 1.84 |
| Extrapolated | $1.2 \times 10^{23}$ | $5.1 \times 10^{23}$ | - | -0.1963 | $1.4 \times 10^{23}$ | $3.9 \times 10^{23}$ | - | -0.1911 | - | 3.28 |
| $1.0 \times 10^{-4}$ | 199609 | 372869 | -0.15415 | -0.19010 | 180638 | 267708 | -0.14558 | -0.17787 | 5.38 | 7.67 |
| $7.5 \times 10^{-5}$ | 317682 | 603672 | -0.16021 | -0.19264 | 281562 | 422181 | -0.15082 | -0.18003 | 5.90 | 7.91 |
| $5.0 \times 10^{-5}$ | 587999 | 1138209 | -0.16752 | -0.19583 | 543338 | 828687 | -0.15784 | -0.18304 | 6.07 | 8.02 |
| $2.5 \times 10^{-5}$ | 1648308 | 3278017 | -0.17797 | -0.20037 | 1541226 | 2402169 | -0.16738 | -0.18716 | 6.64 | 8.29 |
| Extrapolated | $1.2 \times 10^{23}$ | $5.1 \times 10^{23}$ | - | -0.2174 | $1.4 \times 10^{23}$ | $3.9 \times 10^{23}$ | - | -0.2019 | - | 9.73 |
| HCISCF(2) $^c$ | - | 2133424 | -0.1567 | - | - | 1450271 | -0.1457 | - | 6.90 | - |
| Extrapolated | - | - | - | -0.1996 | - | - | - | -0.1965 | - | 1.93 |
| ASCISCF(2) $^d$ | - | 500000 | -0.2044 | - | - | 500000 | -0.2315 | - | -17.01 | - |
| Extrapolated | - | - | - | -0.2561 | - | - | - | -0.28688 | - | -19.27 |

$^a$ See Table 3 for additional explanations.
$^b$ The $4d_{x^2-y^2}$ orbitals are kept frozen in the active space.
$^c$ Ref. 24
$^d$ Ref. 27

The iCISCF-CAS(44, 44) energies are documented in Table 6. In all calculations with different $C_{\text{min}}$, the $3B_{1g}$ state is predicted to be the ground state. However, the presently extrapolated iCISCF(2) energy gap (9.7 kcal/mol) between $5A_g$ and $3B_{1g}$ is significantly larger than that (1.9 kcal/mol) by HCISCF(2).$^{24}$ The latter is even smaller than the gap (3.3 kcal/mol) obtained by iCISCF(2) with $4d_{x^2-y^2}$ frozen. Close inspections reveal that, although the HCISCF gap (6.9 kcal/mol) is very much the same as the iCISCF one (6.6 kcal/mol) with $C_{\text{min}} = 2.5 \times 10^{-5}$, the HCISCF energies for $5A_g$ and $3B_{1g}$ are actually close to the iCISCF ones with $C_{\text{min}} = 1.0 \times 10^{-4}$, given dramatic differences in the num-
bers of SDs. It can therefore be concluded that the HCISCF calculations\textsuperscript{24} are far from convergence. Note also that ASCISCF-CAS(44, 44)\textsuperscript{27} predicts much lower variational energies but still incorrect spin ordering, which was ascribed to spatial symmetry breaking. To investigate such symmetry-breaking effects, we repeated the calculations using $C_{2v}$ instead of $D_{2h}$. Indeed, localized symmetry-breaking active orbitals are observed (cf. Fig. S3), leading to lower energies than those with $D_{2h}$.

Some representative active orbitals from iCISCF-CAS(40, 42) calculations are plotted in Fig. S4. As can be seen from the energetics in Table 7, both iCISCF and iCISCF(2) predict the correct ground state with different $C_{\text{min}}$. And in this case, there exist perfect agreements between iCISCF and ASCISCF\textsuperscript{27} for both the extrapolated total and relative energies. Yet, rather unexpectedly, the iCISCF-CAS(40, 42) energies are even lower than the iCISCF-CAS(44, 44) ones (cf. Table 6), reflecting the importance of rational construction of active spaces (for which the iCAS method is a good choice).

| $C_{\text{min}}$ | $N_{\text{CSF}}$ | $N_{\text{SD}}$ | $E_{\text{iCISCF}}$ | $E_{\text{iCISCF(2)}}$ | $N_{\text{CSF}}$ | $N_{\text{SD}}$ | $E_{\text{iCISCF}}$ | $E_{\text{iCISCF(2)}}$ | Gap (kcal/mol) |
|-----------------|-----------------|--------------|-----------------|-----------------|-----------------|--------------|-----------------|-----------------|-----------------|
| $1.0 \times 10^{-4}$ | 199810 | 370332 | -0.15477 | -0.19185 | 176251 | 259571 | -0.15428 | -0.18806 | 0.31 | 2.38 |
| $7.5 \times 10^{-5}$ | 314006 | 591402 | -0.16086 | -0.19468 | 279206 | 416350 | -0.16002 | -0.19072 | 0.52 | 2.48 |
| $5.0 \times 10^{-5}$ | 595172 | 1143717 | -0.16882 | -0.19838 | 535154 | 811146 | -0.16738 | -0.19412 | 0.91 | 2.67 |
| $2.5 \times 10^{-5}$ | 1686557 | 3331667 | -0.18018 | -0.20369 | 1566899 | 2429062 | -0.17800 | -0.19907 | 1.37 | 2.90 |
| Estimated | - | 500000 | -0.1587 | - | - | 500000 | -0.1617 | - | -1.87 | - |
| Extrapolated | $7.3 \times 10^{21}$ | $3.0 \times 10^{22}$ | - | -0.2242 | $8.5 \times 10^{21}$ | $2.2 \times 10^{22}$ | - | -0.2173 | - | 4.34 |
| ASCISCF(2)\textsuperscript{b} | - | 500000 | -0.1671 | - | - | 500000 | -0.1699 | - | -1.76 | - |
| Extrapolated | - | - | - | -0.2208 | - | - | - | -0.2137 | - | 4.46 |

\textsuperscript{a} See Table 3 for additional explanations.
\textsuperscript{b} Ref.\textsuperscript{27}

### 3.4 A rational design of active space for Fe-porphyrin

Although the FeP complexes have been studied by many groups utilizing different active spaces, there are not many works explaining how their active spaces for FeP are designed.
It has been proved that the iCAS method developed by some of us is a useful tool to design and generate initial guess MOs for MCSCF calculations.\cite{35} In this section, we would like to design a few active spaces from small to large utilizing the iCAS algorithm. All initial guess MOs in this section are generated based on the ROHF wave function of $^5A_g$ state.

One of the smallest active space to describe various spin states of FeP is CAS(6, 5), which contains only the 3$d$ orbitals and electrons of Fe$^{2+}$. It has been proved that this small active space is not able to describe the strong interaction between Fe$^{2+}$ and porphyrin anion.\cite{57} More orbitals and electrons have to be included in the active space. By comparing the results of CAS(32, 29) and CAS(40, 42) in Sec. 3.3, it is evident that the $\pi$ orbitals of porphyrin do not influence the spin splitting of Fe$^{2+}$ as significantly as the ligand orbitals and $4s4p4d$ orbitals of Fe do. Usually, the ligand orbitals interact with the metal centre strongly. Thus, in the first step, the five 3$d$ orbitals of Fe, the 2$s$, 2$p_x$, 2$p_y$ orbitals of the four N atoms are used to generate pre-LMOs and the subsequent LMOs guesses for iCISCF calculations. Besides the five 3$d$ orbitals, 12 LMOs, eight doubly occupied MOs (DOMOs) and four virtual MOs, are generated by the iCAS as active MOs. In fact, not all the 12 LMOs are spatially close to the Fe$^{2+}$. By checking their coefficients, we found that only four doubly occupied LMOs are mixed with the atomic orbitals of Fe. The four ligand LMOs are exhibited in Fig. \ref{fig:LMOs} together with their significant MOs coefficients. If only the four LMOs and the Fe 3$d$ orbitals are considered as active MOs, the active space will be CAS(14,9). However, such an active space only contains DOMOs and SOMOs, and does not have any virtual orbitals to relax the electrons in the active space. By analyzing the coefficients of the four LMOs, another 3 atomic orbitals are added, the 4$s$, 4$p_x$ and 4$p_y$ orbital of Fe$^{2+}$. Thus, a CAS(14,12) active space is generated by the iCAS method. Moreover, to account for the doubles-shell effects, the 4$d$ orbitals of Fe atom could be considered, resulting in iCISCF-CAS(14,17) calculations.

Although the $\pi$ orbitals of porphyrin are not spatially adjacent to Fe$^{2+}$, some studies
showed that they do differentially stabilize the triplet states over quintet states of FeP.\textsuperscript{58}

For the low-lying excited states of FeP, the 24 $\pi$ orbitals are distributed to four different irreps of $D_{2h}$ symmetry, six $B_{3g}$ MOs (three DOMOs), six $B_{2g}$ MOs (three DOMOs), five $A_u$ MOs (two DOMOs), and seven $B_{1u}$ MOs (five DOMOs). To consider the influence of the $\pi$ orbitals, it may not be necessary to include all 24 $\pi$ MOs in the active space. In principle, the $\pi$ orbitals with close energies as the HOMO and LUMO, should interact with the Fe$^{2+}$ more strongly. Thus, the 24 $\pi$ LMOs, constructed from the pre-LMOs, are recanonicalized based on their Fock matrix (the Fock matrix of DOMOs or virtual MOs are diagonalized separately), which is called regional LMOs. After the canonicalization, the eigenvalues of the Fock matrix within each subspace can be considered as approximate orbital energies. The 24 $\pi$ regional LMOs with their irreps and energies are given in Fig. 8. Thus, for the first step, ten orbitals (from the 9$^{th}$ to 18$^{th}$ MOs in Fig. 8) are added to the CAS(14,17) active space, including two $B_{3g}$ MOs (one DOMO), two $B_{2g}$ MOs (one DOMO), two $A_u$ MOs (one DOMO), and four $B_{1u}$ MOs (two DOMOs). Moreover, we found that the orbital dominated by the 4$p_z$ orbital of Fe with $B_{1u}$ symmetry has lower orbital energy than the frontier virtual $\pi$ orbital in Fig. 8 (the 14$^{th}$ MO), which could be included in the active space as well. Thus, two sets of guess MOs with and without the 4$p_z$ orbital of Fe centre, CAS(14,28) and CAS(14,27), are generated as well. To consider the influence of more $\pi$ orbitals, another seven orbitals (from the 5$^{th}$ to 8$^{th}$ and from 19$^{th}$ to 21$^{th}$ in Fig. 8) could be taken into account. Thus, on top of CAS(24,28), eight more electrons and seven more active MOs are added to the active space, resulting in iCISCF-CAS(32,35) calculations. Finally, by adding the remaining valence $\pi$ orbital of porphyrin to the active space, we arrive at the active space proposed by Levine and coworkers, CAS(40,42). The distribution of the core and active orbitals of calculations with the above mentioned seven different active spaces are given in Table 8.

Using all active spaces in Table 8, the $^3A_{2g}$ ($^3B_{1g}$ in $D_{2h}$), $^3E_g$ ($^3B_{2g}+^3B_{3g}$ in $D_{2h}$) and $^5A_{1g}$ ($^5A_g$ in $D_{2h}$) state of FeP are computed. Note that for the Cartesian coordinates of-
ferred by Groenhof and coworkers, the $D_{4h}$ symmetry is not applied during the geometry optimization. Thus, the degenerate $^3E_g$ state is split to two states in $D_{2h}$ symmetry, $^3B_{2g}$ and $^3B_{3g}$. The three triplet and one quintet states computed using various active space are given in Table 9. The results show that with the two smallest active space, CAS(6,5) and CAS(14,12), the $^5A_g$ state is predicted to be the ground state. Thus, to include only the ligand orbitals in the active space, the triplet states are not stabilized over the quintet state very much. However, by taking into account the double-shell effects (iCISCF-CAS(14,17) results in Table 8), the $^5A_g - ^3B_{1g}$ splitting amounts to -0.55 kcal/mol. Compared to that with CAS(14,12), the $^5A_g - ^3B_{1g}$ gap increases 13.90 kcal/mol. Moreover, the excitation energies of $^3B_{2g}$ and $^3B_{3g}$ state with respect to the $^3B_{1g}$ state are close to that delivered by the iCISCF-CAS(40,42) calculations as well. Thus, it is the five $4d$ orbitals destabilizing the quintet states with respect to the $^3B_{1g}$ state more significantly.

To include some $\pi$ orbitals of porphyrin or the $4p_z$ orbital of Fe in the active space, iCISCF results using four different active spaces are reported in Table 8 as well. Compared to CAS(24,27), the relative energies computed by iCISCF-CAS(24,28) are in good agreement with the most accurate ones, iCISCF-CAS(40,42). The deviations of excitation energies computed by the extrapolated iCISCF results are less than 1.0 kcal/mol. Further increase the active space to CAS(32,35), more accurate $^5A_g - ^3B_{1g}$ gaps are predicted. However, the relative energies of $^3B_{2g}$ and $^3B_{3g}$ states with respect to the $^3B_{1g}$ state are getting worse. Nevertheless, the absolute deviations of extrapolated results are still less than 1.0 kcal/mol with respect to the iCISCF-CAS(40,42) results.

The results in Table 8 show that the $4d$ orbitals are the most important to differentially stabilize the triplet states over the $^5A_g$ state. Although the $\pi$ orbitals of porphyrin are essential to deliver correct spin ordering, it may not be necessary to take all the 24 $\pi$ orbitals into consideration. The active space CAS(24,28) can already predict qualitatively correct results for the four states, which could be used as starting points for the subsequent dynamic calculations.
Table 8: Distributions of orbitals of FeP in irreducible representations of $D_{2h}$ for some iCISCF calculations

| active space    | $A_g$ | $B_{3g}$ | $B_{2g}$ | $B_{1g}$ | $A_u$ | $B_{3u}$ | $B_{2u}$ | $B_{1u}$ |
|-----------------|-------|----------|----------|----------|-------|----------|----------|----------|
| (6, 5) core     | 23    | 3        | 3        | 14       | 2     | 19       | 19       | 7        |
| active          | 2     | 1        | 1        | 1        | 0     | 0        | 0        | 0        |
| (14, 12) core   | 21    | 3        | 3        | 14       | 2     | 18       | 18       | 7        |
| active          | 5     | 1        | 1        | 1        | 0     | 2        | 2        | 0        |
| (14, 17) core   | 21    | 3        | 3        | 14       | 2     | 18       | 18       | 7        |
| active          | 7     | 2        | 2        | 2        | 0     | 2        | 2        | 0        |
| (24, 27) core   | 21    | 2        | 2        | 14       | 1     | 18       | 18       | 5        |
| active          | 7     | 4        | 4        | 2        | 2     | 2        | 2        | 0        |
| (24, 28) core   | 21    | 2        | 2        | 14       | 1     | 18       | 18       | 5        |
| active          | 7     | 4        | 4        | 2        | 2     | 2        | 2        | 5        |
| (32, 35) core   | 21    | 1        | 1        | 14       | 0     | 18       | 18       | 4        |
| active          | 7     | 6        | 6        | 2        | 4     | 2        | 2        | 6        |
| (40, 42) core   | 21    | 0        | 0        | 14       | 0     | 18       | 18       | 2        |
| active          | 7     | 8        | 8        | 2        | 5     | 2        | 2        | 8        |

Figure 7: The four ligand orbitals close to the Fe centre. Their significant MO coefficients are listed as well.
Figure 8: The 24 \( \pi \) regional LMOs of porphyrin constructed by the iCAS method, ordered by their orbital energies (in \( E_h \)).
Table 9: The energies of lowest $^3B_{1g}$ state of FeP (in $E_h$) using seven different active spaces, the relative energies of $^3B_{2g}$, $^3B_{3g}$, and $^5A_g$ state w.r.t. the $^3B_{1g}$ state are given in kcal/mol

| $C_{min}$  | $^3B_{1g}$ | $E_{ICISCF}$ | $^3B_{2g}$ | $E_{ICISCF}(2)$ | $^3B_{3g}$ | $^5A_g$ | $E_{ICISCF}$ | $^5A_g$ | $^3B_{1g}$ | $E_{ICISCF}$ | $^5A_g$ |
|-----------|-----------|-------------|-----------|----------------|-----------|--------|-------------|--------|-----------|-------------|--------|
| 1.0 $\times$ 10^{-4} | -2244.72472 | 4.33 | 4.19 | -17.55 | -2244.72472 | 4.33 | 4.19 | -17.55 | -2244.72472 | 4.33 | 4.19 | -17.55 |
| 0.0 | -2244.72472 | 4.33 | 4.19 | -17.55 | -2244.72472 | 4.33 | 4.19 | -17.55 | -2244.72472 | 4.33 | 4.19 | -17.55 |
| 1.0 $\times$ 10^{-4} | -2244.76054 | -0.06 | -0.24 | -14.45 | -2244.76057 | -0.08 | -0.26 | -14.45 | -2244.76057 | -0.08 | -0.26 | -14.45 |
| 0.0 | -2244.76057 | -0.08 | -0.26 | -14.45 | -2244.76057 | -0.08 | -0.26 | -14.45 | -2244.76057 | -0.08 | -0.26 | -14.45 |
| 1.0 $\times$ 10^{-4} | -2244.86467 | 1.94 | 1.68 | -0.74 | -2244.86554 | 1.80 | 1.54 | -0.58 | -2244.86554 | 1.80 | 1.54 | -0.58 |
| 7.5 $\times$ 10^{-5} | -2244.86487 | 1.90 | 1.63 | -0.67 | -2244.86556 | 1.80 | 1.54 | -0.57 | -2244.86556 | 1.80 | 1.54 | -0.57 |
| 5.0 $\times$ 10^{-5} | -2244.86507 | 1.86 | 1.60 | -0.65 | -2244.86558 | 1.80 | 1.53 | -0.57 | -2244.86558 | 1.80 | 1.53 | -0.57 |
| 2.5 $\times$ 10^{-5} | -2244.86532 | 1.84 | 1.58 | -0.60 | -2244.86559 | 1.80 | 1.53 | -0.57 | -2244.86559 | 1.80 | 1.53 | -0.57 |
| Extrapolated | - | - | - | - | -2244.86562 | 1.79 | 1.54 | -0.55 | -2244.86562 | 1.79 | 1.54 | -0.55 |
| 1.0 $\times$ 10^{-4} | -2244.98960 | 2.14 | 1.76 | 1.79 | -2244.99602 | 1.95 | 1.56 | 2.79 | -2244.99602 | 1.95 | 1.56 | 2.79 |
| 7.5 $\times$ 10^{-5} | -2244.99090 | 2.32 | 1.88 | 1.98 | -2244.99634 | 2.02 | 1.61 | 2.86 | -2244.99634 | 2.02 | 1.61 | 2.86 |
| 5.0 $\times$ 10^{-5} | -2244.99233 | 2.16 | 1.76 | 2.17 | -2244.99668 | 1.95 | 1.56 | 2.91 | -2244.99668 | 1.95 | 1.56 | 2.91 |
| 2.5 $\times$ 10^{-5} | -2244.99420 | 2.06 | 1.65 | 2.45 | -2244.99706 | 1.89 | 1.51 | 2.97 | -2244.99706 | 1.89 | 1.51 | 2.97 |
| Extrapolated | - | - | - | - | -2244.99792 | 1.81 | 1.44 | 3.17 | -2244.99792 | 1.81 | 1.44 | 3.17 |
| 1.0 $\times$ 10^{-4} | -2245.09504 | 2.57 | 2.08 | 1.85 | -2245.00255 | 2.36 | 1.86 | 2.99 | -2245.00255 | 2.36 | 1.86 | 2.99 |
| 7.5 $\times$ 10^{-5} | -2245.09656 | 2.78 | 2.27 | 2.09 | -2245.00297 | 2.45 | 1.94 | 3.07 | -2245.00297 | 2.45 | 1.94 | 3.07 |
| 5.0 $\times$ 10^{-5} | -2245.09827 | 2.62 | 2.15 | 2.32 | -2245.00343 | 2.37 | 1.89 | 3.15 | -2245.00343 | 2.37 | 1.89 | 3.15 |
| 2.5 $\times$ 10^{-5} | -2245.00052 | 2.50 | 2.02 | 2.63 | -2245.00395 | 2.31 | 1.83 | 3.22 | -2245.00395 | 2.31 | 1.83 | 3.22 |
| Extrapolated | - | - | - | - | -2245.00516 | 2.21 | 1.75 | 3.47 | -2245.00516 | 2.21 | 1.75 | 3.47 |
| 1.0 $\times$ 10^{-4} | -2245.15477 | 4.21 | 3.94 | 0.31 | -2245.19185 | 3.11 | 2.78 | 2.38 | -2245.19185 | 3.11 | 2.78 | 2.38 |
| 7.5 $\times$ 10^{-5} | -2245.16086 | 3.60 | 3.29 | 0.52 | -2245.19468 | 3.05 | 2.67 | 2.48 | -2245.19468 | 3.05 | 2.67 | 2.48 |
| 5.0 $\times$ 10^{-5} | -2245.16882 | 3.48 | 3.14 | 0.91 | -2245.19838 | 2.88 | 2.50 | 2.67 | -2245.19838 | 2.88 | 2.50 | 2.67 |
| 2.5 $\times$ 10^{-5} | -2245.18018 | 3.29 | 2.95 | 1.37 | -2245.20369 | 2.79 | 2.38 | 2.90 | -2245.20369 | 2.79 | 2.38 | 2.90 |
| Extrapolated | - | - | - | - | -2245.22419 | 2.57 | 1.99 | 4.34 | -2245.22419 | 2.57 | 1.99 | 4.34 |

$^a$ See Table 3 for additional explanations.
4 Conclusions and Outlook

A nearly exact CASSCF approach, iCISCF, has been proposed to treat strongly correlated systems that are beyond the capability of CASSCF. It combines the selected iCI for the active space solver and the hybrid JR+QN algorithm for orbital optimization. Upon convergence, an inner-space second-order perturbation step (i.e., iCISCF(2)) can further be taken to improve the energy estimate. The current implementation of iCISCF/iCISCF(2) can handle ca. 50 active orbitals in conjunction with more than 1000 basis functions, as shown by the showcases of polyacenes and Fe(II)-porphyrin. Further developments of iCISCF will include (1) the use of iCAS for automatic construction and localization of CAS, (2) extrapolation/interpolation schemes for speedup of orbital optimization, (3) analytic energy gradients (which are operationally precisely the same as those of CASSCF), and (4) stochastic treatment of dynamic correlation from the complementary space Q.

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Data Availability Statement

The data that supports the findings of this study are available within the article.
A Orbital gradients and diagonal Hessian

By virtue of the basic commutator

$$\left[ \hat{E}_{pq}, \hat{E}_{rs} \right] = \delta_{qr} \hat{E}_{ps} - \delta_{ps} \hat{E}_{rq},$$  \hspace{1cm} (A.1)

the following commutators can be derived

$$\left[ \hat{E}_{pq}, \hat{H} \right] = (1 - P_{pq}c.c.) \sum_{\sigma} a_{pr}^{\dagger}[a_{qr}, H]$$ \hspace{1cm} (A.2)

$$\left[ \hat{E}_{pq}, \hat{H} \right] = \left\{ \hat{E}_{pr} h_{rq} + \hat{e}_{pr, st} g_{rq, st} \right\} - \left\{ h_{pr} \hat{E}_{rq} + g_{pr, st} \hat{e}_{rq, st} \right\},$$ \hspace{1cm} (A.3)

$$\left[ \hat{E}_{pq}, \hat{H} \right] = [\hat{E}_{pq}, \hat{H}] + c.c.$$ \hspace{1cm} (A.4)

$$\left[ \hat{E}_{pq}, \hat{H} \right] = \left\{ (\hat{E}_{pr} + \hat{E}_{rp}) h_{rq} + (\hat{e}_{pr, st} + \hat{e}_{rp, st}) g_{rq, st} \right\}$$

$$\left[ \hat{E}_{pq}, \hat{H} \right] = \left\{ h_{pr} (\hat{E}_{rq} + \hat{E}_{qr}) + g_{pr, st} (\hat{e}_{rq, st} + \hat{e}_{qr, st}) \right\},$$ \hspace{1cm} (A.5)

in terms of which the orbital gradients (15), the $\hat{H}_k$ Hamiltonian (27), and the sigma vectors (31) and (32) can readily be obtained. Further in view of the following identities

$$D_{ip} = 2\delta_{ip},$$ \hspace{1cm} (A.6)

$$\Gamma_{pq,ij} = 2\delta_{ij} D_{pq} - \delta_{iq} D_{pj},$$ \hspace{1cm} (A.7)

$$\Gamma_{pi,jq} = 4\delta_{ip}\delta_{jq} - \delta_{ij} D_{pq},$$ \hspace{1cm} (A.8)
the explicit expressions for the orbital gradients (15) and the diagonal elements of the
orbital Hessian (24) (which are required by the BFGS algorithm) can readily be derived

\[ G_{ia}^0 = 4f_{ia}^c + 4f_{ia}^a, \]  
\[ G_{it}^0 = 4f_{it}^c + 4f_{it}^a - 2F_{ti}, \]  
\[ G_{ia}^0 = 2F_{ia}, \]  
\[ G_{ut}^0 = 2(F_{ut} - F_{tu}), \]  
\[ E_{ia,ia}^{oo} = 4\{f_{ia}^c + f_{ia}^a - f_{ii}^c - f_{ii}^a + 3K_{aa}^{ii} - J_{aa}^{ii}\}, \]  
\[ E_{it,it}^{oo} = 4\{f_{it}^c + f_{it}^a - f_{ii}^c - f_{ii}^a + \frac{1}{2}f_{tt}^c D_{tt} - \frac{1}{2}F_{tt}\} \]
\[ + \sum_u (\delta_{iu} - D_{tu})(3K_{iu}^{ii} - J_{tu}^{ii}) + \frac{1}{2} \sum_{u,v} J_{ii}^{uv} P_{tt}^{uv} + \sum_{u,v} K_{ii}^{uv} Q_{tt}^{uv}\}, \]  
\[ E_{ia,ia}^{oo} = 4\{\frac{1}{2}D_{tt}f_{aa}^c + \frac{1}{2} \sum_{u,v} P_{tt}^{uv} J_{aa}^{uv} + \sum_{u,v} Q_{tt}^{uv} K_{aa}^{uv} - \frac{1}{2}F_{tt}\}, \]  
\[ E_{iu,it}^{oo} = 2(1 + P_{iu}) W_{iu,it} - 4W_{iu,it} - 2(F_{tt} + F_{uu}), \quad \forall t > u, \]  

where

\[ f_{pq}^c = h_{pq} + \sum_i (2j_{pq}^{ii} - K_{pq}^{ii}), \]  
\[ f_{pq}^a = \sum_{u,t} (J_{pq}^{tu} - \frac{1}{2} K_{pq}^{tu}) D_{ut}, \]  
\[ F_{pp} = \sum_v D_{uv} f_{vp}^{pc} + \sum_{u,v} P_{uu}^{uv} f_{vp}^{pc}, \]  
\[ W_{iu,it} = D_{it} f_{au}^c + \sum_{rs} P_{it}^{rs} f_{uu}^c + 2 \sum_{rs} Q_{iu}^{rs} K_{uu}^{st}, \]  
\[ W_{iu,it} = D_{it} f_{ut}^c + \sum_{rs} P_{it}^{rs} f_{ut}^c + 2 \sum_{rs} Q_{iu}^{rs} K_{ut}^{st}, \]  
\[ Q_{tu}^{vv} = \frac{1}{2} (\Gamma_{tv,uw} + \Gamma_{vt,uw}) = Q_{tu}^{vw}, \]  
\[ K_{pq}^{rs} = g_{pr, sq} = K_{qp}^{sr}. \]
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automatic selection and localization of active orbitals by iCAS

- do selected iCI
- converged?
- Yes
- No
- generate RDMs
- JR update of $\kappa_{tr}$
- BFGS update of $\kappa_{at}$, $\kappa_{tt}$, $\kappa_{tt}$
- update MOs and integrals