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Journal

The Journal of chemical physics, 141(4)

ISSN

0021-9606

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Publication Date

2014-07-01

DOI

10.1063/1.4889918

Peer reviewed

Increasing spin-flips and decreasing cost: Perturbative corrections for external singles to the complete active space spin flip model for low-lying excited states and strong correlation

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Abstract

An approximation to the spin-flip extended configuration interaction singles (SF-XCIS) method is developed using a second-order perturbation theory approach. In addition to providing significant efficiency advantages, the new framework is general for an arbitrary number of spin-flips, with the current implementation being applicable for up to around 4 spin-flips. Two new methods are introduced: one which is developed using non-degenerate perturbation theory, SF-CAS(S), and a second quasidegenerate perturbation theory method, SF-CAS(S)₁. These two approaches take the spin-flip complete active-space (SF-CAS) wavefunction as the reference, and then perturbatively includes the effect of single excitations. For the quasidegenerate perturbation theory method, SF-CAS(S)₁, the subscripted “1” in the acronym indicates that a truncated denominator expansion is used to obtain an energy-independent down-folded Hamiltonian. We also show how this can alternatively be formulated in terms of an extended Lagrangian, by introducing an orthonormality constraint on the first-order wavefunction. Several numerical examples are provided, which demonstrate the ability of SF-CAS(S) and SF-CAS(S)₁ to describe bond dissociations, singlet-triplet gaps of organic molecules, and exchange coupling parameters for binuclear transition metal complexes.

I. INTRODUCTION

One of the central interests in quantum chemistry is the computationally efficient recovery of electron correlation which is lost in the mean-field Hartree-Fock (HF) approximation. This electron correlation is usually defined as the energy difference between the full configuration interaction (CI) energy and the HF energy. At least conceptually, the electron correlation can be divided into two contributing components: *dynamical correlation* which refers to the energy stabilization that occurs when two electrons are allowed to avoid each other explicitly, and *strong correlation* (or static correlation) which refers to the complete breakdown of the mean-field approach due to near degeneracies. Strong correlation arises when multiple electronic configurations are needed to obtain even a qualitatively correct picture.

While many clear-cut strategies exist for recovering dynamical correlation, such as configuration interaction (CI), coupled cluster theory (CC), and many-body perturbation theory (MBPT),¹⁻⁴ methods capable of systematically describing strong correlation have been far more elusive. Most successful approaches to this problem are true multireference methods which use reference orbitals optimized for multiple electronic configurations, with the most popular of these approaches being the complete active-space self-consistent field theory (CASSCF and CASPT2).⁵ More recently, other approaches have been developed such as pairing theories based on coupled-cluster theory,⁶⁻¹³ density matrix renormalization theory,¹⁴⁻¹⁷ reduced density matrix theory,¹⁸⁻²⁰ and improved antisymmetric geminal power wavefunctions.²¹

The spin-flip family of methods provide a relatively simpler, single reference strategy for tackling strong correlation.²²⁻²⁵ Spin-flip is a CI approach in which the excitation operators not only promote electrons into unoccupied orbitals, but also changes their spin function from α to β . The reference orbitals are obtained from a Hartree-Fock (UHF/ROHF) calculation for the high-spin configuration, which is often easily described with a single determinant.⁷¹ This avoids, entirely, the challenge of multiconfigurational orbital optimization. Furthermore, the resulting low-spin basis determinants are treated in a more balanced manner. This is easily seen by considering a single σ -bond dissociation. In the conventional approach, the $|\sigma\bar{\sigma}\rangle$ configuration is taken as the reference. Both single and double excitations to this reference are thus required to generate the $|\sigma\sigma^*\rangle$, $|\sigma^*\bar{\sigma}\rangle$, and $|\sigma^*\sigma^*\rangle$ determinants needed for proper bond-breaking. In contrast, all four of these determinants are obtained

from a *single* spin-flip excitation from a high-spin configuration, $|\sigma\sigma^*\rangle$. Expanding the bare Hamiltonian in the basis of determinants obtained from SF excitation operators yields the SF-CI methods.^{23–26} Alternatively, the high-spin similarity transformed Hamiltonian can be used to yield the spin-flip coupled cluster methods.^{24,27}

Although the SF methods have been useful in studying strongly correlated problems, the spin asymmetry of the reference introduces spin-contamination, which can become quite large in magnitude. Sears et al. provided an initial solution to this with the spin-complete spin-flip configuration interaction singles (SC-SF-CIS) method.²⁸ While SC-SF-CIS successfully removed spin-contamination, certain excitations were still absent, and the SF-XCIS method was introduced to correct this.²⁹

SF-XCIS contains all the excitations that make up SF-CIS, but with additional double and triple excitations which provide spin-pure wavefunctions. For the one spin-flip case (1SF), for which SF-XCIS is defined, the additional configurations increase the computational cost relative to SF-CIS by a factor of about 13. If the SF-XCIS were to be extended to larger number of spin-flips, relative computational cost would, however, increase.

To enable multiple spin-flips in a spin-pure fashion, while maintaining computational efficiency, the Restricted Active-Space with n -spin-flips (RAS- n SF) method was developed.^{30–32} RAS- n SF contains all n -spin-flipping excitations within an orbital active-space, in addition to all possible single excitations from the doubly occupied orbitals into the active-space, and from the active space into the virtual orbitals. For the 1SF case, the RAS-1SF wavefunction is a subset of the SF-XCIS wavefunction, such that all direct excitations from doubly occupied to virtual orbitals are neglected, which reduces the computational cost substantially. The RAS- n SF method is defined and implemented for an arbitrary number of spin-flip cases, and has been demonstrated to provide qualitative accuracy for a number of strongly correlated problems.^{30,32–38}

In a recent paper, referred to throughout as Paper I,³⁹ we introduced an approximation, termed SF-CAS(h,p)₁, to simplify the RAS- n SF method. By treating the excitations into and out of the active space with perturbation theory, the SF-CAS(h,p)₁ method provides a simplification to the RAS- n SF approach. Speedups of several orders of magnitude were obtained, with little loss of accuracy.

RAS- n SF and SF-CAS(h,p)₁ are active-space methods, so a definition for the active-space orbitals must be supplied by the user. However, unlike conventional active-space

methods, there is a default, almost "black-box", choice for the active-space: the singly occupied orbitals of the high spin ROHF reference. Unfortunately, there are examples where this default, minimal active space was not sufficient for qualitative accuracy, and larger active-spaces had to be defined.³⁰ This is a result of missing electronic excitations which are included by increasing the active-space. One way to maintain the minimal active-space would be to increase the number of excitations outside of the active-space. SF-XCIS provides a definition of the minimal additional set of excitations, which include the direct "singles-like" excitations from doubly occupied to virtual levels. However, this method would not only be comparatively expensive, but has also only been defined and implemented for a single spin-flip.

The motivation for this paper is thus three-fold. We aim to develop a method which: (a) is general for arbitrary number of spin-flips, (b) improves the performance for the minimal, default active-space (c) maintains relative computational efficiency. To this end, we present a method which can equivalently be considered either as an extension of SF-CAS(h,p)₁ to include all single-excitations, or as a perturbative approximation to a generalized n SF-XCIS method. The current method is defined in the following section.

II. THEORY

Being a truncated CI method, the SF-XCIS wavefunction is a linear combination of determinants whose expansion coefficients are variationally optimized. To discuss this method explicitly, we first divide the orbital space into doubly-occupied, singly-occupied, and virtual orbital blocks. We use I, J and i, j as indices for occupied orbitals in the doubly-occupied and singly-occupied orbital blocks, respectively. Analogously, a, b and A, B denote unoccupied orbitals in the singly-occupied and virtual orbital blocks, respectively. The SF-XCIS determinant expansion can then be written as:

$$\begin{aligned} |\Psi^{\text{SF-XCIS}}\rangle = & (a_i^{\bar{a}} \hat{r}_i^{\bar{a}} + a_I^{\bar{a}} \hat{r}_I^{\bar{a}} + a_{i\bar{I}}^{\bar{a}\bar{b}} \hat{r}_{i\bar{I}}^{\bar{a}\bar{b}} + a_i^{\bar{A}} \hat{r}_i^{\bar{A}} \\ & + a_{ij}^{\bar{a}A} \hat{r}_{ij}^{\bar{a}A} + a_I^{\bar{A}} \hat{r}_I^{\bar{A}} + a_{iI}^{\bar{a}A} \hat{r}_{iI}^{\bar{a}A} \\ & + a_{i\bar{I}}^{\bar{a}\bar{A}} \hat{r}_{i\bar{I}}^{\bar{a}\bar{A}} + a_{ij\bar{I}}^{\bar{a}\bar{b}A} \hat{r}_{ij\bar{I}}^{\bar{a}\bar{b}A}) |^3\phi^{\text{ROHF}}\rangle \end{aligned} \quad (1)$$

where an unrestricted orbital notation is used (orbitals are, however, still ROHF), with β orbitals being distinguished from α using an overbar, and implicit summation is assumed over repeated indices.

If the above determinant expansion is reduced to include only true single excitations, $\hat{r}_i^{\bar{a}}$, $\hat{r}_I^{\bar{a}}$, $\hat{r}_i^{\bar{A}}$, and $\hat{r}_I^{\bar{A}}$, the SF-CIS method would be recovered. The double and triple excitations are, however, necessary for obtaining proper spin eigenstates.

By labelling the doubly occupied orbitals as “holes (h)” and virtual orbitals as “particles (p)”, the determinants in the above expansion can then be categorized based on the number of hole and particle indices:

$$\begin{aligned} |\Psi^{\text{nSF-XCIS}}\rangle = & \sum_A c_A \phi_A + \sum_h c_h \phi_h + \sum_p c_p \phi_p \\ & + \sum_{hp} c_{hp} \phi_{hp}, \end{aligned} \quad (2)$$

where ϕ_h , ϕ_p , and ϕ_{hp} correspond to the full set of low-spin configurations with 1 hole, 1 particle, or 1 hole and 1 particle, respectively. Neglect of the ϕ_{hp} determinants in Eq. 2 reduces to the RAS- n SF wavefunction. Just as RAS- n SF can be considered as a spin-flip variant of a difference dedicated CI method, DDCI1,^{40,41} the generalized n SF-XCIS method can likewise be thought of as a spin-flip version of CAS+S.⁴²

As mentioned above, the n SF-XCIS method would be useful as either a generalization of the SF-XCIS method for multiple strongly correlated electrons, or as a more accurate extension of RAS- n SF. However, the computational cost of this method would be considerably higher. In order to include the effect of the ϕ_{hp} determinants, but at a much reduced computational cost, we now develop a perturbative approximation to the n SF-XCIS method just discussed.

Using the Löwdin partitioning technique,^{43–45} we can divide up the n SF-XCIS determinant space into a small but important *model space* (A) and a larger but less-important *external space* (X). As was done in Paper I³⁹, we regroup the resulting Schrödinger equation into two separate equations, and down-fold the effect of the external space into an energy-dependent effective Hamiltonian.

$$\mathcal{H}_{AA,s}(E_s) = \mathbf{H}_{AA} + \mathbf{H}_{AX} [E_s - \mathbf{H}_{XX}]^{-1} \mathbf{H}_{XA} \quad (3)$$

The model space, A , consists of all determinants obtained by distributing the $n^\alpha + n^\beta$ electrons among the active-space orbitals. This is the SF-CAS-CI space and is denoted by ϕ_A . The external space, X , consists of the remaining determinants, ϕ_h , ϕ_p , and ϕ_{hp} .

Although the exact energy E_s can be obtained by diagonalizing this energy-dependent

effective Hamiltonian, the formation of $\mathcal{H}_{AA,s}$ is more expensive than the original CI problem, since it requires iteratively inverting the large $\mathbf{H}_{XX}$ block of the Hamiltonian for each state.

Assuming that the states of interest are primarily composed of model space determinants (a statement often true for low-lying excited states and strongly correlated states), we can use the following perturbative expansion of the Hamiltonian:

$$\begin{aligned}\bar{\mathbf{H}} &= \mathbf{H} - E_0^{(0)} \mathbf{I} \\ &= \bar{\mathbf{H}}^{(0)} + \lambda \bar{\mathbf{H}}^{(1)}\end{aligned}\tag{4}$$

$$\bar{\mathbf{H}}^{(0)} = \left(\begin{array}{c|c} \hat{H} - \langle |\hat{H}| \rangle & 0 \\ \hline 0 & \hat{F} - \langle |\hat{F}| \rangle + \eta \end{array} \right)\tag{5}$$

$$\bar{\mathbf{H}}^{(1)} = \left(\begin{array}{c|c} 0 & \hat{V} \\ \hline \hat{V} & \hat{V} - \langle |\hat{V}| \rangle - \eta \end{array} \right).\tag{6}$$

The Hamiltonian operator, Fock operator, and fluctuation potential are denoted by $\hat{H}$, $\hat{F}$, and $\hat{V}$, respectively. The ground state SF-CAS-CI wavefunction is taken as the reference state,⁴⁶ $|\rangle$, and an arbitrary level-shift parameter, η , is also included. This was found to increase both stability and accuracy of the perturbative expansion in Paper I,³⁹ so we have included η in the current work as well.⁷²

Inserting this perturbative expansion into $\mathcal{H}_{AA,s}$ (Eq. 3) and collecting common orders of λ yields the following second-order effective Hamiltonian:

$$\bar{\mathcal{H}}_{ab,s}^{(2)}(\omega_s) = \bar{H}_{ab} + \sum_x \frac{H_{ax} H_{xb}}{\omega_s - \omega_x^{(0)}}\tag{7}$$

where the indices refer to determinants $a, b \in A$ and $x \in X$. The energy differences are defined as:

$$\omega_s = E_s - \langle |\hat{H}| \rangle\tag{8}$$

$$\omega_x^{(0)} = \langle X | \hat{F} | X \rangle - \langle |\hat{F}| \rangle + \eta\tag{9}$$

A non-degenerate perturbative correction (NDPT) can be obtained by taking the expectation value of the Hamiltonian in Eq. 7, using the zeroth-order eigenvectors and state energies, $\omega_s^{(0)}$.

$$E_s^{\text{SF-CAS(S)}} = E_s^{(0)} + \sum_{abx} \frac{C_{as}^{(0)} H_{ax} H_{xb} C_{bs}^{(0)}}{\omega_s^{(0)} - \omega_x^{(0)}}\tag{10}$$

This NDPT method will be referred to as SF-CAS(S) throughout the rest of the paper.

SF-CAS(S) provides a correction for each state, but neglects any remixing of the SF-CAS-CI determininants due to the presence of the singles excitations. Alternatively, we can account for ϕ_A re-mixing, by adopting a quasidegenerate perturbation theory (QDPT) approach, in which an effective Hamiltonian is diagonalized to yield the perturbed and energies and coefficients.

The effective Hamiltonian, $\bar{\mathcal{H}}_{ab,s}^{(2)}(\omega_s)$, in Eq. 7, unfortunately, is both state specific (s) and energy dependent (ω_s), which makes this both expensive and computationally awkward. As was done in the CIS(D) $_n$ methods,⁴⁷ a multistate, energy independent, effective Hamiltonian, is obtained by expanding the denominator in the following series, keeping the n -th term:

$$\frac{1}{\omega_s - \omega_x^{(0)}} = - \sum_{n=0}^{\infty} \frac{(\omega_s)^n}{(\omega_x^{(0)})^{n+1}}, \quad (11)$$

This is convergent provided that $|\omega_s| < |\omega_x^{(0)}|$. For the low-lying excited states in which we are interested, this assumption is usually valid. A truncation of Eq. 11 at $n = 0$ yields the SF-CAS(S) $_0$ method, for which the energy is obtained by the following diagonalization.

$$\bar{\mathcal{H}}_{ab}^{(2)} C_b = \omega_s C_a \quad (12)$$

Where

$$\bar{\mathcal{H}}_{ab}^{(2)} = \bar{H}_{ab} - \sum_x \frac{H_{ax} H_{xb}}{\omega_x^{(0)}} \quad (13)$$

By carrying the Eq. 11 to the first two terms (up to $n = 1$) the SF-CAS(S) $_1$ method is obtained. Although the expansion now contains the energy, ω_s , this can be factored out into a metric, $\mathcal{S}_{ab}$.

$$\bar{\mathcal{H}}_{ab}^{(2)} C_b = \omega_s \mathcal{S}_{ab} C_b \quad (14)$$

With the metric being defined as:

$$\mathcal{S}_{ab} = \delta_{ab} + \sum_x \frac{H_{ax} H_{xb}}{\omega_x^{(0)} \omega_x^{(0)}} \quad (15)$$

These are the same equations presented in Paper I for the SF-CAS(h,p) $_n$ methods, with the only difference being that the index, x , now runs over all ϕ_h , ϕ_p , and ϕ_{hp} determinants.

Although the SF-CAS(S)₁ denominator truncation is based on a well motivated algebraic approximation, it is perhaps interesting to ask what physical significance the quadratic denominator term has in the expression for the metric. This can be easily answered by considering the following Lagrangian function:

$$\mathcal{L} = C_a \bar{\mathcal{H}}_{ab}^{(2)} C_b - \omega_s (C_a C_a - 1) \quad (16)$$

Setting $\partial \mathcal{L} / \partial C_a = 0$ yields an eigenvalue equation which minimizes the expectation value of $\bar{\mathcal{H}}_{ab}^{(2)}$ subject to the constraint that the zeroth-order part of the wavefunction is normalized. This is simply the SF-CAS(S)₀ method.

If, however, the Lagrangian is modified such that the constraint now requires the entire wavefunction (zeroth-order plus first-order) to be normalized,

$$\begin{aligned} \mathcal{L} &= C_a \bar{\mathcal{H}}_{ab}^{(2)} C_b - \omega_s (C_a C_a + C_x C_x - 1) \\ &= C_a \bar{\mathcal{H}}_{ab}^{(2)} C_b - \omega_s \left(C_a C_a + \frac{C_a H_{ax} H_{xb} C_b}{\omega_x^{(0)} \omega_x^{(0)}} - 1 \right) \\ &= C_a \bar{\mathcal{H}}_{ab}^{(2)} C_b - \omega_s (C_a \mathcal{S}_{ab} C_b - 1), \end{aligned} \quad (17)$$

the result is the same generalized eigenvalue problem in Eq. 14. Therefore, the SF-CAS(S)₁ method can be thought of as a variational minimization of the same multi-state effective Hamiltonian that is used in the SF-CAS(S)₀ method, but subject to the constraint that the entire wavefunction remains normalized. This physical interpretation is thus independent of the actual convergence properties of the denominator expansion in Eq. 11, and thus might prove useful even in situations where divergences occur.

Like the fully variational SF-XCIS, the SF-CAS(S) and SF-CAS(S)_n methods provide size-intensive energies such that the excitation energies are not affected by a non-interacting system. However, in addition to size-intensivity, the SF-CAS(S) and SF-CAS(S)₀ methods also have a loosened criteria for size-consistency. While SF-XCIS requires the unpaired electrons to be localized on one fragment for strict additive separability, the SF-CAS(S) and SF-CAS(S)₀ methods do not require this. Like SF-XCIS, however, the SF-CAS(S)₁, still requires the active space to be localized to one fragment during separation. This is due to the implicit energy dependence in the SF-CAS(S)₁ method.⁷³

Just as with the SF-XCIS and SF-CAS(h,p)_n methods, the SF-CAS(S)_n methods are void of any spin-contamination. This is guaranteed by the spin-free formulation and the use of ROHF orbitals. For the default case in which the active-space is defined as simply the singly

occupied orbitals, the SF-CAS(S) $_n$ energies have the same orbital invariance properties as the underlying ROHF energy.

III. IMPLEMENTATION

The SF-CAS(S) and SF-CAS(S) $_n$ methods were implemented in a development version of Q-Chem 4.0.⁴⁸ Compared to Paper I, the main difference for the current work is that more two-electron integrals are needed, and that the contraction to form $\bar{\mathcal{H}}_{ab}^{(2)}$ is now much larger. Using lowercase letters for active space indices, I for doubly-occupied orbitals, and A for virtual orbitals, the $(pq|rs)$, $(Ip|Aq)$, and $(IA|pq)$ integrals are computed and stored in memory using the resolution of the identity approximation (RI).^{49,50} This increases the computational cost from $\mathcal{O}(N^3)$ for SF-CAS(h,p) $_1$ to $\mathcal{O}(N^4)$.

Because p, q, r , and s are active space orbital indices, they do not grow with system size, and the resulting memory requirements for in-core storage is only $\mathcal{O}(N^2)$.

Although the integral computation presents the highest scaling step, the contraction to form the $\bar{\mathcal{H}}_{ab}^{(2)}$ matrix has a much larger prefactor. This step also incurs an order of magnitude increase in scaling, going from $\mathcal{O}(N^1)$ for SF-CAS(h,p) $_1$ to $\mathcal{O}(N^2)$. This contraction step can often become the bottleneck for multiple spin-flip calculations. However, the H_{ax} matrix becomes increasingly sparse when the active space is increased, and sparse matrix multiplication techniques can be used to make this faster. Currently, our code gives the user the option to use the sparse matrix multiplication tools implemented in the Armadillo linear algebra C++ package.⁵¹

In the current implementation, we build and diagonalize the full $\bar{\mathcal{H}}_{ab}^{(2)}$ matrix, which is only $A \times A$ in size. However, because of the inherent factorial scaling of CAS-CI methods, our code is limited in practice to 3-4 spin-flip calculations. Future implementations designed for larger numbers of spin-flips will use matrix-free diagonalization techniques.

IV. COMPUTATIONAL DETAILS

The calculations in the hydrogen fluoride example in Section V A were performed using the aug-cc-pVTZ basis set.⁵² In Section V B, geometry optimizations were performed at the UB3LYP/6-31g* level, with the subsequent singlet-triplet gap calculations using the

aug-cc-pVDZ basis set.⁵²

In Section V C, several bimetallic complexes were studied. Geometries for each complex were taken from experimental data, with any refinement described in the discussion. The reported spin-flip calculations were then performed using the VTZ basis set for all atoms. Cartesian coordinates for complexes are provided in the Supporting Information.⁷⁴

As demonstrated in Paper I,³⁹ a level-shift parameter, η , was useful for stabilizing the QDPT method, SF-CAS(h,p)₁. In that paper, a value of 107 mH was found to be optimal for reproducing the RAS-nSF results, to which SF-CAS(h,p)₁ is an approximation. In the current work we consider different values for the level-shift, and denote the value used in brackets, i.e., SF-CAS(S)₁ [100 mH]. The NDPT method, SF-CAS(h,p), however, did not benefit from a level-shift, and so no level-shift is used for the SF-CAS(S) method.

All calculations were performed using a modified version of the Q-Chem 4.0 electronic structure package.⁴⁸

V. NUMERICAL TESTS

In the following examples, we examine the performance of the NDPT method, SF-CAS(S), and the QDPT method, SF-CAS(S)₁. As these are perturbative approximations to the *n*SF-XCIS method described above, the most meaningful performance assessment would be made by direct comparison to *n*SF-XCIS. However, because only the 1SF-XCIS method has been implemented, we can only compare to 1SF-XCIS when performing one spin-flip calculations. For systems requiring multiple spin-flips, we resort to a comparison with available experimental or high-level ab initio data.

A. Hydrogen fluoride Potential Energy Curve

Computing the potential energy surface (PES) along a bond-breaking coordinate, is a stringent test for electronic structure methods. This is due to the fact that the nature of the electronic wavefunction changes dramatically during bond cleavage, and any method aiming to provide accurate results along this coordinate must be capable of describing both the large dynamical correlation effects near equilibrium, and the large static correlation near the bond-breaking region.

FIG. 1: Hydrogen fluoride PES. SF-CAS shown as grey solid line. RAS-SF shown as blue solid line. SF-CAS(S) shown as hatched red line. SF-CAS(S)₁ [100 mH] shown as light red dashed line. SF-CAS(S)₁ [300 mH] shown as medium red dashed line. SF-CAS(S)₁ [500 mH] shown as dark red dashed line. SF-XCIS shown as dark red solid line. SF-EOM-CCSD(dT) shown as black solid line. Grey area represents total correlation energy recovered by SF-XCIS. Minimal (2,2) active space and one spin-flip used. Level-shifts are shown in brackets. The NDPT method, SF-CAS(S), is not level-shifted.

TABLE I: Spectroscopic properties for HF.

Theory	D_e , kcal/mol	r_e , Å
SF-CAS	-69.7	1.05
RAS-SF	-97.0	0.98
SF-CAS(S)	-126.1	0.92
SF-CAS(S) ₁ [100 mH]	-124.6	0.95
SF-CAS(S) ₁ [300 mH]	-118.8	0.96
SF-CAS(S) ₁ [500 mH]	-114.1	0.97
SF-XCIS	-123.8	0.94
SF-EOM-CCSD(dT)	-140.7	0.92
Exp	141.0 ^a	0.9168 ^b

^a $D_0 = 135.1$,⁵³ ZPE=5.92⁵⁴^bRef. 54.

In recent papers, the RAS- n SF and SF-CAS(h,p)₁ methods were used to compute the hydrogen-fluoride PES and it was concluded that the single spin-flip calculations were insufficient.^{30,39} Consequently, both of these studies appended the lone-pairs of the F atom to the active-space, resulting in a (6,4) active-space. This is interesting because the lone-pair orbitals do not mix directly with the singly-occupied orbitals. For instance, if only SF-CAS is used to compute the PES, the (6,4) curve is identical to the (2,2) curve. The larger active-space only contributes when excitations out of the active-space are included.

This is ultimately due to the fact that certain ϕ_{hp} excitations from F lone-pairs become important, but remain neglected in (2,2) active-space RAS-SF and SF-CAS(h,p)₁. By bringing these lone-pair orbitals into the active-space, the relevant ϕ_{hp} excitations become re-classified as ϕ_p excitations, which are included in both RAS- n SF and SF-CAS(h,p)₁. Although the RAS-1SF(6,4) results are satisfactory, it is preferable to retain the minimal active-space while still achieving comparable accuracy.⁷⁵ Alternatively, SF-XCIS naturally includes these ϕ_{hp} excitations, and the minimal active-space description becomes sufficient. This makes the HF molecule a demanding test of our perturbative treatment, since the ϕ_{hp} determinants have an observed strong effect in this system.

In Fig. 1 we compare the minimal active-space SF-CAS, RAS- n SF, SF-CAS(S), SF-

CAS(S)₁, and SF-XCIS methods. To highlight energy stabilization provided by SF-XCIS, difference between the SF-CAS and SF-XCIS curves is filled in with grey. The binding energy and bond lengths are given in Table I. The UHF-based EOM-SF-CCSD(dT) curve is shown as a black solid line.

Having only four degrees of freedom, the SF-CAS method underestimates the binding by half. Inclusion of the ϕ_h and ϕ_p determinants by RAS-SF increases the binding by about 30 kcal/mol. However, even though the ϕ_h and ϕ_p excitations might intuitively be expected to be the most important single excitations, inclusion of the $\phi_h p$ excitations (via SF-XCIS) has a comparable effect, increasing the binding by yet another 30 kcal/mol. As a reference value in the current basis set, EOM-SF-CCSD(dT)/aug-cc-pVTZ provides an accurate estimation of the experimental binding energy of 141 kcal/mol.

Considering now the perturbative results, we look first at the NDPT curve (hatched red line). It is apparent that the SF-CAS(S) method provides a accurate approximation to the entire SF-XCIS curve. Although SF-CAS(S) slightly overestimates the binding energy and underestimates the bond-length, the performance of SF-CAS(S) in the bond-breaking region is quantitatively accurate.

Turning our attention to the QDPT curves (dashed red lines), SF-CAS(S)₁ shows significant dependence on the value of the level-shift parameter. Although a small level-shift parameter ($\eta = 100$ mH) provides an accurate description of the equilibrium region, the bond-breaking region is significantly overestimated by SF-CAS(S)₁. Because spin-flip methods are designed for describing strong correlation, it is most important that the SF-CAS(S)₁ curve accurately approximates the SF-XCIS curve in the bond-breaking region. Consequently, a much larger level-shift of 500 mH is needed to bring the SF-CAS(S)₁ curve to similar accuracy as the SF-CAS(S) curve.

From these results one would suggest that while the NDPT method, SF-CAS(S), is used without a level-shift, the QDPT method, SF-CAS(S)₁, should be used with a large level-shift. As discussed in section II, this has the effect of penalizing large amplitude perturbations when relaxing the SF-CAS coefficients in a constrained variational minimization of the effective Hamiltonian expectation value. Throughout the rest of the paper, the remaining SF-CAS(S)₁ calculations are performed with $\eta = 500$ mH.

It is perhaps surprising that the SF-CAS(S), SF-CAS(S)₁, and SF-XCIS methods recover so much of the binding energy, despite being designed as a single electron excitation theory on

FIG. 2: Molecules used to generate data for computing singlet-triplet gaps.

top of SF-CAS. In comparison, Hartree-Fock yields a binding energy of only 97.1 kcal/mol. Because there is a set of single excitations for each configuration in the model space, the net result does include some small number of double and triple excitations. However, because this set of double and triple excitations is so small, quantitative agreement with the very accurate EOM-SF-CCSD(dT) is not yet made, and the remaining binding energy (≈ 15 kcal/mol), is due to this missing dynamical correlation.

B. Singlet-Triplet Gaps

One of the more useful applications of the spin-flip approach has been in the computation of singlet-triplet gaps in biradical systems. Therefore, if a biradical is well characterized as a coupling of only two electrons, a one spin-flip (2,2) calculation should provide a decent description of the gap. However, because the orbitals are optimized for a high-spin configuration (ROHF triplet), there is an initial bias for the triplet state compared to the singlet,

FIG. 3: Singlet-Triplet Gaps (Δ^{ST}). Series data plotted on y-axis. SF-XCIS data plotted on x-axis. Units in kcal/mol.

and the $^3E - ^1E$ differences (Δ^{ST}) at the SF-CAS level are too small.

In the RAS-SF (or SF-CAS(h,p)₁) method, Δ^{ST} is increased by including the ϕ_h and ϕ_p excitations which provide the orbital relaxation effects of the low-spin states, leaving the highest-spin state unchanged from the SF-CAS description (which also has the same energy as the ROHF reference).

By adding the remaining set of single excitations (ϕ_{hp}) with SF-XCIS (or SF-CAS(S)₁),

TABLE II: Mean Unsigned Error (MUE) for Singlet-Triplet gaps (Δ^{ST}) as compared to SF-XCIS. Units in kcal/mol. Number of molecules in each data set given in the Number column.

Data Set	Number	SF-CAS	RAS-SF	SF-CAS(S)1 [500 mH]	SF-CAS(S)
(a)	15	7.32	2.13	2.69	1.97
(b)	15	7.77	2.32	2.80	1.79
(c)	15	2.57	1.70	0.37	0.55
(d)	11 ^a	1.62	1.13	0.24	0.32
(e)	25	13.01	9.46	7.56	5.61
(f)	25	7.65	11.58	9.64	11.72
(g)	15	19.67	14.65	11.82	9.48
Total	121	9.04	7.03	5.77	5.32
Total (noXyl) ^b	56	5.05	1.87	1.62	1.22

^aOriginally 15, but four removed as mentioned in text.

^bThe large deviations for the xylylene-based systems are explained in the text.

both the high-spin and the low-spin states relax, with the sign of the effect on Δ^{ST} being system dependent.

To evaluate the ability of SF-CAS(S)₁ to approximate the SF-XCIS Δ^{ST} values, we have taken a few different biradical spin-coupling motifs, Fig. 2(a)-(g), and varied the attached (X,Y)-groups to generate a spread of values. The data is then plotted in Fig. 3. To ensure a meaningful comparison, only minimal (2,2) active-spaces were used in the SF-CAS(S)₁ calculations. Zero deviation from SF-XCIS would result in a data point lying directly on top of the solid diagonal line, with overestimations and underestimations of the ST gap lying above and below the diagonal line, respectively. Any data in the +,- or -,+ quadrants indicate an incorrect sign of Δ^{ST} .

a. Analysis of all data sets Upon inspection of Fig. 3, the most immediate observation is that SF-CAS has four catastrophic failures, with errors larger than 30 kcal/mol and with the wrong sign. These failures correspond to the four mono-chlorinated members of data series (d). For these systems, the ub3lyp/6-31g* optimized geometries reveal that the C-Cl bond essentially breaks, lengthening to around 2.4 Å, and moving nearly normal to the ring plane above the formally attached carbon. The two unpaired electrons are no longer on the

two carbons, as shown in Fig. 2(d). Instead, one unpaired electron localizes on the Cl atom, while the other is delocalized across the three carbons at the top of the ring, being stabilized by two resonance structures. Because these four systems are characterized by geometries which are not commensurate with the geometric motifs in Fig. 2, they have been left out of the error statistics.

From Table II, we see that both SF-CAS(S) and SF-CAS(S)₁ provide an improved description of the Δ^{ST} gaps when compared to RAS-SF, with the NDPT method performing the best. For several of the data sets, (a)-(d), the deviations are less than 3 kcal/mol. However, for systems bridged by benzene, most notably the *m*-xylylene series (f), the errors are consistent and large in magnitude. The *m*-xylylene data is highlighted in Fig. 3. This has been discussed by other authors,^{55,56} and we analyze this in more detail below. Overall, the SF-CAS(S) method performs the best and provides a satisfactory level of agreement with the SF-XCIS results, barring the xylylene data.

As a rough measure of the computational efficiency gains afforded by the perturbative approach, we compare the time required to compute the disilane substituted *p*-xylylene Δ^{ST} (data series (g)). For SF-XCIS the wall time, neglecting the SCF calculation, took 1151 minutes. In comparison, the SF-CAS(S)₁ calculation took only 4.5 minutes, a relative speed-up of 255x. While some of the speed-up is coming from the use of RI integrals, the inherent simplicity of the current method has clear computational advantages, which will only become amplified when considering multiple spin-flip calculations.

b. Analysis of m-xylylene data set, (f) The consistent and large errors in the *m*-xylylene systems, indicate a fundamental problem with treating this system using a 1SF calculation. Intuitively, the high-spin ROHF reference orbitals would seem capable of describing this biradical quite well. However, if one computes the $\langle S^2 \rangle$ value of the analogous UHF triplet wavefunction, a value of 2.62 is obtained, which is significantly larger than the expected value of 2. This spin contamination comes from higher multiplicity states mixing into the triplet, indicating a multiconfigurational character. It is thus understandable why perturbation theory fails for this case,⁵⁸ since the underlying assumption is that the reference state is well described by a single reference. To correct this, one may try to find a high-spin state that does not suffer much spin-contamination upon spin unrestriction. The next highest spin-state, the quintet, is also spin contaminated, with $\langle S^2 \rangle = 6.37$, non-negligibly higher than the expected value of 6. Continuing, one gets to the heptet, which has less

TABLE III: Vertical Singlet-Triplet gaps for *m*-xylylene for different numbers of spin-flips. Energies obtained for each theory listed using the aug-cc-pvdz basis set. Units in eV.

Theory	1 Spin-Flip	2 Spin-Flip	3 Spin-Flip
SF-CAS	0.34	0.66	0.57
SF-CAS(h,p) ₁	0.25	0.37	0.46
RAS-SF	0.21	0.34	0.48
SF-CAS(S)	0.23	0.26	0.39
SF-CAS(S) ₁ [500]	0.29	0.47	0.47
SF-XCIS	0.70	—	—
Experiment ^a	0.42		

^aExperimental adiabatic singlet-triplet gap. From Ref. 57

contamination than the previous states. Here $\langle S^2 \rangle = 12.12$, and while this is still not zero, the contamination is significantly decreased, especially considering relative values. Taking this as evidence that the heptet is relatively single determinantal, we use the heptet ROHF as our reference. A 3SF calculation is then required to recouple the electrons into a singlet. The singlet-triplet gaps as a function of number of spin-flips are provided in Table III.

While the above discussion used the spin-contamination of the unrestricted calculation as a guide for determining the appropriate number of spin-flips needed, one might also find the heptet reference to be ideal from a different course. Problems with a minimal (2,2) active-space description of *m*-xylylene have actually been the topic of a few papers recently,^{55,56} and the problem has been described as coming from the active-space orbitals, which are too strongly localized on the CH₂ moieties. Consequently, MRCI results exhibit slow convergence of singlet-triplet gaps when a (2,2) active-space was used.⁵⁶ In efforts to maintain the (2,2) active-space, Malrieu and coworkers were able to obtain better orbitals with improved convergence, through an iterative procedure based on DDCI natural orbitals.⁵⁶

In a recent review paper, Malrieu et al. paint a clear picture of the physics introduced with the different classes of excitations.⁴² They describe the $\phi_{h\bar{p}}$ excitations as providing spin-polarization, which can become large for biradicals with ligands containing low-lying triplet states, such as those with conjugated bridging ligands. While the triplet state of benzene

FIG. 4: Structures for bimetallic complexes. **A** $[(\text{Et}_5\text{dien})_2\text{Cu}_2(\mu\text{-C}_2\text{O}_4)]^{2+}$. **B** $[\text{Cu}_2(\mu\text{-OH})_2(\text{bipym})_2]^{5+}(\text{NO}_3)_2(\text{H}_2\text{O})_4$. **C** $[(\mu\text{-OCH}_3)\text{V}^{\text{IV}}\text{O}(\text{maltolato})]_2$. **D** $[\text{Cr}_2(\text{NH}_3)_{10}(\text{O})]^{4+}$. **E** $[\text{Cr}_2(\text{NH}_3)_{10}(\text{OH})]^{5+}$. **F** $[\text{Mn}^{\text{II}}(\text{NH}_3)_4\text{Cu}^{\text{II}}(\text{oxpn})]^{2+}$. All xyz coordinates are provided in the Supporting Information.

would not be classified as being particularly low in energy, the SF-XCIS method appears to exhibit a significant amount of mixing between the triplet state in the singly occupied orbitals and the triplet state of the bridging benzene. This mixing is not being described well with second order perturbation theory in the SF-CAS(S)₁ method. To include the triplet state of the benzene properly, we would need to include both the doubly degenerate HOMO and LUMO orbitals. A 3SF calculation brings all of these orbitals into the singly occupied block, thus improving the results.

Although the actual magnitude of the deviations seems worse for 3SF-CAS than 1SF-CAS, the 3SF-CAS results overestimate the experimental numbers, which is the expected behaviour. This overestimation can then be cleaned up with the single excitations in both the RAS-3SF and the 3SF-CAS(S) methods, with the latter providing the best agreement to experiment.

C. Spin Coupling in TM Complexes

Transition metal complexes often exhibit important characteristics such as high catalytic activity, rich photochemistry, molecular magnetism, etc. These useful properties stem from

TABLE IV: Exchange coupling constants, J , for bimetallic compounds shown in Fig. 4. Units in cm^{-1} . Cartesian coordinates are provided in supporting information. Number of spins flipped are shown in the first row. Red numbers indicate wrong sign of J .

	A	B	C	D	E	F
Number of spin-flips	1	1	1	3	3	3
SF-CAS	-3.5	14.4	3.3	-45.2	-2.3	-1.8
RAS-SF	-4.1	14.0	1.1	-64.3	-3.8	-3.2
SF-CAS(S) ₁ [100 mH]	303.1	19.1	-586.1	-342.2	-18.3	7.8
SF-CAS(S) ₁ [300 mH]	-35.7	19.0	-77.8	-199.7	-12.1	-155.2
SF-CAS(S) ₁ [500 mH]	-20.4	18.6	-40.9	-150.1	-9.4	-15.1
SF-CAS(S)	-9.2	19.7	-22.5	-115.8	-7.7	-5.0
SF-XCIS	-11.4	30.8	-29.4	—	—	—
Experiment	-37.0 ^a	57.0 ^b	-107.0 ^c	-225.0 ^d	-15.8 ^e	-16.0 ^f

^aReference 59.

^bReference 60.

^cReference 61.

^dReference 62.

^eReference 63.

^fReference 64.

their atomic electronic structures, which often contain an abundance of low-lying electronic states. This, unfortunately, complicates attempts at modelling transition metal complexes with quantum chemical methods. A system of interacting, dynamically correlated electronic states is quite removed from the mean-field model, upon which most of standard approaches are based. Although not formally capable of describing strong correlation, density functional theory (DFT) has been used, to varying degrees of success, for the computation of J values. This is usually done in the context of broken-symmetry DFT with an approximate projection scheme, but other approaches have been successful,^{65,66} such as constrained-DFT.⁶⁷ However, all of these approaches are plagued by the problem of functional choice. Ab initio methods capable of describing strong correlation in a systematically improvable manner, such as the spin-flip methods, are especially useful in their application to transition metal compounds.

In molecules containing multiple open-shell transition metal atoms, the local spins on the metals can couple either ferromagnetically, or antiferromagnetically. This coupling of two radical centers is often described phenomenologically by a Heisenberg Hamiltonian of the form,

$$\hat{H} = -2 \sum_{i < j} J_{ij} \hat{S}_i \hat{S}_j \quad (18)$$

where the multiplicity of the ground state depends on the sign of the exchange coupling parameter, J , with negative values indicating antiferromagnetic coupling, and positive values indicating ferromagnetic coupling.

In this section, we assess the accuracy of the SF-CAS(S) and SF-CAS(S)₁ methods as a tool for computing J coupling constants for a variety of bimetallic transition metal complexes, shown in Fig. 4. Complexes **A-C** are 1 spin-flip calculations, which permits direct comparison to the SF-XCIS target. Complexes **D-F** are 3 spin-flip calculations (6 total unpaired electrons), which prevents comparison to SF-XCIS. Results are tabulated for the various methods and experiment in Table IV.

In Sec. V A, a level-shift of $\eta = 500$ mH, was found to be necessary for damping the overestimation of the QDPT (S)₁ correction in the bond-breaking region of the PES. However, this is perhaps a surprisingly large addition to the denominator. To provide a comparative numerical test of this large level-shift, we have included SF-CAS(S)₁ results in Table IV using both $\eta = 100$ mH and $\eta = 300$ mH, in addition to $\eta = 500$ mH.

Complex A

Looking first at **A**, we see that while SF-CAS predicts the correct sign of J , the magnitude is roughly a factor 10 too small. Adding variational ϕ_h and ϕ_p excitations, via RAS-SF, the magnitude increases only slightly from the SF-CAS starting point. Using perturbation theory to add these excitations in addition to the ϕ_{hp} excitations produces a more pronounced effect. Looking first at the QDPT results, it is immediately obvious that the level-shift parameter has a large effect on the results, with the value ($\eta = 500$ mH) chosen based on the bond-breaking of hydrogen fluoride in Section V A clearly preferred (on the basis of fidelity to SF-XCIS, which it perturbatively approximates). For small values of η , the ionic configurations, which are poorly described by high-spin orbitals, are significantly overcorrected by the QDPT correction, such that the high-lying model space configurations drop

to the bottom of the spectrum of the effective Hamiltonian, strongly mixing with the true ground electronic states. A large level-shift parameter pushes those perturbed states back up in energy. In contrast, the NDPT method, SF-CAS(S), does not suffer from this same problem as the coefficients are not remixed after perturbing. Consequently, SF-CAS(S) provides a good approximation (9 cm^{-1}) to the SF-XCIS benchmark value of 11.4 cm^{-1} , and a qualitatively accurate approximation to experiment.

Complex B

As the only ferromagnetically coupled complex in this set, the behavior is significantly different than the previous dicopper complex. RAS-SF provides a nearly negligible change relative to SF-CAS, and inclusion of perturbative singles improves the results by only around 5 cm^{-1} . The QDPT results are virtually independent of the level-shift used, and is in close agreement with the NDPT value. While SF-CAS(S) and SF-CAS(S) [500 mH] underestimate J compared to SF-XCIS, both provide more accurate results than SF-CAS and RAS-SF.

Complex C

For the divanadate complex, both SF-CAS and RAS-SF fail at predicting the correct sign of J . Including the ϕ_{hp} excitations corrects this, and both SF-CAS(S) and SF-CAS(S)₁ [500 mH] predict the correct sign. However, as with **A**, the QDPT results are found to be very sensitive to the value of η , with the large 500 mH value providing the best results. Again, SF-CAS(S) provides the best approximation to SF-XCIS, which itself underestimates experiment by roughly a factor of three.

Complexes D-E

Recently,³² the RAS-SF method was used to compute the J coupling parameter in two dichromium compounds, **D** and **E**. In both of these molecules, the Cr atom assumes a III oxidation state, which, in an octahedral ligand field, results in two local quartets. Having six unpaired electrons, the ROHF heptet orbitals are the proper reference for a subsequent three spin-flip calculation. The RAS-SF calculations provided the correct sign of the J coupling,

but the magnitude was severely underestimated in both molecules.³² To obtain improved results, the active-space was increased to include the bridging oxo (or hydroxo) ligand orbitals. A better solution, of course, would be to improve the accuracy while maintaining the minimal active space.

All methods considered predict the correct sign of J . Similar to the RAS-SF results, SF-CAS underestimates the coupling significantly. Both SF-CAS(S) and SF-CAS(S)₁ [500 mH] improve upon this considerably. However, as with most of the transition metal systems, the QDPT results are quite sensitive to the value of η . Although the 3SF-XCIS code has not yet been implemented, we might expect its value to fall somewhere between the NDPT and QDPT results (between -116 and -150 cm⁻¹).

Complex F

This complex has one and five unpaired electrons on the Cu and Mn centers, respectively. Having six total unpaired electrons defining the active-space, 3 spin-flips are required to arrive at the desired $m_s = 0$ determinants. As with the previous compounds, both SF-CAS and RAS-SF significantly underestimate the experimental value. Again, the dependence of SF-CAS(S)₁ on the value of η is rather pronounced, and for small values the sign is either wrong, or the magnitude is far too large. However, both SF-CAS(S) and SF-CAS(S)₁ [500 mH] provide qualitatively accurate values of J .

From this collection of bimetallic transition metal complexes, several observations can be made. Perhaps most obviously, is that small values of η lead to a very unstable perturbative correction when the QDPT framework is desired. If a NDPT approach is sufficient, as was the case in these systems, the SF-CAS(S) method provides better accuracy without any level-shift parameter. Compared to both SF-CAS and RAS-SF, the SF-CAS(S) and SF-CAS(S)₁ [500 mH] methods provide more accurate J values, while being significantly more efficient than SF-XCIS.

VI. CONCLUSIONS

Previous applications of the RAS-SF method have found it sometimes necessary to add additional orbitals to the naturally defined minimal active-space, (the ROHF singly occupied

orbitals). SF-XCIS contains the excitations required to maintain a minimal active-space, but has two drawbacks: it is computationally expensive compared to RAS-SF, and is only defined for one spin-flip. In the current work, we present two methods which provide a solution to of these issues: a non-degenerate perturbation theory method, SF-CAS(S), and a quasi-degenerate perturbative method, SF-CAS(S)₁. Taking the SF-CAS as a starting point, which enables multiple spin-flips, we include the effect of all singles excitations using second-order perturbation theory. For the one spin-flip case, the resulting first-order wavefunction contains the same excitations as the parent SF-XCIS method, but is no longer variational. The SF-CAS(S)₁ energies have the same size-consistency and orbital-invariance properties as SF-XCIS, whereas SF-CAS(S) also has the additional property of additive-separability.

The performance of SF-CAS(S) and SF-CAS(S)₁ was assessed through a number of examples: hydrogen fluoride potential energy curves, singlet-triplet gaps in organic diradicals, and exchange coupling parameters for bimetallic complexes.

For the organic diradical singlet-triplet gaps, a systematic set of molecules was generated for comparing singlet-triplet gap calculations between the RAS-SF, SF-CAS(S), and SF-CAS(S)₁, and the SF-XCIS methods. For these molecules, both SF-CAS(S) and SF-CAS(S)₁ provided an improvement over RAS-SF, as compared to SF-XCIS. The subset of data consisting of substituted *m*-xylylene systems, test set (f), was found to be poorly described by all methods. However, consideration of the corresponding UHF wavefunction found the triplet to be significantly spin contaminated, indicating that the triplet ROHF orbitals might be problematic as a reference. In contrast, the heptet UHF determinant was significantly less contaminated, and the resulting 3 spin-flip calculations provided accurate results with the heptet ROHF orbitals.

The exchange coupling parameter, J , was computed for a series of bimetallic transition metal complexes. Compared to RAS-SF, both SF-CAS(S) and SF-CAS(S)₁ provide J values which are larger in magnitude, and closer to both SF-XCIS and experiment. If a quasi-degenerate perturbation theory is desired, we recommend a level-shift of 500 mH to be used with the SF-CAS(S)₁ method. If the molecule being studied has isolated ground spin states, then it appears to be consistently preferable to choose the non-degenerate perturbation theory method, SF-CAS(S), which does not use a level-shift.

Overall, the SF-CAS(S) and SF-CAS(S)₁ methods stand as a promising tools for understanding and predicting the electronic structure of low-lying, strongly correlated electronic

states.

Acknowledgement

Support for this work was provided through the Scientific Discovery through Advanced Computing (SciDAC) program funded by the U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research, and Basic Energy Sciences.

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- ⁷¹ For systems which do not have an easily accessible and uncorrelated high-spin state, methods which change the number of particles (such as EOM-IP/EA-CCSD/CISD) can offer a useful alternative,⁶⁸ and similar low-cost SF/IP/EA-CAS(X) analogues are under development.

- ⁷² Although we are taking the pragmatic approach of damping large perturbations via the level-shift, other approaches such as multipartitioning may provide an interesting alternative.^{69,70}
- ⁷³ This implicit energy dependence makes the SF-CAS(S)₁ resemble an approximate Brillouin-Wigner perturbation theory. Because of this reason, the use of the metric in Eq. 15 would not be appropriate for methods containing excitations that are disconnected from the active-space, i.e. a full doubles correction, $\hat{r}_{IJ}^{AB}$.
- ⁷⁴ See Supplementary Material Document No. ....
- ⁷⁵ In fact, it was observed that the RAS-1SF(6e,4o) PES lies almost directly on top of the SF-XCIS PES.³⁰