

# Resolving the Notorious Case of Conical Intersections for Coupled Cluster Dynamics

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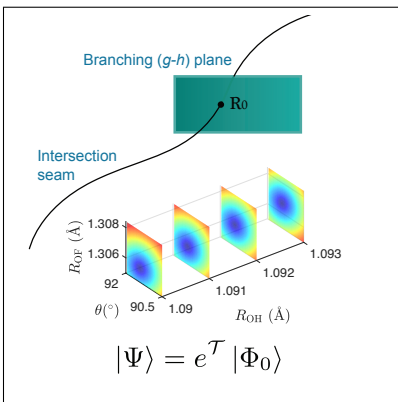
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## Abstract

The motion of electrons and nuclei in photochemical events often involve conical intersections, degeneracies between electronic states. They serve as funnels in nuclear relaxation processes where the electrons and nuclei couple nonadiabatically. Accurate *ab initio* quantum chemical models are essential for interpreting experimental measurements of such phenomena. In this Letter we resolve a long-standing problem in coupled cluster theory, presenting the first formulation of the theory that correctly describes conical intersections between excited electronic states of the same symmetry. This new development demonstrates that the highly accurate coupled cluster theory can be applied to describe dynamics on excited electronic states involving conical intersections.

## Graphical TOC Entry



Conical intersections, or electronic degeneracies, are widely recognized as central to the motion of nuclei and electrons in photochemical events.<sup>1,2</sup> They have been implicated in a range of chemical reactions, from the ring-opening reaction of 1,3-cyclohexadiene<sup>3</sup> and the proton transfer reaction in hydroxybenzaldehyde<sup>4</sup> to the cis-trans isomerization thought to be the primary photochemical event in human vision.<sup>5</sup> Our understanding of nuclear dynamics is firmly rooted in the often accurate Born-Oppenheimer approximation, where the motion of the electrons create potential energy surfaces to which the nuclei in turn respond.<sup>6</sup> However, the approximation breaks down completely when a molecule approaches a conical intersection, where the dynamics involves an intricate interplay between nuclear and electronic motion.<sup>7</sup> Advances in pump-probe techniques have made this phenomenon increasingly open to experimental investigation.<sup>8</sup>

Rapid developments in *ab initio* quantum chemistry was spurred by the realization that nonadiabaticity is the norm in photochemistry. These include assessments of the potential energy surfaces close to electronic degeneracies,<sup>9,10</sup> attempts to incorporate nonadiabaticity in dynamics simulations by solving the time-dependent Schrödinger equation explicitly,<sup>7,11</sup> implementations of nonadiabatic coupling elements,<sup>12-14</sup> and schemes for constructing quasi-diabatic representations based on *ab initio* data<sup>15,16</sup>. A major overarching goal of this research is the reliable prediction of nonadiabatic dynamics, which will enable one to monitor, in real-time, processes—such as electron density fluctuations<sup>7</sup>—not directly accessible by experiment.<sup>1</sup> Since the Schrödinger equation cannot be solved exactly for many-electron molecular systems, such predictions must be grounded in approximate treatments of electronic correlation, or electron-electron interactions.<sup>17</sup>

The most successful treatment of electronic correlation is provided by coupled cluster theory,<sup>18,19</sup> a model now routinely applied to chemically interesting systems in spite of its steep computational scaling.<sup>20</sup> Nevertheless, as is true for all quantum chemical models, the theory is not globally accurate and may fail to describe certain regions of the potential energy surfaces. The standard coupled cluster ground state wave function, which is based on a

closed-shell Hartree-Fock reference, is less accurate in regions where the exact wave function has multireference character (*e.g.*, when a molecule dissociates into fragments). Accurately describing multireference ground states within a coupled cluster framework is still an active research area.<sup>21,22</sup> In the following, we restrict ourselves to excited electronic states, where multireference character is not an issue<sup>23</sup> but where other problems have hindered the theory from being applied to conical intersections. About a decade ago, Hättig<sup>24</sup> argued that Hermitian symmetry—a property that coupled cluster theory does not have—is needed to describe conical intersections between states of the same symmetry. The unphysical complex energies, predicted to exist due to the nonsymmetric eigenvalue problem,<sup>24</sup> were later found in coupled cluster singles and doubles (CCSD)<sup>25</sup> and triples (CCSDT)<sup>26,27</sup> calculations.<sup>28</sup> More recently, complex energies were encountered in dynamics simulations using the perturbative doubles (CC2)<sup>29</sup> model, illustrating their relevance in realistic applications.<sup>30</sup> Moreover, since the vast majority of degeneracies are same-symmetry conical intersections,<sup>2</sup> coupled cluster theory has been of limited use for conical intersections in general.

The state-of-the-art theories for conical intersections are complete active space (CAS) models, such as CASSCF and CASPT2.<sup>31</sup> However, while they give a physically correct description of conical intersections by their Hermitian symmetry (see, *e.g.*, Ben-Nun *et al.*<sup>11</sup>), their ability to account for dynamic correlation is limited.<sup>32</sup> The same can be said for the algebraic diagrammatic construction (ADC)<sup>33</sup> theory advocated by some groups.<sup>24,34</sup> The ground state wave function in ADC, obtained by Møller-Plesset perturbation theory, is known to have a limited domain of validity.<sup>35,36</sup> For large systems, computational chemists often resort to density functional theory (DFT), which is less computationally demanding than *ab initio* theories, but also less accurate.<sup>37,38</sup> On the other hand, coupled cluster theory accurately accounts for dynamic correlation effects and multireference character in excited states. A formulation of the theory able to treat conical intersections will therefore be a highly desirable addition to current methodologies.

A notable example is the  $\pi\pi^*$  nuclear relaxation in thymine, where theoretical investiga-

tions by various methods have provided inconsistent predictions.<sup>39</sup> Some simulations predict that relaxation proceeds first to a local minimum of the  $\pi\pi^*$  state within 100 femtoseconds, followed by slow internal conversion from the  $\pi\pi^*$  state to the  $n\pi^*$  state (CASPT2)<sup>40</sup> or to the ground state (CASSCF);<sup>41</sup> others predict fast barrierless  $\pi\pi^*/n\pi^*$  relaxation (TD-DFT)<sup>38</sup> or direct  $\pi\pi^*/$ ground state relaxation within a few hundred femtoseconds (CASPT2).<sup>42</sup> Evidently, accurate quantum chemical predictions are essential for reliable predictions in dynamics simulations. The accuracy of coupled cluster theory was recently shown in experiments confirming ultrafast  $\pi\pi^*/n\pi^*$  conversion, emphasizing the need for highly accurate methods in excited state dynamics.<sup>43</sup>

In a recent paper, we showed that nonsymmetric theories provide a correct description of conical intersections if they are nondefective, a mathematical property that ensures non-parallel eigenstates.<sup>44</sup> Here we demonstrate that coupled cluster theory can be constrained to be nondefective, thereby resolving the long-standing intersection issues.<sup>24</sup> The modified theory, named similarity constrained coupled cluster theory, provides a correct description of same-symmetry conical intersections. In particular, we illustrate numerically that this is the case for a conical intersection in hypofluorous acid. This new development shows that coupled cluster theory can be applied to nonadiabatic photochemical processes.

The coupled cluster ground state wave function is written  $|\Psi\rangle = e^T |\Phi_0\rangle$  for the Hartree-Fock state  $|\Phi_0\rangle$ , where  $T = \sum t_\mu \tau_\mu$ , the cluster operator, consists of excitation operators,  $\tau_\mu$ , weighted by amplitudes,  $t_\mu$ .<sup>19,45</sup> The  $n$ th excitation energy and electronic state,  $\omega_n$  and  $\mathbf{r}_n$ , are determined from

$$\mathbf{A} \mathbf{r}_n = \omega_n \mathbf{r}_n, \quad A_{\mu\nu} = \langle \Phi_\mu | (\bar{H} - E_0) | \Phi_\nu \rangle, \quad |\Phi_\mu\rangle = \tau_\mu |\Phi_0\rangle, \quad \tau_0 = \mathbb{I}, \quad (1)$$

where  $E_0 = \langle \Phi_0 | \bar{H} | \Phi_0 \rangle$  and  $\bar{H} = e^{-T} H e^T$  is the similarity transformed Hamiltonian.<sup>46,47</sup> For notational convenience, we assume that  $\{|\Phi_\mu\rangle\}$  is an orthonormal basis. In the CCSD model, the cluster operator is restricted to one- and two-electron excitations, with amplitudes

determined by projection onto the corresponding excited determinants.<sup>25</sup>

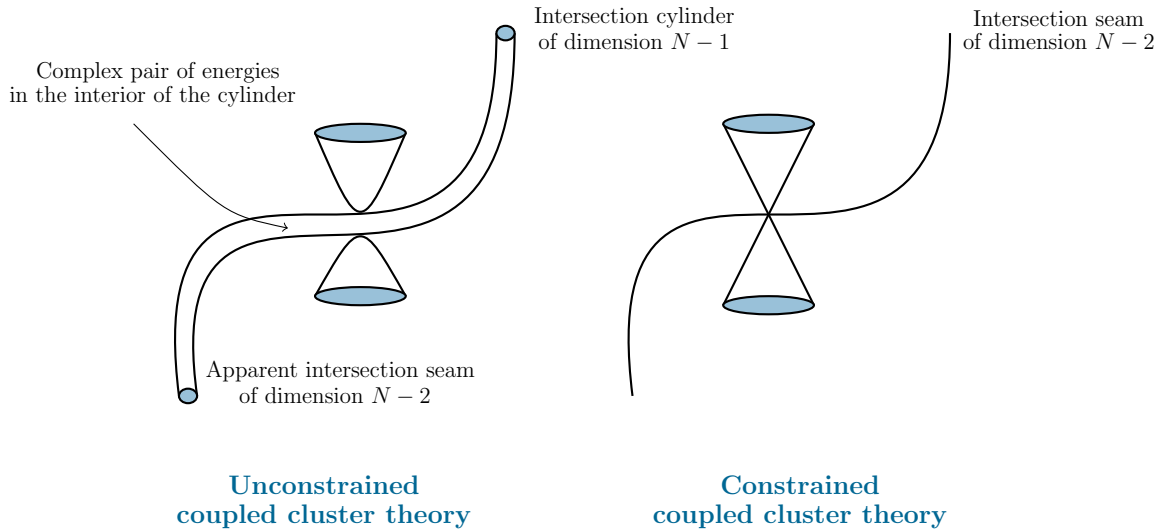


Figure 1: Conical intersections in coupled cluster theory. The illustrated shapes are for three vibrational degrees of freedom ( $N = 3$ ), appropriate for hypofluorous acid and other three-atomic molecules. Superimposed on the illustrated vibrational space are potential energy surfaces in the plane orthogonal to the seams at a point of intersection.

We recently traced the unphysical artifacts, observed using coupled cluster methods at same-symmetry conical intersections,<sup>28</sup> to defects in the nonsymmetric matrix  $\mathbf{A}$ .<sup>44</sup> Matrices are known as defective when they are impossible to diagonalize, *i.e.* when two or more of their eigenvectors are parallel.<sup>48</sup>

Considering a representation of  $\mathbf{A}$  in a basis of the intersecting states,  $J_{ij}(\mathbf{R})$ ,  $i, j = 1, 2$ , where  $\mathbf{R}$  is a nuclear coordinate, Hättig<sup>24</sup> argued that at a degeneracy of a nondefective and nonsymmetric  $\mathbf{J}$ ,

$$J_{11} = J_{22}, \quad J_{12} = 0, \quad J_{21} = 0, \quad (2)$$

and concluded, as others have since,<sup>9,28</sup> that the intersections of coupled cluster theory are qualitatively wrong. This is because equation (2), for real  $H$ , has one more condition than in quantum mechanics,<sup>49,50</sup> and might therefore be expected to give intersections of dimension  $N - 3$ , where  $N$  is the number of vibrational degrees of freedom. These three conditions are redundant for nondefective matrices, however. It can be shown that the  $\mathbf{R}$  satisfying them

are expected to inhabit a space of the correct dimension<sup>44</sup>  $N - 2$ .

In practice,  $\mathbf{A}$  is defective with intersections where  $(J_{11} - J_{22})^2 + 4 J_{12} J_{21} = 0$ , an equation obeyed in a space of dimension<sup>24</sup>  $N - 1$ . While this dimensionality is incorrect, the degeneracy is folded on itself. The intersection is a cylinder instead of a curve for  $N = 3$ , for instance, resembling a seam of dimension  $N - 2$ . See Figure 1. Inside the cylinder the excitation energies are complex and on its surface  $\mathbf{A}$  is defective.<sup>28,44</sup>

When the cluster operator is complete (*i.e.*, includes all excitation operators),  $\mathbf{A} + E_0 \mathbf{I}$  is mathematically similar to a representation  $\mathbf{H}$  of the electronic Hamiltonian  $H$ . It can then be shown that if  $\mathbf{c}_n$  is an eigenvector of  $\mathbf{H}$ , where  $H_{\mu\nu} = \langle \Phi_\mu | H | \Phi_\nu \rangle$ , then  $\mathbf{c}_n = \mathbf{Q} \mathbf{r}_n$ , where  $Q_{\mu\nu} = \langle \Phi_\mu | e^T | \Phi_\nu \rangle$ . The orthogonality of the  $\mathbf{c}_n$ , implied by the symmetric  $\mathbf{H}$ , translates to a generalized orthogonality for the eigenvectors  $\mathbf{r}_n$  of  $\mathbf{A}$ :

$$\mathbf{c}_k^T \mathbf{c}_l = \mathbf{r}_k^T \mathbf{Q}^T \mathbf{Q} \mathbf{r}_l = 0, \quad k \neq l. \quad (3)$$

As this is a relation only satisfied for a complete cluster operator, some of the eigenvectors  $\mathbf{r}_n$  may and indeed do become parallel at same-symmetry intersections in truncated coupled cluster methods. In the full space limit, the left eigenvectors  $\mathbf{l}_k$  and  $\mathbf{l}_l$  are similarly orthogonal over the inverse of the above metric,  $(\mathbf{Q}^T \mathbf{Q})^{-1}$ .

The wave function of similarity constrained CCSD (SCCSD) is defined by including an additional triple excitation in cluster operator  $\mathcal{T}$ :

$$\mathcal{T} = \sum_{ai} t_i^a \tau_i^a + \frac{1}{2} \sum_{aibj} t_{ij}^{ab} \tau_{ij}^{ab} + \zeta \tau_{IJK}^{ABC}. \quad (4)$$

The amplitudes  $t_i^a$ ,  $t_{ij}^{ab}$ , and  $\zeta$  are determined such that *i*) equation (3) is valid for the two intersecting states, and *ii*) the projected equations of the CCSD model are satisfied. This leads to a coupled set of equations that may be solved self-consistently. The implementation is described in more detail in the Supporting Information.

Note that generalized orthogonality over a positive definite matrix is sufficient to ensure

that the theory is nondefective. Indeed, since  $\mathbf{Q}^T \mathbf{Q}$  is positive definite, parallel eigenvectors cannot satisfy equation (3). The theory is consequently nondefective.

The additional term in the cluster operator  $\mathcal{T}$  may equivalently be viewed as performing a second similarity transformation of  $H$ . This similarity transformation,

$$\bar{H} = e^{-\zeta \tau_{IJK}^{ABC}} \bar{H}_{\text{ccsd}} e^{\zeta \tau_{IJK}^{ABC}}, \quad (5)$$

is chosen such that  $\bar{H}$  guarantees the validity of the generalized orthogonality condition, where  $\bar{H}_{\text{ccsd}}$  is the standard CCSD similarity transformed Hamiltonian. Imposing constraints on the matrix elements of model Hamiltonians is an idea that dates back to Linderberg<sup>51</sup>.

As first shown by Köhn and Tajti,<sup>28</sup> the lowest singlet excited states of  $A_1$  symmetry in formaldehyde have a defective conical intersection. Here we reproduce their findings and compare them with the predictions of the similarity constrained theory. The results are shown in Figure 2, where we have used the same geometry as in the original study.<sup>28</sup>

The unphysical behavior of CCSD is evident. The states become degenerate at 1.3515 Å and 1.3570 Å, giving a complex pair of energies in-between ( $E_{\pm} = E_{\text{real}} \pm i E_{\text{imag}}$ ). Such artifacts are absent in the constrained model, where the defective intersection becomes an avoided crossing. If it exists, the conical intersection of the theory is located elsewhere in nuclear space.

The lowest singlet excited states of  $A'$  symmetry in hypochlorous acid intersect.<sup>52</sup> We investigate this conical intersection in hypofluorous acid. This three-atomic molecule (H–O–F) provides a pedagogical illustration of the model, allowing direct comparisons with Figure 1. After locating a point of intersection, we performed a scan in the branching plane, the plane orthogonal to the intersection seam.<sup>53</sup> The results are shown in Figure 3.

In a recent paper, we showed that nondefective coupled cluster models exhibit the correct first-order branching plane energy gap linearity,<sup>44</sup> that is, their intersections are conical.<sup>53</sup> From Figure 3, we see that the energy surfaces have the physically correct conical appearance;

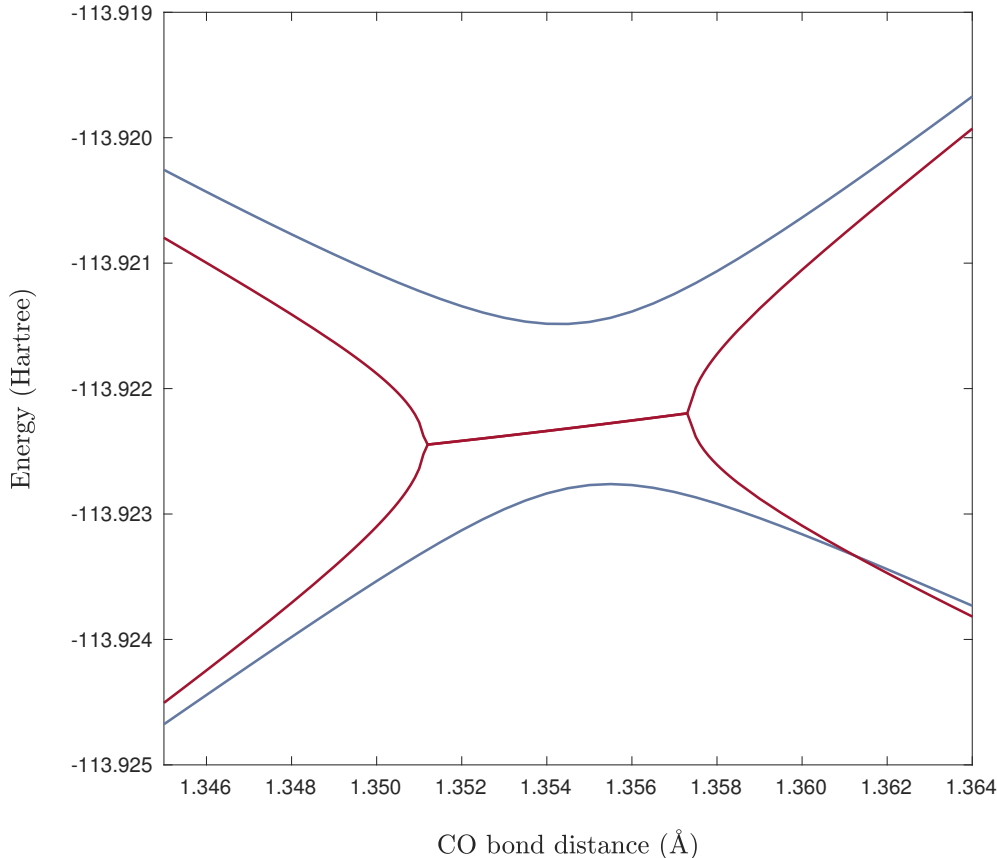


Figure 2: The  $2^1A_1$  and  $3^1A_1$  excited states of formaldehyde using CCSD (red) and SCCSD (blue) with an aug-cc-pVDZ basis. The real part of the CCSD energies is shown. An imaginary pair of energies is obtained for the C=O bond distances 1.3515–1.3570 Å.

the energy gap linearity is satisfied. Note the contrast to calculations on formaldehyde using CCSD, where the energy gradient changes more rapidly close to the intersection; this can be seen from Figure 2 in the vicinity of the CO bond distances 1.3515 Å and 1.3570 Å.

In this initial development, we have used a conceptually simple cluster operator  $\mathcal{T}$  that preserves the size-extensive structure of the ground state wavefunction and energy as well as the size-intensive structure of  $\mathbf{A}$ .<sup>54</sup> Aiming for a small correction of the wave function  $|\Psi\rangle = e^{\mathcal{T}}|\Phi_0\rangle$ , we selected the excitation, from the dominant single and double excitations contributing to the two states, such that the  $\zeta$  parameter was sufficiently small (we used 2 as a threshold). The excitation was selected at a particular geometry and kept unchanged in

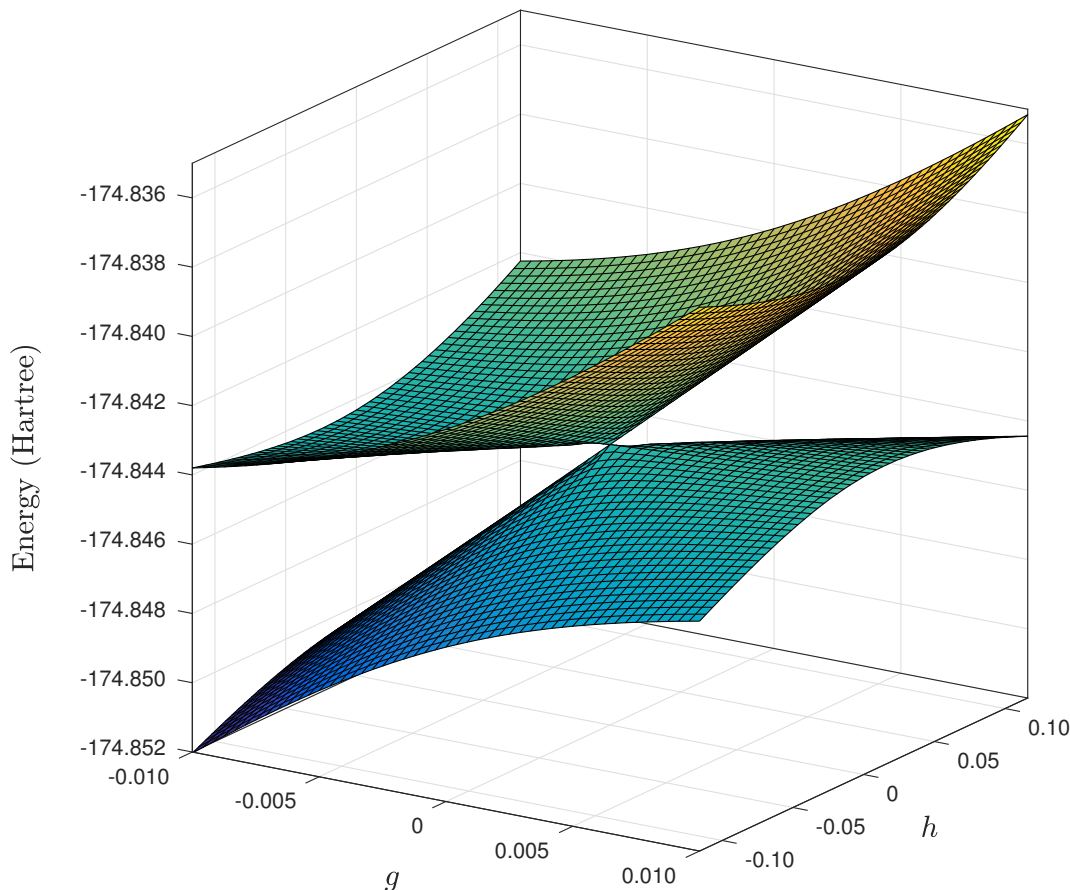


Figure 3: A branching plane in hypofluorous acid (SCCSD/aug-cc-pVDZ) between the  $2^1A'$  and  $3^1A'$  excited states.

subsequent calculations. This selection procedure can easily be made black-box; in the initial geometry of the simulation, one can identify an appropriate excitation from an automated test of several excitations.

We have considered variations in the energies for twelve choices of triple excitation, see Table S2 in the Supporting Information. The energies are found to differ from CCSD by less than five milliHartrees for all excitations, and the energy gaps are similar to the CCSD and CC3 gaps (but different from the CC2 gap). In terms of quality and the location of the intersection seam, the constrained model is thus similar but not identical to CCSD. This behavior is as expected this close to seam, given the proximity to the unphysical cylinder

(see Figure 1). For a numerical illustration of the cylinder, see our recent paper.<sup>44</sup>

While conceptually simple, the single triple excitation in  $\mathcal{T}$  implies a loss of orbital invariance and does not guarantee continuous potential energy surfaces. Other formulations preserving the  $N^6$  scaling are indeed possible where the cluster operator is also orbital invariant. For instance, this can be achieved by defining the triples contribution in  $\mathcal{T}$  to be the product of the singles and doubles contributions in one of the states. This definition also guarantees continuity of the potential energy surfaces. Let  $r_{\mu_1}$  and  $r_{\mu_2}$  denote the singles and doubles contributions in the state  $\mathbf{r}$ . The cluster operator is then defined as

$$\mathcal{T} = T_1 + T_2 + \zeta \sum_{\mu_1 \mu_2} r_{\mu_1} r_{\mu_2} \tau_{\mu_1} \tau_{\mu_2}, \quad (6)$$

where the  $\zeta$  parameter is used to enforce the generalized orthogonality in equation (3). In equation (6), only one of the intersecting states is selected. However, both can be included to give a balanced operator, state invariant with respect to the intersecting states. Alternatively, the states can provide two parameters,  $\zeta_1$  and  $\zeta_2$ , which will allow generalized orthogonality to be enforced between the left and right eigenvectors simultaneously. For the theory to be nondefective, however, orthogonality between either sets of eigenvectors is sufficient. A generalization for three-state intersections is straight-forward. In this case, the three states can each provide a parameter,  $\zeta_1$ ,  $\zeta_2$ , and  $\zeta_3$ , that may be used to enforce generalized orthogonality among the left or right eigenvectors.

*Concluding remarks.* Similarity constrained coupled cluster theory (SCCSD) gives a physically correct description of an  $2^1A'/3^1A'$  same-symmetry conical intersection in hypofluorous acid, with both the proper dimensionality of the intersection seam as well as the correct energy gap linearity in the branching plane.<sup>2</sup> Confirming our predictions from a recent paper<sup>44</sup> and resolving a long-standing problem in coupled cluster theory,<sup>24</sup> this finding demonstrates that the model can properly describe, with minor modifications, same-symmetry conical intersections between electronic excited states.

Nonadiabatic coupling elements and energy gradients govern the dynamics close to a conical intersection.<sup>55</sup> Implementing these quantities in the similarity constrained theory is thus necessary for it to be applied in *ab initio* dynamics simulations. These developments are within reach in the near future, although some controversies for the nonadiabatic coupling elements remains to be settled.<sup>14,56</sup> On the other hand, techniques for energy gradients are well-established.<sup>54,57</sup> For use in dynamics simulations on larger systems, the model should be extended to the lower levels in the coupled cluster hierarchy. Particularly relevant is a perturbative doubles model (SCC2, analogous to CC2<sup>29</sup>), which should scale as  $N^5$ , where  $N$  is the number of orbitals. Further developments include implementations of cluster operators which ensure orbital invariance, state invariance among the intersecting states, and continuity of the potential energy surfaces.

As a closing remark, we note that the approach adopted in this paper, namely to enforce a feature of the exact wave function (*i.e.*, nondefectiveness), could potentially have more wide-reaching applications. The standard philosophy in *ab initio* quantum chemistry is to solve ever more accurate representations of the Schrödinger equation (the coupled cluster hierarchy results by expanding the subspace onto which the equation is projected). Yet many desirable features of the wave function—such as gauge invariance, the related origin invariance,<sup>58</sup> and the correct scaling of molecular properties and transition moments<sup>54,59</sup>—are only valid for a complete cluster operator, and in some cases a complete one-electron basis. Constraining the approximate wave function to satisfy exact properties may turn out to be very useful.

*Computational details.* Calculations were carried out using the Dalton quantum chemistry program.<sup>60</sup> We converged energies and residuals to within  $10^{-8}$ . The orthogonality in equation (3) was converged to within  $10^{-6}$ , giving energies correct to approximately  $10^{-6}$  Hartrees. The energies in Figures 2 and 3 are obtained by  $\tau_{IJK}^{ABC} = \tau_{8,8,7}^{7,2,3}$  and  $\tau_{IJK}^{ABC} = \tau_{7,5,8}^{10,2,2}$ , respectively, where the canonical orbitals are ordered according to their energy, from low to high. Complex energies were converged with a modified Davidson algorithm.<sup>28</sup>

A branching plane in hypofluorous acid was identified as follows. First we located a point of intersection. By searching along three orthonormal vibrational coordinates, we then found the intersection seam vector  $\mathbf{s}$ , the direction in which the degeneracy is preserved. To obtain an orthogonal basis of the branching plane (the orthogonal complement to  $\mathbf{s}$ ), we chose the direction in which the energy difference increased most (denoted  $\mathbf{g}$ , where  $\mathbf{g} \perp \mathbf{s}$ ) and the vector orthogonal to  $\mathbf{s}$  and  $\mathbf{g}$  (denoted  $\mathbf{h}$ ). The normal modes used in the above procedure, as well as cartesian coordinates of  $\mathbf{s}$ ,  $\mathbf{g}$ ,  $\mathbf{h}$ , and of the intersection geometry  $\mathbf{R}_0$ , are given in the Supporting Information.

For formaldehyde, we performed the scan  $R_{\text{CO}} = 1.3450 : 0.0005 : 1.3550 \text{ \AA}$ . Some additional points were included for CCSD. For hypofluorous acid (where  $\mathbf{g}_{\text{scan}} = g \mathbf{g}$  and  $\mathbf{h}_{\text{scan}} = h \mathbf{h}$ ),  $g = -0.010 : 0.001 : 0.010$  and  $h = -0.1160 : 0.0116 : 0.1160$ . Interpolated values are shown in both figures.

The triples excitations used are as follows. In formaldehyde, the excitation is the product of the second-largest singles and the largest doubles excitations in the lower state at  $1.3450 \text{ \AA}$ . In hypofluorous acid, the excitation is the product of the largest singles and doubles excitations in the lower states at the geometry given by  $R_{\text{OH}} = 1.1400 \text{ \AA}$ ,  $R_{\text{OF}} = 1.3184 \text{ \AA}$ , and  $\vartheta_{\text{HOF}} = 91.06^\circ$ .

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### Notes

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## Supporting information available:

The supporting information includes a derivation of the generalized orthogonality condition, an analysis of the size scaling properties of the model, and a detailed description of the model equations and their implementation. Also included are more details on the performed calculations and the energies obtained using different triple excitations in hypofluorous acid.

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