

# Supporting information: Resolving the notorious case of conical intersections for coupled cluster dynamics

Eirik F. Kjørstad<sup>†,‡</sup> and Henrik Koch<sup>\*,†,‡</sup>

<sup>†</sup>*Department of Chemistry, Norwegian University of Science and Technology, 7491  
Trondheim, Norway*

<sup>‡</sup>*Department of Chemistry and the PULSE Institute, Stanford University, Stanford,  
California 94305, USA*

E-mail: [henrik.koch@ntnu.no](mailto:henrik.koch@ntnu.no)

# Derivation of the generalized orthogonality in the full space limit

The energies of the coupled cluster model are equal to the eigenvalues of the matrix

$$(\mathbf{A} + E_0 \mathbf{I})_{\mu\nu} = \langle \Phi_\mu | e^{-T} H e^T | \Phi_\nu \rangle, \quad E_0 = \langle \Phi_0 | e^{-T} H e^T | \Phi_0 \rangle, \quad (\text{S1})$$

where  $T$  has been determined from the amplitude equations (see, *e.g.*, Purvis and Bartlett<sup>1</sup>), and where  $\mu, \nu \geq 0$ . In the limit where  $\mu$  and  $\nu$  run over all excitations, the identity operator can be written  $\mathbb{I} = \sum_{\mu \geq 0} |\Phi_\mu\rangle \langle \Phi_\mu|$ , where we assume that  $\{|\Phi_\mu\rangle\}_\mu$  is an orthonormal basis. Inserting this resolution of  $\mathbb{I}$  before and after  $H$  leads to the following expression for  $\mathbf{A} + E_0 \mathbf{I}$ :

$$\begin{aligned} (\mathbf{A} + E_0 \mathbf{I})_{\mu\nu} &= \sum_{\tau\sigma \geq 0} \langle \Phi_\mu | e^{-T} | \Phi_\tau \rangle \langle \Phi_\tau | H | \Phi_\sigma \rangle \langle \Phi_\sigma | e^T | \Phi_\nu \rangle \\ &= \sum_{\tau\sigma \geq 0} Q_{\mu\tau}^{-1} H_{\tau\sigma} Q_{\sigma\nu} \\ &= (\mathbf{Q}^{-1} \mathbf{H} \mathbf{Q})_{\mu\nu}. \end{aligned} \quad (\text{S2})$$

That  $\mathbf{Q}^{-1}$  is the inverse of  $\mathbf{Q}$  is straightforwardly verified:

$$(\mathbf{Q}^{-1} \mathbf{Q})_{\mu\nu} = \sum_{\tau \geq 0} \langle \Phi_\mu | e^{-T} | \Phi_\tau \rangle \langle \Phi_\tau | e^T | \Phi_\nu \rangle = \langle \Phi_\mu | e^{-T} e^T | \Phi_\nu \rangle = \delta_{\mu\nu}. \quad (\text{S3})$$

It follows from equation (S2) that the left and right eigenvectors of  $\mathbf{A} + E_0 \mathbf{I}$ , and therefore of  $\mathbf{A}$ , satisfy (up to normalization)

$$\mathbf{l}_k^T (\mathbf{Q}^T \mathbf{Q})^{-1} \mathbf{l}_l = \delta_{kl}, \quad \mathbf{r}_k^T \mathbf{Q}^T \mathbf{Q} \mathbf{r}_l = \delta_{kl}, \quad (\text{S4})$$

because the eigenvectors of the symmetric matrix  $\mathbf{H}$  are orthogonal.

## System size scaling properties

For a non-interacting only system  $AB$  with a conical intersection on the  $A$  system, the cluster operator has the form  $\mathcal{T} = \mathcal{T}_A + T_B$ , where  $\mathcal{T}_A$  and  $T_B$  only contains excitations within the subsystems  $A$  and  $B$ , respectively. As a consequence, the similarity transformed Hamiltonian separates in the usual size-extensive manner,  $\bar{H} = \bar{H}_A + \bar{H}_B$ . The energy is  $E = \langle R_A | \bar{H}_A | R_A \rangle + \langle R_B | \bar{H}_B | R_B \rangle = E_A + E_B$  and the ground state equations reduce to the amplitude equations for each subsystem. The size-intensive compound block structure of the Jacobian  $\mathbf{A}$  then follows from the amplitude equations (see p. 683 in Helgaker *et al.*<sup>2</sup>), providing excitation energies and excited state vectors belonging to the correct blocks of  $\mathbf{A}$ , *i.e.*  $\mathbf{A}_{A,A}$  and  $\mathbf{A}_{B,B}$ .

However, the metric  $\mathbf{Q}^T \mathbf{Q}$  contains a non-zero  $AB$  coupling term. An implication is that, while the energy, the wavefunction, and the excited states contain no coupling terms, the energies for an isolated  $A$  system are not identical to those obtained for the  $AB$  system. Note that the energies of the  $B$  system remain unchanged. Asymptotically, the  $AB$  coupling term becomes independent of the number of  $B$  fragments, giving a constant error for the  $A$  system in the limit of an infinite number of  $B$  fragments. There are many alternative approximations of  $\mathbf{Q}^T \mathbf{Q}$  without  $AB$  terms. For instance,  $\mathbf{Q}^T \mathbf{Q}$  could be approximated by  $\mathbf{Q}^T \mathbf{P} \mathbf{Q}$ , where  $\mathbf{P}$  is a projection matrix onto the space of the reference and the two excited states of interest,  $\{|R\rangle, |r_1\rangle, |r_2\rangle\}$ . In practice, the effect of the  $AB$  term appears to be small, however. By positioning a Helium-atom at a distance of 100 Å from HOF, we obtained energy changes that are negligible compared to CISD (see Table S1).

## Implementation

The model was implemented in a local version of the Dalton quantum chemistry suite,<sup>3</sup> and a local coupled cluster program currently in the initial phases of development.

**Table S1: Differences in SCCSD and CISD energies of HOF compared to energies obtained when a He atom is positioned 100 Å from HOF. We list the absolute errors, in Hartrees, of the ground state and first two  $A'$  excited state energies,  $\Delta E_0(\text{HOF})$ ,  $\Delta E_1(\text{HOF})$ , and  $\Delta E_2(\text{HOF})$ . A convergence threshold of  $10^{-10}$  has been used. The HOF geometry is  $R_{\text{OH}} = 1.14$  Å,  $R_{\text{OF}} = 1.32$  Å, and  $\vartheta_{\text{HOF}} = 91.0^\circ$ .**

	$\Delta E_0(\text{HOF})$	$\Delta E_1(\text{HOF})$	$\Delta E_2(\text{HOF})$
CISD	0.00566816	0.03384339	0.03383982
SCCSD	$2.9 \cdot 10^{-9}$	$5 \cdot 10^{-10}$	$6 \cdot 10^{-10}$

## The projection vector and the coupled cluster Jacobian

In similarity constrained CCSD (SCCSD), an additional triple excitation and amplitude is added to the cluster operator,  $\mathcal{T}$ . With this cluster operator, both the projection vector,  $\Omega_\mu = \langle \Phi_\mu | e^{-\mathcal{T}} H e^{\mathcal{T}} | \Phi_0 \rangle$ , and the Jacobian matrix,  $A_{\mu\nu} = \langle \Phi_\mu | e^{-\mathcal{T}} [H, \tau_\nu] e^{\mathcal{T}} | \Phi_0 \rangle$ , are modified relative to CCSD. We refer to the literature for detailed expressions of  $\Omega$  and  $\mathbf{A}$  in CCSD.<sup>1,4</sup>

First we introduce a spin-adapted biorthonormal excitation manifold in which to express our matrices. We use the elementary basis (see p. 691-692 in Helgaker *et al.*<sup>2</sup>)

$$\left| \begin{matrix} a \\ i \end{matrix} \right\rangle = E_{ai} |\Phi_0\rangle, \quad \left| \begin{matrix} ab \\ ij \end{matrix} \right\rangle = E_{ai} E_{bj} |\Phi_0\rangle \quad (\text{S5})$$

as the right basis, where  $E_{ai} = a_{a\alpha}^\dagger a_{i\alpha} + a_{a\beta}^\dagger a_{i\beta}$ , and

$$\left\langle \begin{matrix} a \\ i \end{matrix} \right| = \frac{1}{2} \langle \Phi_0 | E_{ai}^\dagger, \quad \left\langle \begin{matrix} ab \\ ij \end{matrix} \right| = \frac{1}{1 + \delta_{ai,bj}} \left( \frac{1}{3} \langle \Phi_0 | E_{ai}^\dagger E_{bj}^\dagger + \frac{1}{6} E_{aj}^\dagger E_{bi}^\dagger \right) \quad (\text{S6})$$

as the left basis.

We may now list explicit expressions for the projection vector and the transformation by the coupled cluster Jacobian, as well as its transpose:  $\Omega$ ,  $\boldsymbol{\rho} = \mathbf{A} \mathbf{c}$ , and  $\boldsymbol{\sigma} = \mathbf{A}^T \mathbf{b}$ . Let

$T = T_1 + T_2 + T_3$ , where  $T_3$  is general for now:

$$T_1 = \sum_{ai} t_i^a E_{ai}, \quad T_2 = \frac{1}{2} \sum_{aibj} t_{ij}^{ab} E_{ai} E_{bj}, \quad T_3 = \frac{1}{6} \sum_{aibjck} t_{ijk}^{abc} E_{ai} E_{bj} E_{ck}. \quad (\text{S7})$$

For  $\boldsymbol{\rho} = \mathbf{A} \mathbf{c}$  we have  $\rho_{ai} = \rho_{ai}^{\text{CCSD}}$  and

$$\begin{aligned} \rho_{aibj} - \rho_{aibj}^{\text{CCSD}} = \frac{1}{1 + \delta_{ai,bj}} \mathcal{P}_{ij}^{ab} \left( \sum_{ck} (t_{ijk}^{abc} - t_{ikj}^{abc}) X_{kc} - \sum_{ckl} (2t_{jkl}^{bac} - t_{lkj}^{bac} - t_{jlk}^{bac}) Y_{lcki} \right. \\ \left. + \sum_{cdk} (2t_{jik}^{bcd} - t_{kij}^{bcd} - t_{jki}^{bcd}) Z_{ackd} \right), \end{aligned} \quad (\text{S8})$$

where

$$X_{ld} = \sum_{ck} L_{kcld} c_{ck}, \quad Y_{kclj} = \sum_d g_{kcld} c_{dj}, \quad Z_{ackd} = - \sum_k g_{kcld} c_{ak}. \quad (\text{S9})$$

In the above, we have introduced  $\mathcal{P}_{ij}^{ab}$ , whose effect is to add all permutations of the index pairs  $(ai)$  and  $(bj)$ , and  $g_{pqrs}$ , the two-electron  $T_1$  transformed integrals associated with the  $T_1$  transformed Hamiltonian  $\hat{H}$ . The projection vector has the singles contribution

$$\Omega_{ai} - \Omega_{ai}^{\text{CCSD}} = \sum_{bjck} (t_{ijk}^{abc} - t_{ijc}^{cba}) L_{jbkc}, \quad L_{jbkc} = 2g_{jbkc} - g_{jckb}. \quad (\text{S10})$$

The doubles contribution is identical to that of  $\boldsymbol{\rho}$ , except that the  $X$ ,  $Y$ , and  $Z$  intermediates assume the altered definitions

$$X_{kc} = F_{kc}, \quad Y_{lcki} = g_{lcki}, \quad Z_{ackd} = g_{ackd}. \quad (\text{S11})$$

We have denoted by  $F_{pq}$  the elements of the  $T_1$  transformed Fock operator, which is defined as the ordinary Fock operator but with  $T_1$  transformed integrals. For  $\boldsymbol{\sigma} = \mathbf{A}^T \mathbf{b}$  we have

$\sigma_{aibj} = \sigma_{aibj}^{\text{CCSD}}$  and, finally,

$$\begin{aligned}
\sigma_{ck} - \sigma_{ck}^{\text{CCSD}} &= \sum_{dlemfn} (t_{lmn}^{def} - t_{lnm}^{def}) b_{dlem} L_{kcnf} \\
&+ \sum_{dlemfn} (t_{mln}^{def} + t_{lnm}^{def} - 2t_{lmn}^{def}) b_{dlcn} g_{mekf} \\
&+ \sum_{dlemfn} (t_{lnm}^{def} + t_{nml}^{def} - 2t_{lmn}^{def}) b_{dlek} g_{mcnf}.
\end{aligned} \tag{S12}$$

The expressions listed above are those of coupled cluster singles doubles triples (CCSDT) and are also found in the literature.<sup>5</sup> In the similarity constrained formalism, one particular triple excitation ( $\tau_{IJK}^{ABC}$ ) is selected to be non-zero. We can therefore write

$$t_{ijk}^{abc} = \zeta \mathcal{P}_{IJK}^{ABC} \delta_{aibjck, AIBJCK}, \tag{S13}$$

where  $\zeta$  is the magnitude of the chosen triple amplitude, and substitute this  $t_{ijk}^{abc}$  in the above expressions. Here we have introduced  $\mathcal{P}_{IJK}^{ABC}$ , which permutes the index pairs  $(AI)$ ,  $(BJ)$ , and  $(CK)$ . Doing the substitution results in

$$\Omega_{ai} - \Omega_{ai}^{\text{CCSD}} = \zeta \mathcal{P}_{IJK}^{ABC} (\delta_{ai, AI} L_{JBKC} - \delta_{ai, CI} L_{JBKA}) \tag{S14}$$

for the singles part of  $\Omega$ . The doubles part  $\Omega$  is equal to that of  $\rho$  (with redefined  $X$ ,  $Y$ , and  $Z$ ). For  $\rho$ , we find  $\rho_{ai} = 0$  and

$$\begin{aligned}
\rho_{aibj} - \rho_{aibj}^{\text{CCSD}} &= \frac{\zeta}{1 + \delta_{ai,bj}} \mathcal{P}_{ij}^{ab} \mathcal{P}_{IJK}^{ABC} \left( \delta_{aibj}^{AIBJ} X_{KC} - \delta_{aibj}^{AIBK} X_{JC} \right. \\
&- (2\delta_{bja}^{AIB} Y_{KCJi} - \delta_{baj}^{ABK} Y_{ICJi} - \delta_{bja}^{AIB} Y_{JCKi}) \\
&\left. + 2\delta_{bji}^{AIJ} Z_{aBKC} - \delta_{bij}^{AJK} Z_{aBIC} - \delta_{bji}^{AIK} Z_{aBJC} \right).
\end{aligned} \tag{S15}$$

Finally, for  $\sigma$  we find  $\sigma_{aij} = \sigma_{aij}^{\text{CCSD}}$  and

$$\begin{aligned} \sigma_{ck} - \sigma_{ck}^{\text{CCSD}} = & \zeta P_{IJK}^{ABC} (b_{AIBJ} L_{kcKC} - b_{AIBK} L_{kcJC} \\ & + b_{AJcK} g_{IBkC} + b_{AICJ} g_{KBkC} - 2b_{AICK} g_{JBkC} \\ & + b_{AIBk} g_{KcJC} + b_{AKBk} g_{JcIC} - 2b_{AIBk} g_{JcKC}). \end{aligned} \quad (\text{S16})$$

The equations we have implemented are (S14), for  $\mathbf{\Omega}_1$ , (S15), for  $\mathbf{\Omega}_2$  and  $\boldsymbol{\rho}$ , and (S16), for  $\sigma$ . For completeness, we note that expressions for energy  $E$  and the  $\boldsymbol{\eta}$  vector are unchanged:

$$E = \langle \Phi_0 | e^{-\mathcal{T}} H e^{\mathcal{T}} | \Phi_0 \rangle = E^{\text{CCSD}}, \quad (\text{S17})$$

$$\eta_\nu = \langle \Phi_0 | e^{-\mathcal{T}} [H, \tau_\nu] e^{\mathcal{T}} | \Phi_0 \rangle = \eta_\nu^{\text{CCSD}}. \quad (\text{S18})$$

---

**Algorithm 1** The SCCSD algorithm

---

- 1: Select two states  $k$  and  $l$  and a triple excitation  $\tau_{IJK}^{ABC}$ .
  - 2: Set  $t_{IJK}^{ABC} = 0$ .
  - 3: For the given  $t_{IJK}^{ABC}$ , solve  $\Omega_{\mu_1} = 0$  and  $\Omega_{\mu_2} = 0$  for  $t_{\mu_1}$  and  $t_{\mu_2}$ .
  - 4: Solve the multiplier equation  $\bar{\mathbf{t}}^T \mathbf{A} = -\boldsymbol{\eta}^T$  for the multipliers  $\bar{\mathbf{t}}$ .
  - 5: Solve the eigenvalue equation  $\mathbf{A} \mathbf{r}_i = \omega_i \mathbf{r}_i$  for the excited states  $\mathbf{r}_i$ .
  - 6: Evaluate the generalized overlap  $f(\mathcal{T})$ .
  - 7: **if**  $f(\mathcal{T}) = 0$  **then**
  - 8:     Stop.
  - 9: **else**
  - 10:     Estimate  $\partial f(\mathcal{T}) / \partial t_{IJK}^{ABC}$  by numerical differentiation.
  - 11:     Perform a Newton-Raphson step:  $t_{IJK}^{ABC} = t_{IJK}^{ABC} - f(\mathcal{T}) / (\partial f(\mathcal{T}) / \partial t_{IJK}^{ABC})$ .
  - 12:     Go to 3.
  - 13: **end if**
-

## The generalized overlap

For notational purposes, we denote full space quantities (*i.e.*, with  $\mu, \nu \geq 0$ ) by caligraphic font,  $\mathcal{X}$ , reserving  $X$  for the excited-excited block ( $\mu, \nu > 0$ ). Then we can write

$$\mathcal{A} = \begin{pmatrix} 0 & \boldsymbol{\eta}^T \\ 0 & \mathbf{A} \end{pmatrix} \quad (\text{S19})$$

and

$$\mathcal{Q} = \begin{pmatrix} 1 & 0 \\ \mathbf{q} & \mathbf{Q} \end{pmatrix}, \quad q_\mu = \langle \Phi_\mu | e^T | \Phi_0 \rangle, \quad Q_{\mu\nu} = \langle \Phi_\mu | e^T | \Phi_\nu \rangle. \quad (\text{S20})$$

Note that since we use a biorthonormal basis for  $\mathcal{Q}$  and  $\mathcal{A}$ , the elementary overlap matrix  $\mathcal{S}$  (the overlap of the  $|\Phi_\mu\rangle$ ) enters the expression for the generalized overlap  $f$ :

$$\mathcal{A} + E_0 \mathbf{I} = \mathcal{Q}^{-1} \mathcal{S}^{-1} \mathcal{H} \mathcal{Q}, \quad (\text{S21})$$

where  $\mathcal{H}$  is  $H$  expressed in the elementary basis (the kets  $|\Phi_\mu\rangle$ ). With this notation, the generalized overlap  $f$  between the state vectors  $\mathcal{R}_k$  and  $\mathcal{R}_l$  reads

$$f(\mathcal{T}) = \mathcal{R}_k^T \mathcal{Q}^T \mathcal{S} \mathcal{Q} \mathcal{R}_l, \quad (\text{S22})$$

an overlap over the positive definite matrix  $\mathcal{Q}^T \mathcal{S} \mathcal{Q}$ . In block-form, we moreover have

$$\mathcal{S} = \begin{pmatrix} 1 & 0 \\ 0 & \mathbf{S} \end{pmatrix}. \quad (\text{S23})$$

To derive a useful expression for  $f$ , we separate the reference and excited contributions.

Note that the left and right excited states satisfy

$$\mathcal{A}\mathcal{R}_n = \omega_n \mathcal{R}_n, \quad \mathcal{L}_n^T \mathcal{A} = \omega_n \mathcal{L}_n^T, \quad (\text{S24})$$

where the the left ground state vector is determined from the multiplier equation<sup>4</sup>

$$\mathcal{L}_0^T = (1 \ \bar{\mathbf{t}}^T), \quad \bar{\mathbf{t}}^T \mathbf{A} = -\boldsymbol{\eta}^T. \quad (\text{S25})$$

From this it is straight-forward to show that

$$\mathcal{L}_n^T = (0 \ \mathbf{l}_n^T), \quad \mathcal{R}_n = \begin{pmatrix} -\bar{\mathbf{t}}^T \mathbf{r}_n \\ \mathbf{r}_n \end{pmatrix}, \quad \mathbf{A} \mathbf{r}_n = \omega_n \mathbf{r}_n, \quad \mathbf{l}_n^T \mathbf{A} = \omega_n \mathbf{l}_n^T, \quad n > 0. \quad (\text{S26})$$

Substituting the block forms of  $\mathcal{Q}$  and  $\mathcal{R}_n$  into the expression for  $f$  gives

$$f(\mathcal{T}) = \mathbf{r}_k^T (\mathcal{N} \bar{\mathbf{t}} \bar{\mathbf{t}}^T + \mathbf{Q}^T \mathbf{S} \mathbf{Q} - \mathbf{Q}^T \mathbf{S} \mathbf{q} \bar{\mathbf{t}}^T - \bar{\mathbf{t}} \mathbf{q}^T \mathbf{S} \mathbf{Q}) \mathbf{r}_l = 0, \quad (\text{S27})$$

where  $\mathcal{N} = 1 + \mathbf{q}^T \mathbf{S} \mathbf{q}$ . This is the implemented expression for the generalized overlap. The vector  $\mathbf{q}$  can be evaluated as

$$q_{ai} = t_i^a, \quad q_{aibj} = \frac{1}{1 + \delta_{ai,bj}} (t_{ij}^{ab} + t_i^a t_j^b). \quad (\text{S28})$$

The transformation  $\mathbf{y} = \mathbf{Q} \mathbf{x}$  is

$$y_{ai} = x_{ai}, \quad y_{aibj} = x_{aibj} + \frac{1}{1 + \delta_{ai,bj}} (t_j^b x_{ai} + t_i^a x_{bj}). \quad (\text{S29})$$

The transformation  $\mathbf{y} = \mathbf{Q}^T \mathbf{x}$  can be written

$$y_{ai} = x_{ai} + \sum_{ck} t_k^c x_{aick}, \quad y_{aibj} = x_{aibj}. \quad (\text{S30})$$

Finally,  $\mathbf{y} = \mathbf{S} \mathbf{x}$  can be written

$$y_{ai} = 2x_{ai}, \quad y_{aibj} = 2(1 + \delta_{ai,bj})(2x_{aibj} - x_{ajbi}). \quad (\text{S31})$$

## Implementation tests

The following tests were performed.

- For a given value of  $\zeta$ , the excitation energies  $\omega_n$  derived from the left and right eigenvalue problems are identical. Thus,  $\mathbf{A}$  and  $\mathbf{A}^T$  are internally consistent.
- For a given value of  $\zeta$ , the identity<sup>4</sup>

$$A_{\mu\nu} = \frac{\partial \Omega_\mu}{\partial t_\nu}, \quad (\text{S32})$$

evaluated by numerical differentiation and by transformation of elementary basis vectors, is satisfied for the LiH molecule. Thus,  $\mathbf{\Omega}$  and  $\mathbf{A}$  are internally consistent. Moreover, by the previous test,  $\mathbf{\Omega}$ ,  $\mathbf{A}$ , and  $\mathbf{A}^T$  are internally consistent.

- We confirmed that

$$\bar{\mathbf{t}}^T = \frac{\mathbf{q}^T \mathbf{S} \mathbf{Q}}{1 + \mathbf{q}^T \mathbf{S} \mathbf{q}}, \quad (\text{S33})$$

is satisfied for  $\text{H}_2$ , indicating that the implementation of  $\mathbf{q}$  and  $\mathbf{Q}$  are correct. This identity can be shown to be valid from the completeness of  $T = T_1 + T_2$ .

- For two states of the same symmetry in  $\text{H}_2$ , we confirmed that

$$\mathcal{R}_k^T \mathcal{Q}^T \mathcal{S} \mathcal{Q} \mathcal{R}_l = 0 \quad (\text{S34})$$

is correct to the accuracy that the amplitudes and eigenvectors are converged.

- Noting that

$$Q_{\mu\nu} = Q_{\mu\nu}(\mathcal{T}) = \langle \Phi_\mu | e^{\mathcal{T}} | \Phi_\nu \rangle, \quad Q_{\mu\nu}^{-1} = \langle \Phi_\mu | e^{-\mathcal{T}} | \Phi_\nu \rangle = Q_{\mu\nu}(-\mathcal{T}), \quad (\text{S35})$$

we confirmed that  $\mathbf{Q}(\mathcal{T}) \mathbf{Q}(-\mathcal{T})$  and  $\mathbf{Q}^T(\mathcal{T}) \mathbf{Q}^T(-\mathcal{T})$  equal the identity matrix  $\mathbf{I}$  for the implemented  $\mathbf{Q}$  and  $\mathbf{Q}^T$  transformations.

- We confirmed that  $\mathbf{q}^T \mathbf{S} \mathbf{Q} \mathbf{x}$  and  $\mathbf{x}^T \mathbf{Q}^T \mathbf{S} \mathbf{q}$  are equal, indicating that  $\mathbf{Q}$  and  $\mathbf{Q}^T$  are internally consistent.

## The algorithm

We adopt a self-consistent approach. For a fixed triple amplitude,  $t_{\mu_3}$ , the ground state amplitude equations,  $\mathbf{\Omega} = 0$ , are first solved for  $t_{\mu_1}$  and  $t_{\mu_2}$ . Given the converged singles and doubles amplitudes, the excited states  $\mathbf{r}_i$  are found and the overlap  $f(\mathcal{T})$  evaluated. A Newton-Raphson algorithm, designed to locate a zero of the overlap function  $f(\mathcal{T})$ , then provides the next triple amplitude  $t_{\mu_3}$ . These steps are repeated until both the ground state equations are satisfied and  $f(\mathcal{T}) = 0$ . See Algorithm 1.

## The cluster operator

In the similarity constrained theory, a particular triple excitation is used. In Table S2, we list the energies obtained for hypofluorous acid using twelve different triple excitations.

## Left generalized orthogonality

We have chosen to enforce orthogonality of the right eigenvectors in the present study, but, for completeness, we list the equations necessary to enforce orthogonality among the left

eigenvectors here. The left overlap  $f_L$  can be written

$$f_L(\mathcal{T}) = \mathcal{L}_k^T (\mathcal{Q}^T \mathcal{S} \mathcal{Q})^{-1} \mathcal{L}_l. \quad (\text{S36})$$

By block inversion of  $\mathcal{Q}$  and  $\mathcal{S}$ , we have

$$\mathcal{Q}^{-1} = \begin{pmatrix} 1 & 0 \\ -\mathbf{Q}^{-1}\mathbf{q} & \mathbf{Q}^{-1} \end{pmatrix}, \quad \mathcal{S}^{-1} = \begin{pmatrix} 1 & 0 \\ 0 & \mathbf{S}^{-1} \end{pmatrix}. \quad (\text{S37})$$

and therefore

$$\begin{aligned} (\mathcal{Q}^T \mathcal{S} \mathcal{Q})^{-1} &= \begin{pmatrix} 1 & 0 \\ -\mathbf{Q}^{-1}\mathbf{q} & \mathbf{Q}^{-1} \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & \mathbf{S}^{-1} \end{pmatrix} \begin{pmatrix} 1 & -\mathbf{q}^T \mathbf{Q}^{-T} \\ 0 & \mathbf{Q}^{-T} \end{pmatrix} \\ &= \begin{pmatrix} 1 & -\mathbf{q}^T \mathbf{Q}^{-T} \\ -\mathbf{Q}^{-1}\mathbf{q} & \mathbf{Q}^{-1}(\mathbf{S}^{-1} + \mathbf{q}\mathbf{q}^T)\mathbf{Q}^{-T} \end{pmatrix}. \end{aligned} \quad (\text{S38})$$

Now, because the reference term of  $\mathcal{L}_k$  is zero (it is orthogonal to  $\mathcal{R}_0$ ), we can write

$$f_L(\mathcal{T}) = \mathbf{I}_k^T \mathbf{Q}^{-1} (\mathbf{S}^{-1} + \mathbf{q}\mathbf{q}^T) \mathbf{Q}^{-T} \mathbf{l}_l. \quad (\text{S39})$$

## Hypoflorous acid: intersection point, normal modes, seam, and branching plane vectors

### Intersection point

The studied intersection geometry hypofluorous acid is

$$R_{\text{OH}} = 1.1400000 \text{ \AA}, \quad R_{\text{OF}} = 1.3184215 \text{ \AA}, \quad \vartheta_{\text{HOF}} = 91.0585000^\circ, \quad (\text{S40})$$

where the triple amplitude is  $\zeta = 1.6178960762$ . For this geometry and amplitude, the overlap is below  $10^{-6}$  and the energies degenerate to  $10^{-6}$ :

$$\omega_1 = 0.3163264850 \text{ Hartrees}, \quad \omega_2 = 0.3163274291 \text{ Hartrees.} \quad (\text{S41})$$

## Normal modes

We specify the nuclear cartesian coordinates as

$$\mathbf{R} = (O_x, O_y, O_z, H_x, H_y, H_z, F_x, F_y, F_z) \quad (\text{S42})$$

in the following. From a vibrational Hartree-Fock calculation using the Cfour program,<sup>6</sup> we obtained a set of normal modes,

$$\mathbf{Q}_1 = (0.7370, -0.0071, 0.0000, -0.0070, 0.0211, 0.0000, -0.6750, 0.0017, 0.0000), \quad (\text{S43})$$

$$\mathbf{Q}_2 = (0.0749, -0.2371, 0.0000, -0.7773, 0.5604, 0.0000, 0.1103, 0.0885, 0.0000), \quad (\text{S44})$$

$$\mathbf{Q}_3 = (0.0773, 0.1431, 0.0000, -0.5890, -0.7874, 0.0000, 0.0647, 0.0500, 0.0000). \quad (\text{S45})$$

The cartesian coordinate vector at the intersection point is

$$\begin{aligned} \mathbf{R}_0 = & (-1.308090861096777, 0.135129007453069, 0.000000000000000, \\ & -1.470679327231972, -2.013015024947860, 0.000000000000000, \\ & 1.179309062794356, -0.006980060310293, -0.000000000000000). \end{aligned} \quad (\text{S46})$$

## The seam and branching plane vectors

By performing small displacements in the normal modes  $\mathbf{Q}_i$ , we found the basis  $\{\mathbf{g}, \mathbf{h}\}$  of the branching plane and the seam  $\mathbf{s}$ . In the basis of the normal modes,

$$\mathbf{g} = (0.972636, -0.160489, 0.167996), \quad (\text{S47})$$

$$\mathbf{s} = (0.220983, 0.407941, -0.885862), \quad (\text{S48})$$

$$\mathbf{h} = (0.073639, 0.898745, 0.432243). \quad (\text{S49})$$

Note that these vectors are expected to have some numerical imprecision, arising from the finite number of fixed-point calculations on which they are based ( $\mathbf{s}$  and  $\mathbf{g}$  are nearly but not perfectly orthogonal,  $89.96^\circ$ ) and that the  $\mathbf{Q}_i$  is given to four decimal places.

## References

1. Purvis III, G. D.; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982**, *76*, 1910–1918.
2. Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John Wiley & Sons, 2014.
3. Aidas, K.; Angeli, C.; Bak, K. L.; Bakken, V.; Bast, R.; Boman, L.; Christiansen, O.; Cimiraglia, R.; Coriani, S.; Dahle, P. et al. The Dalton Quantum Chemistry Program System. *WIREs Comput. Mol. Sci.* **2014**, *4*, 269–284.
4. Koch, H.; Jørgensen, P. Coupled Cluster Response Functions. *J. Chem. Phys.* **1990**, *93*, 3333–3344.
5. Koch, H.; Christiansen, O.; Jørgensen, P.; Sanchez de Merás, A. M.; Helgaker, T. The CC3 Model: An Iterative Coupled Cluster Approach Including Connected Triples. *J. Chem. Phys.* **1997**, *106*, 1808–1818.

6. Stanton, J.; Gauss, J.; Harding, M.; Szalay, P.; Auer, A.; Bartlett, R.; Benedikt, U.; Berger, C.; Bernholdt, D.; Bomble, Y. et al. CFOUR, a quantum chemical program package.

**Table S2: Energies obtained by various triple excitations  $\tau_{IJK}^{ABC}$  for the geometry  $R_{\text{OH}} = 1.14 \text{ \AA}$ ,  $R_{\text{OF}} = 1.32 \text{ \AA}$ , and  $\vartheta_{\text{HOF}} = 91.0^\circ$ . We list CC2, SCCSD, CCSD, and CC3 energies given in Hartrees and the aug-cc-pVDZ basis. Dashes (–) denote that we were unable to converge the SCCSD equations. The first excitation listed in the table was used in the paper.**

$\begin{pmatrix} A & B & C \\ I & J & K \end{pmatrix}$	$E_0$	$E_1$	$E_2$	$\omega_1$	$\omega_2$	$\zeta$
$\begin{pmatrix} 10 & 2 & 2 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1605	-174.8452	-174.8440	0.3153	0.3165	1.6688
$\begin{pmatrix} 10 & 2 & 8 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1619	-174.8445	-174.8435	0.3174	0.3184	-0.6551
$\begin{pmatrix} 10 & 2 & 10 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1611	-174.8467	-174.8431	0.3144	0.3180	2.2880
$\begin{pmatrix} 8 & 2 & 2 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1605	-174.8448	-174.8434	0.3157	0.3170	1.6531
$\begin{pmatrix} 8 & 2 & 8 \\ 7 & 5 & 8 \end{pmatrix}$	–	–	–	–	–	–
$\begin{pmatrix} 8 & 2 & 10 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1613	-174.8448	-174.8436	0.3165	0.3176	0.4853
$\begin{pmatrix} 3 & 1 & 1 \\ 8 & 8 & 5 \end{pmatrix}$	-175.1623	-174.8455	-174.8430	0.3168	0.3193	2.7638
$\begin{pmatrix} 10 & 1 & 1 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1639	-174.8445	-174.8416	0.3195	0.3223	-1.3795
$\begin{pmatrix} 10 & 1 & 2 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1616	-174.8451	-174.8441	0.3165	0.3175	-0.4178
$\begin{pmatrix} 10 & 1 & 3 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1639	-174.8438	-174.8428	0.3201	0.3211	-1.0914
$\begin{pmatrix} 8 & 1 & 1 \\ 7 & 5 & 8 \end{pmatrix}$	-175.1597	-174.8469	-174.8453	0.3127	0.3144	1.7677
$\begin{pmatrix} 8 & 1 & 2 \\ 7 & 5 & 8 \end{pmatrix}$	–	–	–	–	–	–
CC2	-175.1590	-174.8600	-174.8440	0.2990	0.3150	–
CCSD	-175.1619	-174.8451	-174.8437	0.3168	0.3181	–
CC3	-175.1745	-174.8585	-174.8558	0.3160	0.3187	–