


Biorthonormal Formalism for Nonadiabatic Coupled Cluster Dynamics

Eirik F. Kjønstad and Henrik Koch*

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ABSTRACT: In coupled cluster theory, the electronic states are biorthonormal in the sense that the left states are orthonormal to the right states. Here, we present an extension of this formalism to a left and right total molecular wave function. Starting from left and right Born–Huang expansions, we derive projected Schrödinger equations for the left and right nuclear wave functions. Observables may be extracted from the resulting wave function pair using standard expressions. The formalism is shown to be invariant under electronic basis transformations, such as normalization of the electronic states. Consequently, the nonadiabatic coupling elements can be expressed with biorthonormal electronic wave functions. Calculating normalization factors that scale as full configuration interaction is not necessary, contrary to claims in the literature. For nonadiabatic nuclear dynamics, we need expressions for the derivative couplings in the biorthonormal formalism. These are derived in a Lagrangian framework.

$$\begin{aligned}\tilde{\Psi}(\mathbf{r}, \mathbf{R}, t) &= \sum_n \tilde{\chi}_n(\mathbf{R}, t) \tilde{\psi}_n(\mathbf{r}; \mathbf{R}) \\ \Psi(\mathbf{r}, \mathbf{R}, t) &= \sum_n \chi_n(\mathbf{R}, t) \psi_n(\mathbf{r}; \mathbf{R}) \\ \langle \Omega \rangle &= \langle \tilde{\Psi} | \Omega | \Psi \rangle, \quad \langle \tilde{\Psi} | \Psi \rangle = 1\end{aligned}$$

INTRODUCTION

Nonadiabatic coupling elements account for electron–nucleus interactions that are neglected in the Born–Oppenheimer¹ (BO) approximation. These elements couple different electronic states through the nuclear kinetic energy operator. While mostly negligible in ground-state chemistry, coupling elements are required when considering molecular dynamics in excited electronic states. Excited-state dynamics often involves regions of nuclear space where electronic states are nearly or exactly degenerate, causing a breakdown of the BO separation.^{2,3} Accurately describing nonadiabatic coupling elements is therefore important for reliable predictions in photochemistry.

Coupled cluster theory is one of the most accurate electronic structure methods, both for ground- and excited-state properties,^{4–7} but it has not found widespread use for predicting nonadiabatic dynamics. This is primarily because standard coupled cluster methods give a nonphysical description of regions close to electronic degeneracies or conical intersections.^{8–10} This issue can be traced to the method's non-Hermiticity, which seems to imply that coupled cluster methods cannot be used for nonadiabatic dynamics. However, this is not the case. As we have shown in recent work, the method can be constrained to give a correct physical description of excited-state conical intersections while retaining the standard non-Hermitian formalism and presumably its accuracy.^{11,12} These developments may lead to renewed interest in simulations of nonadiabatic dynamics that use coupled cluster theory to describe the electronic structure. While ground-state intersections are not easily treated, the method is expected to accurately describe relaxation between excited states.

Nonadiabaticity, as described by coupled cluster methods, has been considered by several authors. The first-order derivative coupling (or vector coupling) was first derived by Christiansen,¹³ who applied the *Z*-vector substitution method¹⁴ on a biorthonormal expression for the coupling,

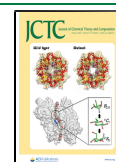
$$\mathbf{F}_{mm}^I = \langle \tilde{\psi}_m | \nabla_I \psi_n \rangle, \quad \langle \tilde{\psi}_m | \tilde{\psi}_n \rangle = \delta_{mn} \quad (1)$$

where $(\tilde{\psi}_l, \psi_k)$ refers to the left and right *k*th electronic states and *I* refers to a nucleus. However, Christiansen's paper¹³ did not include an implementation of the coupling. The vector coupling was later rederived by Tajti and Szalay¹⁵ by differentiating the corresponding *m*-to-*n* transition element of the electronic Hamiltonian. Their derivation is closely related to that given by Ichino *et al.*¹⁶ for the quasidiabatic interstate coupling. Tajti and Szalay¹⁵ also gave an implementation at the coupled cluster singles and doubles (CCSD) level.¹⁷ These papers on the vector coupling^{13,15} did not include a discussion of the nuclear Schrödinger equations in coupled cluster theory, where the coupling elements enter.

The correct formula for the vector coupling has been a subject of some controversy. Tajti and Szalay¹⁵ argued that the biorthonormal formula in eq 1 is incorrect. As they correctly noted, the vector coupling changes with the norm of the left and right states. A similar observation had been made in an

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earlier paper on the diagonal BO correction.¹⁸ Since the vector coupling varies with the norm of the states, the full-CC vector coupling, as given by eq 1, is different from the full configuration interaction (full-CI) limit, where the left and right states are identical and usually normalized. They therefore suggested that normalizing the states was necessary. Furthermore, since the derivative can either act on the left or right state, they suggested using an average of the two.¹⁵ If true, these observations are troubling: because of the normalization factors for the right states, they imply that computing the vector coupling has a computational cost that scales as full-CI. In practice, the normalization factors are therefore approximated. However, it is unfortunate if one must resort to approximations other than the truncation level of the coupled cluster method (e.g., singles and doubles in CCSD). The need for normalization factors was also assumed in the recent CCSD implementation by Faraji *et al.*¹⁹

The first main objective of the present paper is to establish that normalization is not necessary. The reason is that normalization is a special case of an invertible transformation of the electronic basis. Such transformations do not change the expansion space in the Born–Huang expansion²⁰ and therefore do not change the molecular wave function. In particular, the coefficients in the Born–Huang expansion—that is, the nuclear wave functions—absorb the transformation of the electronic states. The vector coupling does depend on normalization, but this quantity is not an observable. Since normalization is not necessary, the biorthonormal formula in eq 1 is a valid option.

In a recent paper, Shamasundar²¹ found, for the rovibrational Schrödinger equation, that normalization does not affect the Born–Oppenheimer product wave function. He noted that this finding should also generalize to nonadiabatic dynamics, that is, the predicted dynamics should not depend on the normalization of the underlying electronic wave functions.²¹

Derivative couplings are readily derived with the Lagrangian approach.^{6,22–24} Here, we use the Lagrangian introduced for CASCI by Hohenstein²⁵ to derive ground-to-excited and excited-to-excited state couplings. This Lagrangian is based on an overlap whose geometrical derivatives are nonadiabatic coupling elements;²⁵ the approach bears some similarities to that used by Hättig *et al.*,^{26,27} who derived transition moments as derivatives of transition moment Lagrangians. We use the Lagrangian approach²⁵ to derive expressions for the vector coupling as well as the second-order derivative coupling (or scalar coupling)

$$G_{mn}^I = \langle \tilde{\psi}_m | \nabla_I^2 \psi_n \rangle \quad (2)$$

The scalar coupling is often omitted in dynamics simulations, but its potential influence on nonadiabatic dynamics has been considered in recent years.³

The second main objective of the paper is to give a framework for nonadiabatic dynamics using coupled cluster methods. In particular, we argue that the biorthonormal formalism for electronic wave functions implies a biorthonormal formalism for the molecular wave function. Hence, we must determine the left and right nuclear wave functions, and the nuclear motion is described by two sets of nuclear Schrödinger equations. The result is a molecular wave function pair ($\tilde{\Psi}, \Psi$). Observable quantities are calculated by the usual biorthonormal formulas.

THEORY

Electronic Wave Functions in Coupled Cluster Theory. In the equation of motion coupled cluster formalism, the n th ($n = 0, 1, 2, \dots$) left and right electronic states are expressed as²⁸

$$\langle \tilde{\psi}_n | = \langle \mathcal{L}_n | \exp(-T) = \sum_{\mu \geq 0} \mathcal{L}_\mu^n \langle \mu | \exp(-T) \quad (3)$$

and

$$| \psi_n \rangle = \exp(T) | \mathcal{R}_n \rangle = \sum_{\mu \geq 0} \exp(T) | \mu \rangle \mathcal{R}_\mu^n \quad (4)$$

where $\langle \tilde{\psi}_m | \psi_n \rangle = \delta_{mn}$. The projection space is defined as

$$| \mu \rangle = \tau_\mu | \text{HF} \rangle \quad (5)$$

$$\langle \mu | = \langle \text{HF} | \tilde{\tau}_\mu^\dagger, \quad \mu \geq 0, \quad \tau_0 = \tilde{\tau}_0 = 1 \quad (6)$$

where τ_μ and $\tilde{\tau}_\mu$ with $\mu > 0$ are the excitation operators relative to the Hartree–Fock state $| \text{HF} \rangle$ and $\langle \mu | \nu \rangle = \delta_{\mu\nu}$. The cluster operator is defined as

$$T = \sum_{\mu > 0} t_\mu \tau_\mu \quad (7)$$

where $\{t_\mu\}$ are scalars called cluster amplitudes.

The right ground state is assumed to have the exponential form

$$| \psi_0 \rangle = | \text{CC} \rangle = \exp(T) | \text{HF} \rangle \quad (8)$$

and projecting the Schrödinger equation onto $\{ \langle \mu | \}_{\mu \geq 0}$ gives the ground state equations

$$E_0 = \langle \text{HF} | \bar{H} | \text{HF} \rangle \quad (9)$$

$$\Omega_\mu = \langle \mu | \bar{H} | \text{HF} \rangle = 0, \quad \mu > 0 \quad (10)$$

where $\bar{H} = \exp(-T) H \exp(T)$. The state amplitudes, \mathcal{L}_n and \mathcal{R}_n , are determined by making the n th energy stationary under the condition $1 = \mathcal{L}_n^T \mathcal{R}_n$. The result is a set of eigenvalue equations

$$\mathcal{L}_n^T \bar{H} = E_n \mathcal{L}_n^T \quad (11)$$

$$\bar{H} \mathcal{R}_n = E_n \mathcal{R}_n \quad (12)$$

where E_n is the energy of the n th state and $\bar{H}_{\mu\nu} = \langle \mu | \bar{H} | \nu \rangle$. Here and throughout, we use bold font (X) to denote vectors (X_μ) and matrices ($X_{\mu\nu}$). In summary, eqs 10–12 are solved to determine the left and right electronic states. The reader is referred to the literature for more details.^{28,29}

Born–Huang Expansion of the Total Wave Function and the Nuclear Schrödinger Equations. The Born–Huang expansion expresses the total wave function in terms of the electronic wave functions. The coefficients of the expansion define the nuclear wave functions. These nuclear wave functions are determined by inserting the expansion in the Schrödinger equation and projecting out the electronic components; the result is a set of nuclear Schrödinger equations. In coupled cluster theory, this implies a biorthonormal description of the total wave function since we can expand in both the left and right electronic wave functions ($\tilde{\psi}_n$ and ψ_n). Hence, we have a left and a right total wave function given by the Born–Huang expansions

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_n \chi_n(\mathbf{R}, t) \psi_n(\mathbf{r}; \mathbf{R}) \quad (13)$$

$$\tilde{\Psi}(\mathbf{r}, \mathbf{R}, t) = \sum_n \tilde{\chi}_n(\mathbf{R}, t) \tilde{\psi}_n(\mathbf{r}; \mathbf{R}) \quad (14)$$

with associated left and right nuclear wave functions $\tilde{\chi}_n$ and χ_n and

$$\begin{aligned} 1 &= \langle \tilde{\Psi} | \Psi \rangle = \sum_{mn} \langle \tilde{\chi}_m | \langle \tilde{\psi}_m | \psi_n \rangle | \chi_n \rangle = \sum_{mn} \delta_{mn} \langle \tilde{\chi}_m | \chi_n \rangle \\ &= \sum_n \langle \tilde{\chi}_n | \chi_n \rangle \end{aligned} \quad (15)$$

where we have assumed biorthonormal electronic states in the third equality: $\langle \tilde{\psi}_m | \psi_n \rangle = \delta_{mn}$. In eqs 13 and 14, the electronic and nuclear coordinates are denoted by \mathbf{r} and \mathbf{R} , respectively, and time by t . Expectation values are defined through the standard expression^{28,29}

$$\langle \Omega \rangle = \langle \tilde{\Psi} | \Omega | \Psi \rangle, \quad \Omega = \Omega^\dagger \quad (16)$$

To derive the equations for the nuclear wave functions, one normally projects the total Schrödinger equation on the electronic basis. In this respect, a biorthonormal description is advantageous; for practical coupled cluster models, where the excitation space is truncated to some excitation order, projection of the right Schrödinger equation is done onto the left electronic basis, leading to computationally tractable expressions that scale as expected for the given model (e.g., $O(N^6)$ for CCSD, where N is the size of the system).

By inserting the Ψ in eq 13 into the time-dependent Schrödinger equation

$$H\Psi = i \frac{d\Psi}{dt} \quad (17)$$

and projecting it onto the left electronic basis, we get a coupled set of equations for the right nuclear wave functions χ_n . These nuclear Schrödinger equations can be expressed as

$$\left(i \frac{d}{dt} - E_m \right) \chi_m = - \sum_{l,n} \frac{1}{2M_l} (\delta_{mn} \nabla_l^2 + G_{mn}^l + 2F_{mn}^l \cdot \nabla_l) \chi_n \quad (18)$$

where we have suppressed the \mathbf{R} and t dependence for readability. The nonadiabatic coupling vectors in eq 18 are given in the biorthonormal basis

$$G_{mn}^l = \langle \tilde{\psi}_m | \nabla_l^2 \psi_n \rangle \quad (19)$$

$$F_{mn}^l = \langle \tilde{\psi}_m | \nabla_l \psi_n \rangle \quad (20)$$

In analogous fashion, we derive the nuclear Schrödinger equations for the left nuclear wave functions from the complex conjugated Schrödinger equation

$$H\tilde{\Psi} = -i \frac{d\tilde{\Psi}}{dt} \quad (21)$$

Inserting eq 14 into 21 and projecting onto the right electronic basis leads to

$$\left(-i \frac{d}{dt} - E_m \right) \tilde{\chi}_m = - \sum_{l,n} \frac{1}{2M_l} (\delta_{mn} \nabla_l^2 + \tilde{G}_{mn}^l + 2\tilde{F}_{mn}^l \cdot \nabla_l) \tilde{\chi}_n \quad (22)$$

$$\tilde{G}_{mn}^l = \langle \nabla_l^2 \tilde{\psi}_m | \psi_n \rangle \quad (23)$$

$$\tilde{F}_{mn}^l = \langle \nabla_l \tilde{\psi}_m | \psi_n \rangle \quad (24)$$

The nuclear Schrödinger equations can be expressed in the more compact matrix notation

$$\left(i \frac{d}{dt} - \mathbf{E} \right) \boldsymbol{\chi} = - \sum_I \frac{1}{2M_I} (\mathbf{I} \nabla_I^2 + \mathbf{G}_I + 2\mathbf{F}_I \cdot \nabla_I) \boldsymbol{\chi} \quad (25)$$

$$\left(-i \frac{d}{dt} - \mathbf{E} \right) \tilde{\boldsymbol{\chi}} = - \sum_I \frac{1}{2M_I} (\mathbf{I} \nabla_I^2 + \tilde{\mathbf{G}}_I + 2\tilde{\mathbf{F}}_I \cdot \nabla_I) \tilde{\boldsymbol{\chi}} \quad (26)$$

where \mathbf{E} is a diagonal matrix with the electronic energies on the diagonal, \mathbf{I} is the identity matrix, $\boldsymbol{\chi}$ is a vector containing the right nuclear wave functions, and \mathbf{G}_I and \mathbf{F}_I are matrices consisting of the scalar and vector couplings of the I th nucleus, respectively. The quantities with a tilde are similarly defined.

This matrix notation has been used to illuminate some relations to gauge theories in the nuclear Schrödinger equations; Pacher *et al.*³⁰ found that the vector coupling can be seen to serve a role analogous to the vector potential in electromagnetism. In the present work, it serves as a useful notation for dealing with basis transformations and the vector algebra needed to demonstrate invariance under such transformations.

Basis Invariance and the Special Case of Norm Invariance. It has been suggested that normalizing the electronic states is necessary when calculating nonadiabatic coupling elements.¹⁵ The reason is that the left and right states are biorthonormal in the coupled cluster theory. Compared to the couplings in the full-CI theory, where the states are normalized, the full coupled cluster limit is “incorrect” because the couplings depend on the geometry-dependent normalization constants. While this suggests that one should normalize the states, doing so is not feasible. The computational cost of the normalization factor scales as full-CI for the right electronic states¹⁵

$$N_R^n = \langle \psi_n | \psi_n \rangle \quad (27)$$

$$N_L^n = \langle \tilde{\psi}_n | \tilde{\psi}_n \rangle \quad (28)$$

Since one cannot evaluate N_R^n in general, some have suggested $N_R^n = (N_L^n)^{-1}$ or $N_R^n = N_L^n = 1$ as alternatives. The former gives the full-CI limit, while the latter is equivalent to assuming the standard biorthonormality.^{15,19}

Biorthonormality is not an issue from the point of view of nonadiabatic dynamics. In fact, normalizing the electronic states is a special case of basis transformation of the electronic basis. As such, the Born–Huang expansion and the nuclear Schrödinger equations are equivalent in the transformed and untransformed bases. Changes in the electronic basis are absorbed in the expansion coefficients, that is, the nuclear wave functions. In the case of normalization, the right electronic wave functions are divided by N_R^n , while the right nuclear wave functions are multiplied by N_R^n . The total wave function does not change.

More precisely, consider invertible transformations of the left and right electronic bases. In vector notation, these transformations can be expressed as

$$\tilde{\boldsymbol{\psi}}' = \tilde{\boldsymbol{\psi}} \mathbf{N} \quad (29)$$

$$\boldsymbol{\psi}' = \boldsymbol{\psi} \mathbf{M} \quad (30)$$

where the matrices \mathbf{M} and \mathbf{N} are assumed to be smooth invertible matrix functions of the nuclear coordinates. For notational simplicity, we have let the left and right wave function vectors be row vectors. Transformed quantities are denoted by a prime. In the transformed basis, the total left and right wave functions have the Born–Huang expansions

$$\Psi'(\mathbf{r}, \mathbf{R}, t) = \sum_n \chi'_n(\mathbf{R}, t) \psi'_n(\mathbf{r}; \mathbf{R}) \quad (31)$$

$$\tilde{\Psi}'(\mathbf{r}, \mathbf{R}, t) = \sum_n \tilde{\chi}'_n(\mathbf{R}, t) \tilde{\psi}'_n(\mathbf{r}; \mathbf{R}) \quad (32)$$

We wish to show that the wave function in the transformed basis is identical to that obtained in the untransformed basis, that is, $\Psi' = \Psi$ and $\tilde{\Psi}' = \tilde{\Psi}$. The conclusion that follows is that the choice of electronic basis does not change the predictions of the theory. In other words, it is perfectly appropriate to use the standard^{28,29} biorthonormal description.

Before proceeding, we define some notation. In the transformed basis, we have to account for the nonunit overlap of the electronic wave functions. Hence, when projecting the time-dependent Schrödinger equation onto the electronic basis, we get electronic overlap matrix elements. In particular

$$\begin{aligned} S_{mn} &= \langle \tilde{\psi}'_m | \psi'_n \rangle = \sum_{kl} \langle \tilde{\psi}'_k N_{km} | \psi'_l M_{ln} \rangle = \sum_{kl} N_{km}^* \delta_{kl} M_{ln} \\ &= (\mathbf{N}^\dagger \mathbf{M})_{mn} \end{aligned} \quad (33)$$

Similarly, the electronic Hamiltonian matrix is not necessarily diagonal

$$\begin{aligned} (\mathbf{H}_e)_{mn} &= \langle \tilde{\psi}'_m | H_e \psi'_n \rangle = \sum_{kl} \langle \tilde{\psi}'_k N_{km} | H_e \psi'_l M_{ln} \rangle \\ &= \sum_{kl} N_{km}^* E_{kl} M_{ln} = (\mathbf{N}^\dagger \mathbf{E} \mathbf{M})_{mn} \end{aligned} \quad (34)$$

We show the equivalence for the right wave functions. The proof for the left wave function is identical. Following the standard procedure, we now insert the transformed wave function in eq 31 into the Schrödinger equation and project onto the transformed left electronic wave functions. The result is the right nuclear Schrödinger equation

$$\left(\mathbf{N}^\dagger \mathbf{E} \mathbf{M} - i \frac{d}{dt} \mathbf{S} \right) \chi' = - \sum_I \frac{1}{2M_I} (\mathbf{S} \nabla_I^2 + \mathbf{G}'_I + 2\mathbf{F}'_I \cdot \nabla_I) \chi' \quad (35)$$

If the total wave function is invariant and $\psi' = \psi \mathbf{M}$, then we must have nuclear wave functions that cancel the transformation of the electronic wave functions, meaning that

$$\chi' = \mathbf{M}^{-1} \chi \quad (36)$$

Indeed, with χ' as given in eq 36, we have

$$\Psi' = \sum_k \psi'_k \chi'_k = \sum_{klm} \psi_l M_{lk} M_{km}^{-1} \chi_m = \sum_l \psi_l \chi_l = \Psi \quad (37)$$

Let us confirm that eq 36 is in fact a solution to the transformed nuclear Schrödinger equation in eq 35. We begin by relating the old and new nonadiabatic coupling terms. The gradients of the electronic wave functions transform as

$$\nabla_I \psi'_l = \sum_m \nabla_I (\psi_m M_{ml}) = \sum_m ((\nabla_I \psi_m) M_{ml} + \psi_m (\nabla_I M_{ml})) \quad (38)$$

Hence, the vector couplings can be written as

$$\begin{aligned} (\mathbf{F}'_I)_{kl} &= \langle \tilde{\psi}'_k | \nabla_I \psi'_l \rangle = \sum_n N_{nk}^* \langle \tilde{\psi}'_n | \nabla_I \psi'_l \rangle \\ &= \sum_{nm} (N_{nk}^* F_{nm}^I M_{ml} + N_{nk}^* \delta_{nm} \nabla_I M_{ml}) \end{aligned} \quad (39)$$

In more compact matrix notation, we have

$$\mathbf{F}'_I = \mathbf{N}^\dagger \mathbf{F}_I \mathbf{M} + \mathbf{N}^\dagger (\nabla_I \mathbf{M}) \quad (40)$$

Similarly, the Laplacian of the electronic wave functions transforms as

$$\begin{aligned} \nabla_I^2 \psi'_l &= \nabla_I \cdot \nabla_I \psi'_l \\ &= \sum_m ((\nabla_I^2 \psi_m) M_{ml} + 2(\nabla_I \psi_m) \cdot (\nabla_I M_{ml}) \\ &\quad + \psi_m (\nabla_I^2 M_{ml})) \end{aligned} \quad (41)$$

implying that the scalar couplings transform as

$$\mathbf{G}'_I = \mathbf{N}^\dagger \mathbf{G}_I \mathbf{M} + 2\mathbf{N}^\dagger \mathbf{F}_I \cdot (\nabla_I \mathbf{M}) + \mathbf{N}^\dagger (\nabla_I^2 \mathbf{M}) \quad (42)$$

The gradient and Laplacian of χ' is derived in the same way as for the electronic states, giving

$$\nabla_I \chi'_l = \sum_m (M_{lm}^{-1} (\nabla_I \chi_m) + (\nabla_I M_{lm}^{-1}) \chi_m) \quad (43)$$

$$\begin{aligned} \nabla_I^2 \chi'_l &= \sum_m (M_{lm}^{-1} (\nabla_I^2 \chi_m) + 2(\nabla_I M_{lm}^{-1}) \cdot (\nabla_I \chi_m) \\ &\quad + (\nabla_I^2 M_{lm}^{-1}) \chi_m) \end{aligned} \quad (44)$$

Thus, we have the following contributions on the right-hand side of the nuclear Schrödinger equation

$$\mathbf{S} \nabla_I^2 \chi' = \mathbf{N}^\dagger (\nabla_I^2 \chi + 2\mathbf{M} (\nabla_I \mathbf{M}^{-1}) \cdot \nabla_I \chi + \mathbf{M} (\nabla_I^2 \mathbf{M}^{-1}) \chi) \quad (45)$$

$$\mathbf{G}'_I \chi' = \mathbf{N}^\dagger (\mathbf{G}_I \chi + 2\mathbf{F}_I \cdot (\nabla_I \mathbf{M}) \mathbf{M}^{-1} \chi + (\nabla_I^2 \mathbf{M}) \mathbf{M}^{-1} \chi) \quad (46)$$

$$\begin{aligned} 2\mathbf{F}'_I \cdot \nabla_I \chi' &= \mathbf{N}^\dagger (2\mathbf{F}_I \cdot \nabla_I \chi + 2\mathbf{F}_I \cdot \mathbf{M} (\nabla_I \mathbf{M}^{-1}) \chi \\ &\quad + 2(\nabla_I \mathbf{M}) \mathbf{M}^{-1} \cdot \nabla_I \chi + 2(\nabla_I \mathbf{M}) \cdot (\nabla_I \mathbf{M}^{-1}) \chi) \end{aligned} \quad (47)$$

Though somewhat involved, most of the terms cancel when added together. In fact, since

$$0 = \nabla_I (\mathbf{M} \mathbf{M}^{-1}) = (\nabla_I \mathbf{M}) \mathbf{M}^{-1} + \mathbf{M} (\nabla_I \mathbf{M}^{-1}) \quad (48)$$

$$\begin{aligned} 0 &= \nabla_I^2 (\mathbf{M} \mathbf{M}^{-1}) \\ &= (\nabla_I^2 \mathbf{M}) \mathbf{M}^{-1} + \mathbf{M} (\nabla_I^2 \mathbf{M}^{-1}) + 2(\nabla_I \mathbf{M}) \cdot (\nabla_I \mathbf{M}^{-1}) \end{aligned} \quad (49)$$

we can write

$$\begin{aligned}
& S\nabla_I^2\chi' + \mathbf{G}'\chi' + 2\mathbf{F}'_I\nabla_I\chi' \\
&= \mathbf{N}^\dagger(\nabla_I^2\chi + \mathbf{G}_I\chi + 2\mathbf{F}_I\nabla_I\chi + 2\nabla_I(\mathbf{M}\mathbf{M}^{-1})\cdot\nabla_I\chi \\
&\quad + \nabla_I^2(\mathbf{M}\mathbf{M}^{-1})\chi + 2\mathbf{F}_I\nabla_I(\mathbf{M}\mathbf{M}^{-1})\chi) \\
&= \mathbf{N}^\dagger(\nabla_I^2\chi + \mathbf{G}_I\chi + 2\mathbf{F}_I\nabla_I\chi) \quad (50)
\end{aligned}$$

In other words, with $\chi' = \mathbf{M}^{-1}\chi$, the right nuclear Schrödinger equation simplifies to

$$\left(\mathbf{N}^\dagger\mathbf{E} - i\frac{d}{dt}\mathbf{N}^\dagger\right)\chi = -\mathbf{N}^\dagger\sum_I\frac{1}{2M_I}(\nabla_I^2 + \mathbf{G}_I + 2\mathbf{F}_I\nabla_I)\chi \quad (51)$$

which, upon premultiplication by $\mathbf{N}^{-\dagger}$, is seen to be equivalent to the original right nuclear Schrödinger equation in eq 25.

Since all of the steps we have made are reversible, we have shown that χ is a solution to the untransformed nuclear Schrödinger equation if and only if χ' is a solution to the transformed Schrödinger equation. The total right wave function is therefore invariant with respect to transformations of the electronic basis, $\Psi' = \Psi$. One consequence of basis invariance is that the nonadiabatic couplings can be expressed in the standard biorthonormal formalism.

In the next section, we derive these in a Lagrangian framework. The couplings have contributions that arise from the geometry-dependence of the many-body operators, where a choice of orbital connection is necessary.^{13,31} These terms are described in Appendix A.

Nonadiabatic Coupled Cluster Couplings in a Lagrangian Formalism. To obtain a Lagrangian for the vector coupling in CASCI, Hohenstein²⁵ defined a partially frozen overlap whose first derivatives are identical to components of the vector coupling. In coupled cluster methods, this overlap can be expressed as

$$O_{mn}(\mathbf{x}) = \langle \tilde{\psi}_m(\mathbf{x}_0) | \psi_n(\mathbf{x}) \rangle \quad (52)$$

in terms of which we have

$$(\mathbf{F}_{mn}^I)_i = \langle \tilde{\psi}_m(\mathbf{x}) | \frac{d}{dx_i} \psi_n(\mathbf{x}) \rangle \Big|_0 = \frac{d}{dx_i} O_{mn}(\mathbf{x}) \Big|_0, \quad i \in I \quad (53)$$

and

$$G_{mn}^I = \langle \tilde{\psi}_m(\mathbf{x}) | \sum_{i \in I} \frac{d^2}{dx_i^2} \psi_n(\mathbf{x}) \rangle \Big|_0 = \sum_{i \in I} \frac{d^2}{dx_i^2} O_{mn}(\mathbf{x}) \Big|_0 \quad (54)$$

We let $i \in I$ mean that x_i is one of the three coordinates of the I th nucleus (x , y , or z). Note that $O_{mn}(\mathbf{x})$ depends on \mathbf{x}_0 . We suppress this dependency to keep the notation simple.

The overlap is expressed in terms of coupled cluster wave functions, which depend not only on \mathbf{x} but also on a set of wave function parameters λ (which themselves depend on \mathbf{x}). Written out in terms of the parameters, we have

$$O_{mn}(\mathbf{x}, \lambda) = \langle \tilde{\psi}_m(\mathbf{x}_0) | \exp(-\kappa) \exp(T) \mathcal{R}_n \rangle \quad (55)$$

where

$$\langle \tilde{\psi}_m(\mathbf{x}_0) | = \langle \mathcal{L}_m | \exp(-T) \Big|_0 \quad (56)$$

and

$$\kappa = \sum_{p>q} \kappa_{pq}(E_{pq} - E_{qp}) = \sum_{p>q} \kappa_{pq} E_{pq}^- \quad (57)$$

The κ operator accounts for orbital rotations, meaning changes in the Hartree–Fock orbitals, where, by definition, we have $\kappa(\mathbf{x}_0) = 0$. Following the standard recipe, we add the equations (denoted by \mathcal{E}_{mn}) that determine the parameters as constraints with associated Lagrangian multipliers (denoted by γ)

$$\mathcal{L}_{mn}(\lambda, \mathbf{x}, \gamma) = O_{mn}(\lambda, \mathbf{x}) + \gamma^T \mathcal{E}_{mn}(\lambda, \mathbf{x}), \quad m \neq n \quad (58)$$

where λ and γ are determined for every \mathbf{x} by the stationarity conditions

$$\frac{\partial \mathcal{L}_{mn}}{\partial \gamma_k} = (\mathcal{E}_{mn})_k = 0 \quad (59)$$

$$\frac{\partial \mathcal{L}_{mn}}{\partial \lambda_k} = 0 \quad (60)$$

The derivatives of this Lagrangian are identical to the derivatives of the frozen overlap (since $\mathcal{E}_{mn} = 0$). One advantage of the Lagrangian formalism is that it automatically incorporates the $2n + 1$ and $2n + 2$ rules for λ and γ , respectively.⁶ In particular, we have

$$(\mathbf{F}_{mn}^I)_i = \frac{d\mathcal{L}_{mn}}{dx_i} \Big|_0 = \frac{\partial \mathcal{L}_{mn}}{\partial x_i} \Big|_0, \quad i \in I \quad (61)$$

where the final equality follows from stationarity, see eqs 59 and 60. Denoting partial derivatives with respect to geometrical coordinates as

$$a^{(i)} = \frac{\partial a}{\partial x_i} \Big|_0, \quad a^{(i,j)} = \frac{\partial^2 a}{\partial x_i \partial x_j} \Big|_0 \quad (62)$$

we can write

$$(\mathbf{F}_{mn}^I)_i = \mathcal{L}_{mn}^{(i)}, \quad i \in I \quad (63)$$

Furthermore, if we let

$$f_\alpha = \frac{\partial \mathcal{L}_{mn}}{\partial \lambda_\alpha} \Big|_{\lambda=\lambda_0}, \quad H_{\alpha\beta} = \frac{\partial^2 \mathcal{L}_{mn}}{\partial \lambda_\alpha \partial \lambda_\beta} \Big|_0 \quad (64)$$

then the scalar coupling can be expressed as (see Appendix B)

$$\begin{aligned}
G_{mn}^I &= \sum_{i \in I} \frac{d^2 \mathcal{L}_{mn}}{dx_i^2} \Big|_0 \\
&= \sum_{i \in I} \left(\mathcal{L}_{mn}^{(i,i)} + \sum_{\alpha\beta} \lambda_\alpha^{(i)} H_{\alpha\beta} \lambda_\beta^{(i)} + 2 \sum_{\alpha} \lambda_\alpha^{(i)} f_\alpha^{(i)} \right) \quad (65)
\end{aligned}$$

Clearly, \mathbf{F}_{mn}^I and G_{mn}^I are similar in complexity to the energy gradient and Hessian. However, G_{mn}^I is somewhat simpler than the energy Hessian because the first derivatives of the parameters ($\lambda^{(i)}$) can be considered one at a time.

To proceed, we must define the Lagrangian \mathcal{L}_{mn} in detail. The conditions \mathcal{E}_{mn} include all equations that must be solved to evaluate the overlap O_{mn} . These are (a) the Hartree–Fock equations, (b) the amplitude equations, and (c) the eigenvalue

equations for the right state amplitudes. Written out in full, we have

$$\begin{aligned}\mathcal{L}_{mn} &= O_{mn} + \gamma^T \mathcal{E}_m \\ &= O_{mn} + \bar{\kappa}^T F_c + \zeta^T \Omega + \beta_n^T (\bar{\mathcal{H}} - E_n) \mathcal{R}_n \\ &\quad + \bar{E}_n (1 - \langle \mathcal{L}_n^0 | \mathcal{R}_n \rangle)\end{aligned}\quad (66)$$

where we have introduced multipliers associated with the different sets of equations, $\bar{\kappa}$, ζ , as well as β_n and \bar{E}_n . We have also introduced the Brillouin condition

$$(F_c)_{pq} = \langle \text{HF} | [E_{pq}^-, H(\kappa)] | \text{HF} \rangle, \quad p > q \quad (67)$$

where

$$H(\kappa) = \exp(\kappa) H \exp(-\kappa) \quad (68)$$

Furthermore, the similarity transformed the Hamiltonian in Ω and $\bar{\mathcal{H}}$ is given by

$$\bar{H} = \bar{H}(\kappa) = \exp(-T) H(\kappa) \exp(T) \quad (69)$$

and the n th electronic energy is defined as

$$E_n = \langle \mathcal{L}_n^{(0)} | \bar{H} | \mathcal{R}_n \rangle \quad (70)$$

With \mathcal{L}_{mn} defined, we can now consider the equations for the zeroth order multipliers. These are determined from the zeroth order terms of the λ stationarity, eq 60. To keep our notation simple, we will denote the zeroth order terms as $\gamma^{(0)} \equiv \gamma$ and $\lambda^{(0)} \equiv \lambda$, where it should be understood from context when these are γ and λ evaluated at \mathbf{x}_0 . Differentiation with respect to the state parameters gives

$$\begin{aligned}\left. \frac{\partial \mathcal{L}_{mn}}{\partial \mathcal{R}_n} \right|_0 &= 0 = \mathcal{L}_m^T + \beta_n^T (\bar{\mathcal{H}} - E_n \mathbf{I}) \\ &\quad - (\bar{E}_n + E_n \beta_n^T \mathcal{R}_n) \mathcal{L}_n^T = 0\end{aligned}\quad (71)$$

To solve this equation, we note that if we let

$$\bar{E}_n = -E_n \beta_n^T \mathcal{R}_n \quad (72)$$

the equation for β_n becomes

$$\beta_n^T (\bar{\mathcal{H}} - E_n \mathbf{I}) = -\mathcal{L}_m^T \quad (73)$$

Thus, we have

$$\beta_n = (E_n - E_m)^{-1} \mathcal{L}_m \quad (74)$$

Next, we consider stationarity with respect to \mathbf{t} . This can be expressed as

$$\left. \frac{\partial \mathcal{L}_{mn}}{\partial \mathbf{t}} \right|_0 = 0 = {}^t \boldsymbol{\eta} + \zeta^T \mathbf{A} \quad (75)$$

where

$${}^t \eta_\mu = \langle \bar{\mathcal{L}}_m | \tau_\mu | \bar{\mathcal{R}}_n \rangle + \langle \bar{\beta}_n | [H, \tau_\mu] | \bar{\mathcal{R}}_n \rangle \quad (76)$$

and where we have introduced the notation

$$|\bar{X}\rangle = \exp(T) |X\rangle \quad (77)$$

$$\langle \bar{X}| = \langle X | \exp(-T) \quad (78)$$

Finally, we have stationarity with respect to κ , which can be written as

$$\left. \frac{\partial \mathcal{L}_{mn}}{\partial \kappa} \right|_0 = 0 = {}^\kappa \boldsymbol{\eta} + \bar{\kappa}^T \mathbf{A}^{\text{HF}} \quad (79)$$

where

$$\begin{aligned}{}^\kappa \eta_{rs} &= -\langle \bar{\mathcal{L}}_m | E_{rs}^- | \bar{\mathcal{R}}_n \rangle + \langle \bar{\zeta} | [E_{rs}^-, H] | \text{CC} \rangle \\ &\quad + \langle \bar{\beta}_n | [E_{rs}^-, H] | \bar{\mathcal{R}}_n \rangle\end{aligned}\quad (80)$$

and

$$A_{pq,rs}^{\text{HF}} = \langle \text{HF} | [E_{pq}^-, [E_{rs}^-, H]] | \text{HF} \rangle \quad (81)$$

With the zeroth order multipliers determined, we can derive the expression for the vector coupling. By partially differentiating \mathcal{L}_{mn} , we find that

$$\begin{aligned}(\mathbf{F}_{mn}^I)_i &= \mathcal{L}_{mn}^{(i)} = (E_n - E_m)^{-1} \langle \mathcal{L}_m | \bar{H}^{(i)} | \mathcal{R}_n \rangle + \langle \zeta | \bar{H}^{(i)} | \text{HF} \rangle \\ &\quad + \langle \text{HF} | [\bar{\kappa}, H^{(i)}] | \text{HF} \rangle, \quad i \in I\end{aligned}\quad (82)$$

where

$$\bar{H}^{(i)} = \exp(-T) H^{(i)} \exp(T) \quad (83)$$

and where quantities at \mathbf{x}_0 are denoted as $y^{(0)} \equiv y$ (e.g., we denote $T^{(0)}$ as T). Here, we have assumed the natural connection, for which there are no contributions to \mathbf{F}_{mn}^I that originate from the many-body operators (see Appendix A and refs 13 and 31).

The vector coupling given in eq 82 has also been identified by other authors. It was derived by Christiansen,¹³ who assumed biorthonormality and used Z-vector substitution¹⁴ on the expression for the vector coupling. Tajti and Szalay¹⁵ identified the same expression indirectly using Z-vector substitution on derivatives of Hamiltonian transition elements. However, they also argued¹⁵ that the coupling should not be given by eq 82 but rather be averaged and expressed with normalized states. As we have shown, eq 82 is a valid choice due to norm invariance and represents the vector coupling in the right nuclear Schrödinger equations. For the left Schrödinger equations, we can make use of the identity

$$\langle \tilde{\psi}_m | \psi_n \rangle = \delta_{mn} \Rightarrow \mathbf{F}_{mn}^I = -\tilde{\mathbf{F}}_{mn}^I \quad (84)$$

Before moving on to the scalar coupling, we note that although the Z-vector substitution method is equivalent to the Lagrangian technique, the latter method gives, in our opinion, an especially elegant way of deriving the coupling elements.

For the scalar coupling, we must determine the first derivatives of the parameters. Equations for these are obtained as the first-order terms of the multiplier stationarity conditions. In the case of \mathbf{t} , we have

$$\left. \frac{d\Omega}{dx_i} \right|_0 = 0 = {}^t \boldsymbol{\xi}^{(i)} + \mathbf{A} \mathbf{t}^{(i)} \quad (85)$$

where

$${}^t \xi_\mu^{(i)} = \langle \mu | \bar{H}^{(i)} | \text{HF} \rangle + \langle \mu | \exp(-T) [\kappa^{(i)}, H] \exp(T) | \text{HF} \rangle \quad (86)$$

In the case of κ , we similarly have

$$\left. \frac{dF_c}{dx_i} \right|_0 = 0 = \kappa \xi^{(i)} + \mathbf{A}^{\text{HF}} \kappa^{(i)} \quad (87)$$

where

$$\kappa \xi_{rs}^{(i)} = \langle \text{HF} | [E_{rs}^-, H^{(i)}] | \text{HF} \rangle \quad (88)$$

The biorthonormality condition implies

$$\left. \frac{d}{dx_i} (1 - \langle \mathcal{L}_n^0 | \mathcal{R}_n \rangle) \right|_0 = 0 = -\mathcal{L}_n^T \mathcal{R}_n^{(i)} \quad (89)$$

while the eigenvalue condition implies

$$\left. \frac{d}{dx_i} ((\bar{H} - E_n) \mathcal{R}_n) \right|_0 = 0 = \mathcal{R}_n \xi^{(i)} + (\bar{H} - E_n) \mathcal{R}_n^{(i)} \quad (90)$$

Here, we have defined

$$\mathcal{R}_n \xi^{(i)} = (\mathcal{Y}^{(i)} - \mathcal{L}_n^T \mathcal{Y}^{(i)} \mathcal{R}_n) \mathcal{R}_n \quad (91)$$

where

$$\begin{aligned} \mathcal{Y}_{\mu\nu}^{(i)} &= \langle \mu | \bar{H}^{(i)} | \nu \rangle + \langle \mu | [\bar{H}, T^{(i)}] | \nu \rangle + \langle \mu | [\kappa^{(i)}, \bar{H}] | \nu \rangle, \\ \mu, \nu &\geq 0 \end{aligned} \quad (92)$$

With the derivatives of the parameters determined, let us next consider $f_{\alpha}^{(i)}$ and $H_{\alpha\beta}$, see eq 64. Recall that the α and β indices refer to the parameters λ_{α} and λ_{β} . The gradient f is given by the zeroth order equations for the multipliers, that is, eqs 71, 75, and 79, with $\lambda = \lambda_0$ but allowing for $\alpha \neq \alpha_0$. Partially differentiating these terms with respect to x_i gives $f^{(i)}$. The blocks of the $\sum_{\alpha} f_{\alpha}^{(i)} \lambda_{\alpha}^{(i)}$ contributions to G_{mn}^I can be written

$$\mathcal{R}_n f_{\mu}^{(i)} (\mathcal{R}_n^{(i)})_{\mu} = \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial x_i \partial (\mathcal{R}_n)_{\mu}} \right|_0 (\mathcal{R}_n^{(i)})_{\mu} = \langle \bar{\beta}_n | H^{(i)} - E_n^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle \quad (93)$$

and

$$\begin{aligned} t f_{\mu}^{(i)} t_{\mu}^{(i)} &= \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial x_i \partial t_{\mu}} \right|_0 t_{\mu}^{(i)} \\ &= \langle \bar{\zeta} | [H^{(i)}, T^{(i)}] | \text{CC} \rangle + \langle \bar{\beta}_n | [H^{(i)}, T^{(i)}] | \bar{\mathcal{R}}_n \rangle \end{aligned} \quad (94)$$

$$\begin{aligned} \kappa f_{pq}^{(i)} \kappa_{pq}^{(i)} &= \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial x_i \partial \kappa_{pq}} \right|_0 \kappa_{pq}^{(i)} \\ &= \langle \bar{\zeta} | [\kappa^{(i)}, H^{(i)}] | \text{CC} \rangle + \langle \bar{\beta}_n | [\kappa^{(i)}, H^{(i)}] | \bar{\mathcal{R}}_n \rangle \\ &\quad + \langle \text{HF} | [\bar{\kappa}, [\kappa^{(i)}, H^{(i)}]] | \text{HF} \rangle \end{aligned} \quad (95)$$

where repeated indices implies summation. For contributions to G_{mn}^I involving $H_{\alpha\beta}$ we have, for terms involving t and κ ,

$$\begin{aligned} t_{\mu}^{(i)} H_{\mu\nu}^{tt} t_{\nu}^{(i)} &= t_{\mu}^{(i)} \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial t_{\mu} \partial t_{\nu}} \right|_0 t_{\nu}^{(i)} \\ &= \langle \bar{\mathcal{L}}_m | (T^{(i)})^2 | \bar{\mathcal{R}}_n \rangle + \langle \bar{\zeta} | [[H, T^{(i)}], T^{(i)}] | \text{CC} \rangle \\ &\quad + \langle \bar{\beta}_n | [[H, T^{(i)}], T^{(i)}] | \bar{\mathcal{R}}_n \rangle \end{aligned} \quad (96)$$

as well as

$$\begin{aligned} \kappa_{rs}^{(i)} H_{rs\nu}^{\kappa t} t_{\nu}^{(i)} &= \kappa_{rs}^{(i)} \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial \kappa_{rs} \partial t_{\nu}} \right|_0 t_{\nu}^{(i)} \\ &= -\langle \bar{\mathcal{L}}_m | \kappa^{(i)} T^{(i)} | \bar{\mathcal{R}}_n \rangle + \langle \bar{\zeta} | [[\kappa^{(i)}, H], T^{(i)}] | \text{CC} \rangle \\ &\quad + \langle \bar{\beta}_n | [[\kappa^{(i)}, H], T^{(i)}] | \bar{\mathcal{R}}_n \rangle \end{aligned} \quad (97)$$

and

$$\begin{aligned} \kappa_{pq}^{(i)} H_{pqrs}^{\kappa\kappa} \kappa_{rs}^{(i)} &= \kappa_{pq}^{(i)} \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial \kappa_{pq} \partial \kappa_{rs}} \right|_0 \kappa_{rs}^{(i)} \\ &= \langle \bar{\mathcal{L}}_m | (\kappa^{(i)})^2 | \bar{\mathcal{R}}_n \rangle + \langle \bar{\zeta} | [\kappa^{(i)}, [\kappa^{(i)}, H]] | \text{CC} \rangle \\ &\quad + \langle \bar{\beta}_n | [\kappa^{(i)}, [\kappa^{(i)}, H]] | \bar{\mathcal{R}}_n \rangle \\ &\quad + \langle \text{HF} | [\bar{\kappa}, [\kappa^{(i)}, [\kappa^{(i)}, H]]] | \text{HF} \rangle \end{aligned} \quad (98)$$

Next, we have terms involving right state and the cluster amplitudes and orbital rotations, *i.e.*

$$\begin{aligned} t_{\mu}^{(i)} H_{\mu\nu}^{t\mathcal{R}_n} (\mathcal{R}_n^{(i)})_{\nu} &= t_{\mu}^{(i)} \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial t_{\mu} \partial (\mathcal{R}_n)_{\nu}} \right|_0 (\mathcal{R}_n^{(i)})_{\nu} \\ &= \langle \bar{\mathcal{L}}_m | T^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle + \langle \bar{\beta}_n | [H, T^{(i)}] | \bar{\mathcal{R}}_n^{(i)} \rangle \\ &\quad - \langle \beta_n | \mathcal{R}_n^{(i)} \rangle \langle \bar{\mathcal{L}}_m | [H, T^{(i)}] | \bar{\mathcal{R}}_n \rangle \end{aligned} \quad (99)$$

$$\begin{aligned} \kappa_{pq}^{(i)} H_{pq\nu}^{\kappa\mathcal{R}_n} (\mathcal{R}_n^{(i)})_{\nu} &= \kappa_{pq}^{(i)} \left. \frac{\partial^2 \mathcal{L}_{mn}}{\partial \kappa_{pq} \partial (\mathcal{R}_n)_{\nu}} \right|_0 (\mathcal{R}_n^{(i)})_{\nu} \\ &= -\langle \bar{\mathcal{L}}_m | \kappa^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle + \langle \bar{\beta}_n | [\kappa^{(i)}, H] | \bar{\mathcal{R}}_n^{(i)} \rangle \\ &\quad - \langle \beta_n | \mathcal{R}_n^{(i)} \rangle \langle \bar{\mathcal{L}}_m | [\kappa^{(i)}, H] | \bar{\mathcal{R}}_n \rangle \end{aligned} \quad (100)$$

Finally, we have the partial derivative of the Lagrangian, which can be written as

$$\begin{aligned} \mathcal{L}_{mn}^{(i,i)} &= -\sum_{pq} \langle \bar{\mathcal{L}}_m | E_{pq} | \bar{\mathcal{R}}_n \rangle \langle \phi_p^{(i)} | \phi_q^{(i)} \rangle + \langle \bar{\zeta} | H^{(i,i)} | \text{CC} \rangle \\ &\quad + \langle \text{HF} | [\bar{\kappa}, H^{(i,i)}] | \text{HF} \rangle + \langle \bar{\beta}_n | H^{(i,i)} | \bar{\mathcal{R}}_n \rangle \end{aligned} \quad (101)$$

Written in compact notation, the scalar coupling is

$$\begin{aligned} G_{mn}^I &= \langle \bar{\mathcal{L}}_m | \bar{\mathcal{R}}_n^{(i,i)} \rangle + \langle \bar{\zeta} | K^{(i,i)} | \text{CC} \rangle + \langle \bar{\beta}_n | K^{(i,i)} | \bar{\mathcal{R}}_n \rangle \\ &\quad + \langle \text{HF} | [\bar{\kappa}, J^{(i,i)}] | \text{HF} \rangle + \langle \bar{\beta}_n | L^{(i)} - \langle L^{(i)} \rangle_n | \bar{\mathcal{R}}_n^{(i)} \rangle \end{aligned} \quad (102)$$

where we have let

$$K^{(i,i)} = J^{(i,i)} + 2J^{(i)}, T^{(i)} + [[H, T^{(i)}], T^{(i)}] \quad (103)$$

$$J^{(i)} = H^{(i)} + [\kappa^{(i)}, H] \quad (104)$$

$$L^{(i)} = 2(H^{(i)} + [\kappa^{(i)}, H] + [H, T^{(i)}]) \quad (105)$$

$$\langle L^{(i)} \rangle_n = \langle \bar{\mathcal{L}}_m | L^{(i)} | \bar{\mathcal{R}}_n \rangle \quad (106)$$

$$J^{(i,i)} = H^{(i,i)} + 2[\kappa^{(i)}, H^{(i)}] + [\kappa^{(i)}, [\kappa^{(i)}, H]] \quad (107)$$

as well as

$$\begin{aligned} \langle \bar{\mathcal{L}}_m | \bar{\mathcal{R}}_n^{(i,i)} \rangle &= \langle \bar{\mathcal{L}}_m | (\kappa^{(i)})^2 - 2\kappa^{(i)}T^{(i)} + (T^{(i)})^2 | \bar{\mathcal{R}}_n \rangle \\ &\quad - 2\langle \bar{\mathcal{L}}_m | \kappa^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle + 2\langle \bar{\mathcal{L}}_m | T^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle \\ &\quad - \sum_{pq} \langle \bar{\mathcal{L}}_m | E_{pq} | \bar{\mathcal{R}}_n \rangle \langle \phi_p^{(i)} | \phi_q^{(i)} \rangle \end{aligned} \quad (108)$$

The final term in eq 108 arises from the orbital connection (see Appendix A).

Throughout the derivations above, we have considered the off-diagonal coupling elements ($m \neq n$). The diagonal terms can be derived from the Lagrangian

$$\begin{aligned} \mathcal{L}_{mn} &= O_{mn} + \gamma^T \mathcal{E}_{mn} \\ &= O_{mn} + \bar{\kappa}^T F_c + \xi^T \Omega + \beta_n^T (\bar{\mathcal{H}} - E_n) \mathcal{R}_n \\ &\quad + \bar{E}_n (1 - \langle \mathcal{L}_n^0 | \mathcal{R}_n \rangle) \end{aligned} \quad (109)$$

which gives the slightly different \mathcal{R}_n stationarity condition

$$0 = (1 + \bar{E}_n - E_n \beta_n^T \mathcal{R}_n) \mathcal{L}_n^T + \beta_n^T (\bar{\mathcal{H}} - E_n) \quad (110)$$

Here, we again select \bar{E}_n to make the first term vanish, giving

$$\beta_n^T = \mathcal{L}_n^T \quad (111)$$

Other than this change, the derivation of the scalar coupling is virtually unchanged. Terms involving differentiation of O_{mn} has the left state $\langle \mathcal{L}_n |$ in the bracket instead of $\langle \mathcal{L}_m |$ (e.g., in the stationarity conditions for the zeroth order multipliers). In particular, the expression in eq 102 is valid with $m = n$.

Unlike for the vector coupling, there is no convenient relationship between G_{mn}^I and \tilde{G}_{mn}^I . To derive the latter quantity, we may consider the Lagrangian

$$\begin{aligned} \mathcal{L}_{mn} &= O_{mn} + \gamma^T \mathcal{E}_{mn} \\ &= O_{mn} + \bar{\kappa}^T F_c + \xi^T \Omega + \mathcal{L}_m^T (\bar{\mathcal{H}} - E_m) \beta_m \\ &\quad + \bar{E}_m (1 - \langle \mathcal{L}_m^0 | \mathcal{R}_m \rangle) \end{aligned} \quad (112)$$

where

$$O_{mn} = \langle \mathcal{L}_m | \exp(-T) \exp(\kappa) | \psi_n(\mathbf{x}_0) \rangle \quad (113)$$

$$E_m = \mathcal{L}_m^T \bar{\mathcal{H}} \mathcal{R}_m^0 \quad (114)$$

The \mathcal{L}_m stationarity then gives

$$0 = \mathcal{R}_n + (\bar{\mathcal{H}} - E_m) \beta_m + (\bar{E}_m - E_m \mathcal{L}_n^T \beta_m) \mathcal{R}_m \quad (115)$$

from which we again have $\bar{E}_m = E_m \mathcal{L}_m^T \beta_m$ and thus

$$\beta_m = -(E_n - E_m)^{-1} \mathcal{R}_n \quad (116)$$

The equations for the zeroth order multipliers are derived as before, with the result that the multipliers change their sign, thus giving the result in eq 84 for the vector coupling. For the derivative of the parameters, we have the same equations for $t^{(i)}$ and $\kappa^{(i)}$. For the derivative of \mathcal{L}_m , we must solve the equation

$$\begin{aligned} \frac{d}{dx_i} (\mathcal{L}_m^T (\bar{\mathcal{H}} - E_m)) \Big|_0 &= 0 = \mathcal{L}_m \xi^{(i)T} \\ &\quad + \mathcal{L}_m^{(i)T} (\bar{\mathcal{H}} - E_m) \end{aligned} \quad (117)$$

which is analogous to eq 90. In contributions involving $\langle \beta_n | \dots | \mathcal{R}_n \rangle$ in G_{mn}^I , we obtain similar expressions involving $\langle \mathcal{L}_m | \dots | \beta_n \rangle$ in the case of \tilde{G}_{mn}^I . The end result is

$$\begin{aligned} \tilde{G}_{mn}^I &= \langle \bar{\mathcal{L}}_m^{(i,i)} | \bar{\mathcal{R}}_n \rangle + \langle \bar{\zeta} | \mathcal{K}^{(i,i)} | \text{CC} \rangle + \langle \bar{\mathcal{L}}_m | \mathcal{K}^{(i,i)} | \bar{\beta}_m \rangle \\ &\quad + \langle \text{HF} | [\bar{\kappa}, J^{(i,i)}] | \text{HF} \rangle + \langle \bar{\mathcal{L}}_m | L^{(i)} - \langle L^{(i)} \rangle_m | \bar{\beta}_m \rangle \end{aligned} \quad (118)$$

with

$$\begin{aligned} \langle \bar{\mathcal{L}}_m^{(i,i)} | \bar{\mathcal{R}}_n \rangle &= \langle \bar{\mathcal{L}}_m | (\kappa^{(i)})^2 - 2T^{(i)} \kappa^{(i)} + (T^{(i)})^2 | \bar{\mathcal{R}}_n \rangle \\ &\quad + 2\langle \bar{\mathcal{L}}_m | \kappa^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle - 2\langle \bar{\mathcal{L}}_m | T^{(i)} | \bar{\mathcal{R}}_n^{(i)} \rangle \\ &\quad - \sum_{pq} \langle \bar{\mathcal{L}}_m | E_{pq} | \bar{\mathcal{R}}_n \rangle \langle \phi_p^{(i)} | \phi_q^{(i)} \rangle \end{aligned} \quad (119)$$

Finally, \tilde{G}_{mn}^I is obtained in a manner similar to G_{mn}^I , see eq 109 and the surrounding text.

This concludes our derivation of the coupled cluster scalar coupling. To the best of our knowledge, equations for this coupling (with $m \neq n$) have not been presented in the literature before. Diagonal terms were also considered by Gauss *et al.*¹⁸ from a different starting point.

CONCLUDING REMARKS

The norm of the electronic states changes the value of nonadiabatic coupling elements but does not change the molecular wave function. The biorthonormal formula assumed by Christiansen¹³ is therefore a valid choice for nonadiabatic dynamics using coupled cluster methods. More generally, we have shown that the total wave function is invariant with respect to smooth and invertible transformations of the electronic basis. Of course, the biorthonormal couplings are not directly comparable to the coupling elements of an Hermitian method with normalized states, such as CI or full-CI. However, this reflects the basis-dependence of the couplings and not the validity of the biorthonormal formalism.

We therefore derive a set of nuclear Schrödinger equations assuming biorthonormal projection onto the electronic basis. Combined with expressions derived for the vector and scalar couplings, these nuclear Schrödinger equations serve as a starting point for the application of coupled cluster methods in simulations of nonadiabatic dynamics.

Our derivations have been restricted to the standard coupled cluster theory. However, the Lagrangian formalism is easily extended to similarity constrained coupled cluster methods,^{11,12} which are suited to describe relaxation through a conical intersection between excited states. The application to ground-state intersections is less straightforward but may be accessible with approaches that use a different reference than the closed-shell Hartree–Fock state.³²

APPENDIX A

Geometry Dependence of the Many-Body Operators

The scalar and vector couplings, see eqs 19 and 20, involve differentiation of the electronic wave functions with respect to the nuclear coordinates \mathbf{x} . To evaluate these, we need to consider the dependence of both the wave function parameters and the many-body operators. For reasons that will become clear, we use the so-called natural connection³¹ to describe the orbital basis at neighboring geometries. Our presentation follows closely that given by of Olsen *et al.*³¹ Using the natural

connection for nonadiabatic coupling elements was also discussed by Christiansen.¹³

To evaluate derivatives at \mathbf{x}_0 , we relate the basis at \mathbf{x}_0 to some basis at $\mathbf{x} = \mathbf{x}_0 + \Delta\mathbf{x}$. Suppose the molecular orbitals (MOs) at \mathbf{x}_0 are

$$\phi_m(\mathbf{x}_0) = \sum_{\alpha} \chi_{\alpha}(\mathbf{x}_0) C_{\alpha m}(\mathbf{x}_0) \quad (120)$$

where $C_{\alpha m}$ are orbital coefficients and χ_{α} are atomic orbitals. The unmodified MOs (UMOs) are defined by freezing the orbital coefficients

$$\phi_m^u(\mathbf{x}) = \sum_{\alpha} C_{\alpha m}(\mathbf{x}_0) \chi_{\alpha}(\mathbf{x}) \quad (121)$$

The UMOs are not orthonormal, however

$$S_{mn}(\mathbf{x}) = \langle \phi_m^u(\mathbf{x}) | \phi_n^u(\mathbf{x}) \rangle, \quad S_{mn}(\mathbf{x}_0) = \delta_{pq} \quad (122)$$

Hence, UMOs are related to orthonormalized MOs (OMOs) through

$$\phi_m(\mathbf{x}) = \sum_n \phi_n^u(\mathbf{x}) T_{nm}(\mathbf{x}) \quad (123)$$

where the connection matrix $T(\mathbf{x})$ satisfies $T(\mathbf{x}_0) = I$ and $T(\mathbf{x})^{\dagger} S(\mathbf{x}) T(\mathbf{x}) = I$.

In the natural connection, T is chosen to be

$$T(\mathbf{x}) = W(\mathbf{x})^{-1} (W(\mathbf{x}) S(\mathbf{x}) W(\mathbf{x})^{\dagger})^{1/2} = W(\mathbf{x})^{-1} \Delta(\mathbf{x}) \quad (124)$$

where

$$W_{mn}(\mathbf{x}) = \langle \phi_m^u(\mathbf{x}_0) | \phi_n^u(\mathbf{x}) \rangle \quad (125)$$

Let us now relate the orbital space at \mathbf{x} to the one at \mathbf{x}_0 . In order to do so, we consider a complete orbital basis (denoted by indices $pq\dots$) partitioned into the OMO basis ($mnn\dots$) and the orthogonal complement orbitals or OCOs ($uv\dots$). For complete bases, we can write

$$\phi_p(\mathbf{x}) = \sum_q \phi_q(\mathbf{x}_0) U_{qp}(\mathbf{x}), \quad U_{qp}(\mathbf{x}) = \langle \phi_q(\mathbf{x}_0) | \phi_p(\mathbf{x}) \rangle \quad (126)$$

Occupation number states at \mathbf{x} can thus be expressed as

$$|\Phi(\mathbf{x})\rangle = U(\mathbf{x}) |\Phi(\mathbf{x}_0)\rangle \quad (127)$$

with

$$U(\mathbf{x}) = \exp(-b(\mathbf{x})), \quad b(\mathbf{x}) = \sum_{pq} b_{pq}(\mathbf{x}) a_p^{\dagger}(\mathbf{x}_0) a_q(\mathbf{x}_0) \quad (128)$$

where $b(\mathbf{x})$ is the anti-Hermitian operator with $b_{pq}(\mathbf{x})$ defined such that $U(\mathbf{x}) = \exp(-b(\mathbf{x}))$. The many-body operators can be expanded as

$$a_p^{\dagger}(\mathbf{x}) = \sum_q a_q^{\dagger}(\mathbf{x}_0) U_{qp}(\mathbf{x}) \quad (129)$$

To evaluate derivatives with respect to some specific component (denoted x), we consider the Taylor expansion of a displacement in this direction, $\mathbf{x} = \mathbf{x}_0 + \Delta\mathbf{x}$, which can be expressed as

$$a_p^{\dagger}(\mathbf{x}) = a_p^{\dagger} + a_p^{(1)\dagger} \Delta x + \frac{1}{2} a_p^{(2)\dagger} (\Delta x)^2 + \dots \quad (130)$$

$$b(\mathbf{x}) = b^{(1)} \Delta x + \frac{1}{2} b^{(2)} (\Delta x)^2 + \dots \quad (131)$$

where $b^{(n)} = \sum_{pq} b_{pq}^{(n)} a_p^{\dagger} a_q$. Here, we have let $a_p^{\dagger} \equiv a_p^{\dagger}(\mathbf{x}_0)$ and suppressed the \mathbf{x}_0 -dependence of the derivatives. It is useful to split operator contributions in the OMO (\parallel) and OCO (\perp) blocks

$$\begin{aligned} a_p^{\dagger}(\mathbf{x}) &= \sum_m a_m^{\dagger}(\mathbf{x}_0) U_{mp}(\mathbf{x}) + \sum_u a_u^{\dagger}(\mathbf{x}_0) U_{up}(\mathbf{x}) \\ &= a_{p\parallel}^{\dagger}(\mathbf{x}) + a_{p\perp}^{\dagger}(\mathbf{x}) \end{aligned} \quad (132)$$

Now, we can evaluate the first derivative contribution

$$f_{IJ} = \langle \Phi_I(\mathbf{x}_0) | \frac{\partial}{\partial x} \Phi_J(\mathbf{x}) \rangle \Big|_0 \quad (133)$$

Using eq 127, we get

$$f_{IJ} = \langle \Phi_I(\mathbf{x}_0) | \frac{\partial U}{\partial x} \Big|_0 | \Phi_J(\mathbf{x}_0) \rangle = -\langle \Phi_I(\mathbf{x}_0) | b^{(1)} | \Phi_J(\mathbf{x}_0) \rangle \quad (134)$$

To simplify further, we note that $U_{mn} = \Delta_{mn}$ is Hermitian in the natural connection. Since the U_{uv} block can similarly be chosen to be Hermitian, we have³¹

$$b_{mn} = b_{uv} = 0 \Rightarrow b_{mn}^{(k)} = b_{uv}^{(k)} = 0 \quad (135)$$

and so

$$f_{IJ} = -\sum_{mn} b_{mn}^{(1)} \langle \Phi_I(\mathbf{x}_0) | a_m^{\dagger} a_n | \Phi_J(\mathbf{x}_0) \rangle = 0 \quad (136)$$

In general, f_{IJ} is non-zero with connections other than the natural connection.

Next, we evaluate the second derivative contribution

$$g_{IJ} = \left\langle \Phi_I(\mathbf{x}_0) \left| \frac{\partial^2}{\partial x^2} \Phi_J(\mathbf{x}) \right. \right\rangle \Big|_0 = \left\langle \Phi_I(\mathbf{x}_0) \left| \frac{\partial^2 U}{\partial x^2} \right. \right\rangle \Big|_0 | \Phi_J(\mathbf{x}_0) \rangle \quad (137)$$

which can be written as

$$\begin{aligned} g_{IJ} &= \langle \Phi_I(\mathbf{x}_0) | -b^{(2)} + b^{(1)} b^{(1)} | \Phi_J(\mathbf{x}_0) \rangle \\ &= \langle \Phi_I(\mathbf{x}_0) | b^{(1)} b^{(1)} | \Phi_J(\mathbf{x}_0) \rangle \end{aligned} \quad (138)$$

In the final equality, we have used eq 135. Now, notice that since

$$\begin{aligned} b^{(1)} &= \sum_{um} b_{um}^{(1)} a_u^{\dagger} a_m + \sum_{mu} b_{mu}^{(1)} a_m^{\dagger} a_u \\ &= -\sum_m a_{m\perp}^{(1)\dagger} a_m + \sum_m a_m^{\dagger} a_{m\perp} \end{aligned} \quad (139)$$

the only non-zero $b^{(1)} b^{(1)}$ contribution is the one that first creates an electron in the complementary space and then destroys it. Thus

$$\begin{aligned}
 g_{IJ} &= -\sum_{mn} \langle \Phi_I(\mathbf{x}_0) | a_m^\dagger a_{m\perp}^{(1)} a_n^{(1)\dagger} a_n | \Phi_J(\mathbf{x}_0) \rangle \\
 &= -\sum_{mn} \langle \Phi_I(\mathbf{x}_0) | a_m^\dagger [a_{m\perp}^{(1)}, a_n^{(1)\dagger}]_+ a_n | \Phi_J(\mathbf{x}_0) \rangle
 \end{aligned}
 \quad (140)$$

The commutator can be expressed as

$$\begin{aligned}
 [a_{m\perp}^{(1)}, a_n^{(1)\dagger}]_+ &= \sum_{uv} U_{um}^{(1)*} U_{vn}^{(1)} [a_u, a_v^\dagger]_+ = \sum_u U_{um}^{(1)*} U_{un}^{(1)} \\
 &= \sum_u \langle \phi_m^{(1)} | \phi_u(\mathbf{x}_0) \rangle \langle \phi_u(\mathbf{x}_0) | \phi_n^{(1)} \rangle
 \end{aligned}
 \quad (141)$$

Moreover, since

$$\langle \phi_m(\mathbf{x}_0) | \phi_n^{(1)} \rangle = U_{mn}^{(1)} = -b_{mn}^{(1)} = 0
 \quad (142)$$

the inner projection in eq 141 is equivalent to the identity and so

$$[a_{m\perp}^{(1)}, a_n^{(1)\dagger}]_+ = \langle \phi_m^{(1)} | \phi_n^{(1)} \rangle
 \quad (143)$$

Hence

$$g_{IJ} = -\sum_{mn} \langle \Phi_I(\mathbf{x}_0) | a_m^\dagger a_n | \Phi_J(\mathbf{x}_0) \rangle \langle \phi_m^{(1)} | \phi_n^{(1)} \rangle
 \quad (144)$$

The formulas for f_{IJ} and g_{IJ} are valid for occupation number states but allow for generalization to general wave functions. We will be concerned with evaluating partial derivatives with respect to x for wave functions of the form

$$|\psi_k(\mathbf{x})\rangle = \sum_I c_{Ik}(\mathbf{x}) |\Phi_I(\mathbf{x})\rangle
 \quad (145)$$

Since c_{Ik} depends implicitly on \mathbf{x} , we have $\partial c_{Ik}/\partial \mathbf{x} = 0$. Thus

$$\begin{aligned}
 f_{kl} &= \left\langle \psi_k(\mathbf{x}_0) \left| \frac{\partial}{\partial \mathbf{x}} \right| \psi_l(\mathbf{x}) \right\rangle \Big|_0 \\
 &= \sum_{IJ} c_{Ik}^*(\mathbf{x}_0) \left\langle \Phi_I(\mathbf{x}_0) \left| \frac{\partial}{\partial \mathbf{x}} \right| \Phi_J(\mathbf{x}) \right\rangle \Big|_0 c_{Jl}(\mathbf{x}_0) \\
 &= \sum_{IJ} c_{Ik}^*(\mathbf{x}_0) f_{IJ} c_{Jl}(\mathbf{x}_0) = 0
 \end{aligned}
 \quad (146)$$

and

$$\begin{aligned}
 g_{kl} &= \left\langle \psi_k(\mathbf{x}_0) \left| \frac{\partial^2}{\partial \mathbf{x}^2} \right| \psi_l(\mathbf{x}) \right\rangle \Big|_0 = \sum_{IJ} c_{Ik}^*(\mathbf{x}_0) g_{IJ} c_{Jl}(\mathbf{x}_0) \\
 &= -\sum_{mn} \langle \psi_k(\mathbf{x}_0) | a_m^\dagger a_n | \psi_l(\mathbf{x}_0) \rangle \langle \phi_m^{(1)} | \phi_n^{(1)} \rangle
 \end{aligned}
 \quad (147)$$

For partial derivatives of the energy, we also have to account for the explicit \mathbf{x} -dependence of the Hamiltonian. We express the OMO Hamiltonian as

$$H = \sum_{pq} h_{pq}(\mathbf{x}) E_{pq}(\mathbf{x}) + \frac{1}{2} \sum_{pqrs} g_{pqrs}(\mathbf{x}) e_{pqrs}(\mathbf{x})
 \quad (148)$$

where both the integrals and the operators depend on \mathbf{x} . However, the dependence of the operators can be ignored in energy derivatives because

$$\begin{aligned}
 \langle \Phi_I(\mathbf{x}) | \Phi_J(\mathbf{x}) \rangle &= \langle \Phi_I(\mathbf{x}_0) | U(\mathbf{x})^\dagger U(\mathbf{x}) | \Phi_J(\mathbf{x}_0) \rangle \\
 &= \langle \Phi_I(\mathbf{x}_0) | \Phi_J(\mathbf{x}_0) \rangle
 \end{aligned}
 \quad (149)$$

In particular, elements involving $E_{pq}(\mathbf{x})$ and $e_{pqrs}(\mathbf{x})$ are linear combinations of such overlaps and therefore give no contributions in energy derivatives.³³ The integrals are related to the UMO basis as

$$h_{pq}(\mathbf{x}) = \sum_{mn} T_{mp}(\mathbf{x})^* h_{mn}^u(\mathbf{x}) T_{nq}(\mathbf{x})
 \quad (150)$$

$$g_{pqrs}(\mathbf{x}) = \sum_{mkl} T_{mp}(\mathbf{x})^* T_{nq}(\mathbf{x})^* g_{mkl}^u(\mathbf{x}) T_{kr}(\mathbf{x}) T_{ls}(\mathbf{x})
 \quad (151)$$

By differentiating $TW = W^\dagger T^\dagger$ and $I = T^\dagger ST$, we find that $T^{(1)} = -W^{(1)}$. Consequently, the partial derivative of the Hamiltonian can be written as

$$H^{(1)} = H_u^{(1)} - \{W^{(1)}, H\}
 \quad (152)$$

where $H_u^{(1)}$ is the derivative of the UMO Hamiltonian and

$$\{W^{(1)}, H\} = \sum_{pq} j_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} j_{pqrs} e_{pqrs}
 \quad (153)$$

where j_{pq} and j_{pqrs} are the sums of one-index transformations of $W_{pq}^{(1)}$ with h_{pq} and g_{pqrs} , respectively.³⁴ The $W^{(1)}$ matrix, given by

$$W_{pq}^{(1)} = \frac{\partial W_{pq}}{\partial \mathbf{x}} \Big|_0 = \sum_{\alpha\beta} C_{\alpha p}(\mathbf{x}_0) C_{\beta q}(\mathbf{x}_0) \int \chi_\alpha(\mathbf{x}_0) \frac{\partial \chi_\beta}{\partial \mathbf{x}} \Big|_0 d\mathbf{r}
 \quad (154)$$

is analogous to $S_{pq}^{(1)} = \partial S_{pq}/\partial \mathbf{x}_0$ in the symmetric connection $T = S^{-1/2}$.

This concludes our discussion of how the geometry dependence of the many-body operators affects energy derivatives and nonadiabatic coupling elements. We refer the reader to the literature for more details.^{31,33}

APPENDIX B

Lagrangian Derivatives

Here, we derive the first and second derivatives of the generic Lagrangian

$$\mathcal{L}(\lambda, \mathbf{x}, \boldsymbol{\gamma}) = \mathcal{O}(\lambda, \mathbf{x}) + \boldsymbol{\gamma}^T \boldsymbol{\varepsilon}(\lambda, \mathbf{x})
 \quad (155)$$

with respect to \mathbf{x} . The parameters and multipliers both depend on \mathbf{x} since they are determined, for a given \mathbf{x} , from the stationarity conditions

$$\frac{\partial \mathcal{L}}{\partial \lambda_k} = 0, \quad \frac{\partial \mathcal{L}}{\partial \gamma_k} = 0
 \quad (156)$$

Using Einstein notation, we can write the Taylor expansion of \mathcal{L} about some \mathbf{x}_0 as

$$\begin{aligned} \mathcal{L}(\lambda, \mathbf{x}, \boldsymbol{\gamma}) = & \mathcal{L}_0 + \left. \frac{\partial \mathcal{L}}{\partial x_k} \right|_0 \Delta x_k + \left. \frac{1}{2} \Delta x_k \frac{\partial^2 \mathcal{L}}{\partial x_k \partial x_l} \right|_0 \\ & \Delta x_l + \left. \frac{1}{2} \Delta \lambda_k \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \lambda_l} \right|_0 \Delta \lambda_l + \left. \Delta \lambda_k \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial x_l} \right|_0 \\ & \Delta x_l + \left. \Delta \gamma_k \frac{\partial^2 \mathcal{L}}{\partial \gamma_k \partial x_l} \right|_0 \Delta x_l + \left. \Delta \lambda_k \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \gamma_l} \right|_0 \Delta \gamma_l \\ & + \dots \end{aligned} \quad (157)$$

where we have ignored terms of order 3 or higher in $\Delta \mathbf{x}$. These terms do not contribute to the first and second derivatives and are therefore not relevant to the analysis given here.

In the first derivative, only the partial derivative survives, *i.e.*

$$\left. \frac{d\mathcal{L}}{dx_i} \right|_0 = \left. \frac{\partial \mathcal{L}}{\partial x_i} \right|_0 \quad (158)$$

This is due to the stationarity conditions since they ensure that there are no linear terms in $\Delta \lambda$ and $\Delta \boldsymbol{\gamma}$ in the Taylor expansion in eq 157. In the second derivative, it is convenient to introduce notation for derivatives with respect to particular components of \mathbf{x} . We let

$$a^{(i)} = \left. \frac{\partial a}{\partial x_i} \right|_0 \quad (159)$$

$$a^{(i,j)} = \left. \frac{\partial^2 a}{\partial x_i \partial x_j} \right|_0 \quad (160)$$

Then, we can write

$$\left. \frac{d\mathcal{L}}{dx_i} \right|_0 = \mathcal{L}^{(i)} \quad (161)$$

and

$$\begin{aligned} \left. \frac{d^2 \mathcal{L}}{dx_i dx_j} \right|_0 = & \mathcal{L}^{(i,j)} + \lambda_k^{(i)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \lambda_l} \right|_0 \lambda_l^{(j)} + \lambda_k^{(j)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial x_i} \right|_0 \\ & + \lambda_k^{(i)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial x_j} \right|_0 + \gamma_k^{(j)} \left. \frac{\partial^2 \mathcal{L}}{\partial \gamma_k \partial x_i} \right|_0 + \gamma_k^{(i)} \left. \frac{\partial^2 \mathcal{L}}{\partial \gamma_k \partial x_j} \right|_0 \\ & + 2\lambda_k^{(i)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \gamma_l} \right|_0 \gamma_l^{(j)} \end{aligned} \quad (162)$$

Now

$$\gamma_l^{(j)} \left(\left. \frac{\partial^2 \mathcal{L}}{\partial x_i \partial \gamma_l} \right|_0 + \lambda_k^{(i)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \gamma_l} \right|_0 \right) = \gamma_l^{(j)} \left. \frac{d\mathcal{E}_l}{dx_i} \right|_0 = 0 \quad (163)$$

by stationarity, so that

$$\begin{aligned} \left. \frac{d^2 \mathcal{L}}{dx_i dx_j} \right|_0 = & \mathcal{L}^{(i,j)} + \lambda_k^{(i)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \lambda_l} \right|_0 \lambda_l^{(j)} + \lambda_k^{(j)} \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial x_i} \right|_0 + \lambda_k^{(i)} \\ & \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial x_j} \right|_0 \end{aligned} \quad (164)$$

To simplify the notation further, we define derivatives with respect to the parameters as


$$f_k = \left. \frac{\partial \mathcal{L}}{\partial \lambda_k} \right|_0, \quad H_{kl} = \left. \frac{\partial^2 \mathcal{L}}{\partial \lambda_k \partial \lambda_l} \right|_0 \quad (165)$$

Thus, we get the final expression for the second derivatives:

$$\left. \frac{d^2 \mathcal{L}}{dx_i dx_j} \right|_0 = \mathcal{L}^{(i,j)} + \lambda_k^{(i)} H_{kl} \lambda_l^{(j)} + \lambda_k^{(j)} f_k^{(i)} + \lambda_k^{(i)} f_k^{(j)} \quad (166)$$

AUTHOR INFORMATION

Corresponding Author

Henrik Koch – *Scuola Normale Superiore, Pisa PI 56126, Italy; Department of Chemistry, Norwegian University of Science and Technology, Trondheim 7491, Norway;*
 orcid.org/0000-0003-0828-4979; Email: henrik.koch@sns.it

Author

Eirik F. Kjønsdal – *Department of Chemistry, Norwegian University of Science and Technology, Trondheim 7491, Norway;*  orcid.org/0000-0002-8367-8727

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jctc.0c00730>

Notes

The authors declare no competing financial interest.

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REFERENCES

- Born, M.; Oppenheimer, R. Zur Quantentheorie der Molekeln. *Ann. Phys.* **1927**, *389*, 457–484.
- Zhu, X.; Yarkony, D. R. Non-adiabaticity: the importance of conical intersections. *Mol. Phys.* **2016**, *114*, 1983–2013.
- Curchod, B. F. E.; Martínez, T. J. Ab Initio Nonadiabatic Quantum Molecular Dynamics. *Chem. Rev.* **2018**, *118*, 3305–3336.
- Bartlett, R. J.; Musiał, M. Coupled-cluster theory in quantum chemistry. *Rev. Mod. Phys.* **2007**, *79*, 291.
- Krylov, A. I. Equation-of-Motion Coupled-Cluster Methods for Open-Shell and Electronically Excited Species: The Hitchhiker's Guide to Fock Space. *Annu. Rev. Phys. Chem.* **2008**, *59*, 433–462.
- Helgaker, T.; Jørgensen, P.; Olsen, J. *Molecular Electronic-Structure Theory*; John Wiley & Sons, 2014.
- Loos, P.-F.; Scemama, A.; Jacquemin, D. The Quest for Highly Accurate Excitation Energies: A Computational Perspective. *J. Phys. Chem. Lett.* **2020**, *11*, 2374–2383.

- (8) Hättig, C. Structure optimizations for excited states with correlated second-order methods: CC2 and ADC (2). *Adv. Quantum Chem.* **2005**, *50*, 37–60.
- (9) Köhn, A.; Tajti, A. Can coupled-cluster theory treat conical intersections? *J. Chem. Phys.* **2007**, *127*, 044105.
- (10) Kjønstad, E. F.; Myhre, R. H.; Martínez, T. J.; Koch, H. Crossing conditions in coupled cluster theory. *J. Chem. Phys.* **2017**, *147*, 164105.
- (11) Kjønstad, E. F.; Koch, H. Resolving the Notorious Case of Conical Intersections for Coupled Cluster Dynamics. *J. Phys. Chem. Lett.* **2017**, *8*, 4801–4807.
- (12) Kjønstad, E. F.; Koch, H. An Orbital Invariant Similarity Constrained Coupled Cluster Model. *J. Chem. Theory Comput.* **2019**, *15*, 5386–5397.
- (13) Christiansen, O. First-order nonadiabatic coupling matrix elements using coupled cluster methods. I. Theory. *J. Chem. Phys.* **1999**, *110*, 711–723.
- (14) Handy, N. C.; Schaefer, H. F., III On the evaluation of analytic energy derivatives for correlated wave functions. *J. Chem. Phys.* **1984**, *81*, 5031–5033.
- (15) Tajti, A.; Szalay, P. G. Analytic evaluation of the nonadiabatic coupling vector between excited states using equation-of-motion coupled-cluster theory. *J. Chem. Phys.* **2009**, *131*, 124104.
- (16) Ichino, T.; Gauss, J.; Stanton, J. F. Quasidiabatic states described by coupled-cluster theory. *J. Chem. Phys.* **2009**, *130*, 174105.
- (17) Purvis, 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.
- (18) Gauss, J.; Tajti, A.; Kállay, M.; Stanton, J. F.; Szalay, P. G. Analytic calculation of the diagonal Born-Oppenheimer correction within configuration-interaction and coupled-cluster theory. *J. Chem. Phys.* **2006**, *125*, 144111.
- (19) Faraji, S.; Matsika, S.; Krylov, A. I. Calculations of non-adiabatic couplings within equation-of-motion coupled-cluster framework: Theory, implementation, and validation against multi-reference methods. *J. Chem. Phys.* **2018**, *148*, 044103.
- (20) Born, M.; Huang, K. *Dynamical Theory of Crystal Lattices*; Clarendon Press, 1954.
- (21) Shamasundar, K. R. Diagonal Born–Oppenheimer correction for coupled-cluster wave-functions. *Mol. Phys.* **2018**, *116*, 1483–1495.
- (22) Helgaker, T.; Jørgensen, P. Configuration-interaction energy derivatives in a fully variational formulation. *Theor. Chim. Acta* **1989**, *75*, 111–127.
- (23) Koch, H.; Jensen, H. J. r. A.; Jørgensen, P.; Helgaker, T.; Scuseria, G. E.; Schaefer, H. F., III Coupled cluster energy derivatives. Analytic Hessian for the closed-shell coupled cluster singles and doubles wave function: Theory and applications. *J. Chem. Phys.* **1990**, *92*, 4924–4940.
- (24) Helgaker, T.; Jørgensen, P.; Handy, N. C. A numerically stable procedure for calculating Møller-Plesset energy derivatives, derived using the theory of Lagrangians. *Theor. Chim. Acta* **1989**, *76*, 227–245.
- (25) Hohenstein, E. G. Analytic formulation of derivative coupling vectors for complete active space configuration interaction wave-functions with floating occupation molecular orbitals. *J. Chem. Phys.* **2016**, *145*, 174110.
- (26) Hättig, C.; Christiansen, O.; Jørgensen, P. Multiphoton transition moments and absorption cross sections in coupled cluster response theory employing variational transition moment functionals. *J. Chem. Phys.* **1998**, *108*, 8331–8354.
- (27) Hättig, C.; Jørgensen, P. Derivation of coupled cluster excited states response functions and multiphoton transition moments between two excited states as derivatives of variational functionals. *J. Chem. Phys.* **1998**, *109*, 9219–9236.
- (28) Stanton, J. F.; Bartlett, R. J. The equation of motion coupled-cluster method. A systematic biorthogonal approach to molecular excitation energies, transition probabilities, and excited state properties. *J. Chem. Phys.* **1993**, *98*, 7029–7039.
- (29) Koch, H.; Jørgensen, P. Coupled cluster response functions. *J. Chem. Phys.* **1990**, *93*, 3333–3344.
- (30) Pacher, T.; Mead, C. A.; Cederbaum, L. S.; Köppel, H. Gauge theory and quasidiabatic states in Mol. Phys. *J. Chem. Phys.* **1989**, *91*, 7057–7062.
- (31) Olsen, J.; Bak, K. L.; Ruud, K.; Helgaker, T.; Jørgensen, P. Orbital connections for perturbation-dependent basis sets. *Theor. Chim. Acta* **1995**, *90*, 421–439.
- (32) Lefrancois, D.; Tuna, D.; Martínez, T. J.; Dreuw, A. The Spin-Flip Variant of the Algebraic-Diagrammatic Construction Yields the Correct Topology of S1/S0 Conical Intersections. *J. Chem. Theory Comput.* **2017**, *13*, 4436–4441.
- (33) Helgaker, T.; Jørgensen, P. *Methods in Computational Molecular Physics*; Wilson, S., Diercksens, G. H. F., Eds.; Springer US: Boston, MA, 1992; pp 353–421.
- (34) Helgaker, T.; Jørgensen, P. *Advances in quantum chemistry*; Elsevier, 1988; Vol. 19; pp 183–245.