Biorthonormal Formalism for Nonadiabatic Coupled Cluster Dynamics

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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 conformational interactions 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.

INTRODUCTION

Nonadiabatic coupling elements account for electron–nucleus interactions that are neglected in the Born–Oppenheimer (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. 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, 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. 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. 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, who applied the Z-vector substitution method on a biorthonormal expression for the coupling,

\[ F_{mn}^i = \langle \tilde{\Psi}_m | \nabla_i | \tilde{\Psi}_n \rangle, \quad \langle \tilde{\Psi}_m | \tilde{\Psi}_n \rangle = \delta_{mn} \quad (1) \]

where \( \langle \tilde{\Psi}_m | \tilde{\Psi}_n \rangle \) refers to the left and right \( k \)th electronic states and \( I \) refers to a nucleus. However, Christiansen’s paper did not include an implementation of the coupling. The vector coupling was later rederived by Tajti and Szalay 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. for the quasidiabatic interstate coupling. Tajti and Szalay also gave an implementation at the coupled cluster singles and doubles (CCSD) level. These papers on the vector coupling 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 Szalay 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
earlier paper on the diagonal BO correction. 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. 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 normalizations do 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.24

Derivative couplings are readily derived with the Lagrangian approach. 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 transition moment Lagrangians. We use the Lagrangian approach to derive expressions for the vector coupling as well as the second-order derivative coupling (or scalar coupling)

$$G_{mn}^{I} = \langle \hat{\psi}_{m} | V_{I} | \hat{\psi}_{n} \rangle$$

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

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 ($\Psi_{l}$,$\Psi_{r}$). 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 ($n = 0, 1, 2, ...$) left and right electronic states are expressed as

$$\langle \hat{\psi}_{n} | = \langle \hat{L}_{n} | \exp(-T) = \sum_{\mu \geq 0} L_{\mu}^{n} | \mu \rangle \exp(-T)$$

and

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

where $| \psi_{n} \rangle = \delta_{nn}$. The projection space is defined as

$$| \mu \rangle = \langle \hat{\mu}_{\mu} \rangle \hat{\mu}$$

and

$$M_{\mu}^{\mu} = \delta_{\mu\mu}$$

where $| \psi_{\mu} \rangle = \delta_{\mu\mu}$. The cluster operator is defined as

$$T = \sum_{\mu > 0} t_{\mu} \mu$$

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

The right ground state is assumed to have the exponential form

$$| \psi_{0} \rangle = | \mu \rangle$$

and projecting the Schrödinger equation onto $| \mu \rangle$ gives the ground state equations

$$E_{0} = \langle \hat{\mu}_{\mu} | \hat{\mu} \rangle$$

where $\hat{\mu} = \exp(-T) \hat{\mu} \exp(T)$. The state amplitudes, $L_{n}$ and $R_{\mu}$, are determined by making the $n$th energy stationary under the condition $1 = L_{n}^{T} R_{\mu}$. The result is a set of eigenvalue equations

$$L_{n}^{T} \hat{\mu} = E_{n} L_{n}$$

$$\mathcal{R}_{\mu}^{n} = E_{n} \mathcal{R}_{\mu}$$

where $E_{n}$ is the energy of the $n$th state and $\hat{\mu} = \langle \mu | \hat{\mu} | \mu \rangle$. Here and throughout, we use bold font (X) to denote vectors ($X_{n}$) and matrices ($X_{\mu}$). 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.

### 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 ($\hat{\psi}_{n}$ and $\psi_{\mu}$). Hence, we have a left and a right total wave function given by the Born–Huang expansions.
\(\Psi(r, R, t) = \sum_n \chi_n(R, t) \psi_n(r; R)\) 
(13)

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

with associated left and right nuclear wave functions \(\tilde{\chi}_n\) and \(\chi_n\), and

\[1 = \langle \tilde{\Psi} | \Psi \rangle = \sum_{mn} \langle \tilde{\chi}_m | \tilde{\psi}_m \rangle \langle \psi_n | \chi_n \rangle = \sum_{mn} \delta_{mn} \langle \tilde{\chi}_m | \psi_n \rangle \]
(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 \(r\) and \(R\), respectively, and time by \(t\). Expectation values are defined through the standard expression:

\[\langle \Omega \rangle = \langle \tilde{\Psi} | \Omega | \Psi \rangle, \quad \Omega = \Omega^I\]
(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 equations; Pacher et al. 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 formalism 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. The reason is that the left and right states are biorthonormal in the coupled cluster theory. Compared to the full-CI limit, while the latter is equivalent to assuming 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 states.

\[N^R_L = \langle \psi_L | \tilde{\psi}_L \rangle\]
(27)

\[N^R_R = \langle \tilde{\psi}_R | \tilde{\psi}_R \rangle\]
(28)

Since one cannot evaluate \(N^R_L\) in general, some have suggested \(N^L_R = (N^R_L)^{-1}\) or \(N^R_L = N^R_R = 1\) as alternatives. The former gives the full-CI limit, while the latter is equivalent to assuming the standard biorthonormality.

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 \(N^R_L\) while the right nuclear wave functions are multiplied by \(N^R_L\). 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

\[\psi' = \psi N\]
(29)

\[\tilde{\psi}' = \tilde{\psi} M\]
(30)
where the matrices $M$ and $N$ 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

$$\Psi'(r, R, t) = \sum_n \chi'_n(r, t)\psi'_n(R)$$

(31)

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

(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 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

$$S_{mn} = \langle \tilde{\psi}'_m | \psi'_n \rangle = \sum_{kl} \langle \tilde{\psi}'_m | N_{kn} | \psi'_n \rangle = \sum_{kl} N_{kn} \delta_{km} = (N^tM)_{mn}$$

(33)

Similarly, the electronic Hamiltonian matrix is not necessarily diagonal

$$(H_e)_{mn} = \langle \tilde{\psi}'_m | H | \psi'_n \rangle = \sum_{kl} \langle \tilde{\psi}'_m | N_{kn} | H | \psi'_n \rangle = \sum_{kl} N_{kn}^* E_{kl} M_{ln} = (N^tEM)_{mn}$$

(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

$$\left(N^tEM - i\frac{d}{dt}\right)\chi' = -\sum_{l} \frac{1}{2M_l^t} (S\psi'^2_l + G_l^t + 2F_l^t \cdot \psi_l')$$

(35)

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

$$\chi' = M^{-1}\chi$$

(36)

Indeed, with $\chi'$ as given in eq 36, we have

$$\Psi' = \sum_k \psi'_k \chi'_k = \sum_{klm} \psi'_k M_{kl} M^{-1}_{lm} \chi' = \sum_k \psi_k' \chi_k = \Psi'$$

(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

$$\nabla_j \psi'_i = \sum_m \nabla_j (\psi'_i M_m) = \sum_m (\nabla_j \psi'_i M_m + \psi'_i (\nabla_j M_m))$$

(38)

Hence, the vector couplings can be written as

$$(F'_j)_{kl} = \langle \tilde{\psi}'_l | \nabla_j \psi'_k \rangle = \sum_m (N_{kl}^* r^t M_m + N_{kl}^* r_{lm} \nabla_j M_m)$$

(39)

In more compact matrix notation, we have

$$F'_j = N^t F_j M + N^t \left( \nabla_j M \right)$$

(40)

Similarly, the Laplacian of the electronic wave functions transforms as

$$\nabla'^2 \psi'_i = \nabla_j \cdot \nabla_j \psi'_i = \sum_m (\nabla^2 \psi'_i M_m) + 2(\nabla \psi'_i) (\nabla_j M_m)$$

(41)

implying that the scalar couplings transform as

$$G'_j = N^t G_j M + 2N^t F_j (\nabla_j M) + N^t (\nabla^2_j M)$$

(42)

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

$$\nabla_l \chi'_i = \sum_m (M^{-1}_{lm} \chi'_m) + (\nabla M^{-1}_{lm}) \chi'_m$$

(43)

$$\nabla'^2 \chi' = \sum_m (M^{-1}_{lm} \nabla^2 \chi'_m) + 2(\nabla M^{-1}_{lm}) (\nabla \chi'_m)$$

(44)

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

$$S\nabla'^2 \chi' = N^t (\nabla^2 \chi') + 2M_j (\nabla_j M^{-1}) \cdot \nabla \chi' + M (\nabla^2_j M^{-1}) \chi'$$

(45)

$$G'_j \chi' = N^t (G_j \chi') + 2F_j (\nabla_j M) M^{-1} \cdot \chi' + (\nabla^2_j M) M^{-1} \chi'$$

(46)

$$2F'_j \cdot \nabla \chi' = N^t (2F_j \cdot \nabla \chi') + 2F_j (\nabla_j M) M^{-1} \chi' + 2(\nabla_j M) M^{-1} \chi'$$

(47)

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

$$0 = \nabla_0 (MM^{-1}) = (\nabla_0 M) M^{-1} + M (\nabla_0 M^{-1})$$

(48)

$$0 = \nabla_j^2 (MM^{-1})$$

(49)

we can write
Nonadiabatic Coupled Cluster Couplings in a Lagrangian Formalism. To obtain a Lagrangian for the vector coupling in CASCI, Hohenstein \(^{25}\) 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

\[
Q_{mn}(x) = \langle \tilde{\psi}_m(x_0)|\psi_n(x) \rangle
\]

in terms of which we have

\[
(F^l_{mn}) = \left( \frac{d}{dx_i} \langle \tilde{\psi}_m(x)|\psi_n(x) \rangle \right)_{x_i} = \frac{d}{dx_i} Q_{mn}(x), \quad i \in I
\]

and

\[
G^l_{mn} = \left( \frac{d^2}{dx_i dx_j} \langle \tilde{\psi}_m(x)|\psi_n(x) \rangle \right)_{x_i x_j} = \sum_{i \in I} \frac{d^2}{dx_i^2} Q_{mn}(x)_{x_i}
\]

We let \(i \in I\) mean that \(x_i\) is one of the three coordinates of the \(i\)th nucleus \((x, y, \text{or} z)\). Note that \(Q_{mn}(x)\) depends on \(x_0\). 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 \(x\) but also on a set of wave function parameters \(\lambda\) (which themselves depend on \(x\)). Written out in terms of the parameters, we have

\[
Q_{mn}(x, \lambda) = \langle \tilde{\psi}_m(x_0)|\exp(-x)\exp(T)|\lambda\rangle
\]

where

\[
\langle \tilde{\psi}_m(x_0) | = \langle \mathcal{L}_m|\exp(-T) \rangle_{x_0}
\]

and

\[
\kappa = \sum_{p \neq q} \kappa_{pq}(E_{pq} - E_{qp}) = \sum_{p \neq q} \kappa_{pq} E_{pq}^{-}
\]

The \(\kappa\) operator accounts for orbital rotations, meaning changes in the Hartree–Fock orbitals, where, by definition, we have \(\kappa(x_0) = 0\). 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 \(\gamma\))

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

where \(\lambda\) and \(\gamma\) are determined for every \(x\) by the stationarity conditions

\[
\frac{\partial \mathcal{L}_{mn}}{\partial \gamma_k} = (\mathcal{E}_{mn})_k = 0
\]

\[
\frac{\partial \mathcal{L}_{mn}}{\partial \lambda_k} = 0
\]

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 \(2m + 2\) rules for \(\lambda\) and \(\gamma\), respectively.\(^{6}\) In particular, we have

\[
(F^l_{mn})_{x_i} = \left( \frac{dL_{mn}}{dx_i} \right)_{x_i}
\]

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

\[
a^{(i)} = \frac{\partial a}{\partial x_i} \bigg|_0, \quad a^{(i,i)} = \frac{\partial^2 a}{\partial x_i \partial x_j} \bigg|_0
\]

we can write

\[
(F^l_{mn})_{x_i} = L^{(i)}_{mn}, \quad i \in I
\]

Furthermore, if we let

\[
f_\alpha = \left( \frac{\partial L_{mn}}{\partial \lambda_\alpha} \right)_{x_i \lambda_\beta} \quad H_{\alpha \beta} = \left( \frac{\partial^2 L_{mn}}{\partial \lambda_\alpha \partial \lambda_\beta} \right)_{x_i \lambda_\beta}
\]

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

\[
G^l_{mn} = \sum_{i \in I} \frac{d^2 L_{mn}}{dx_i^2} + \sum_{\alpha \neq \beta} \lambda_\alpha^{(i)} H_{\alpha \beta}^{(i)} + 2 \sum_{\alpha} \lambda_\alpha^{(i)} J_\alpha^{(i)}
\]

Clearly, \(F^l_{mn}\) and \(G^l_{mn}\) are similar in complexity to the energy gradient and Hessian. However, \(G^l_{mn}\) 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 \(Q_{mn}\). 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
\[
\mathcal{L}_{mn} = O_{mn} + \gamma^T E_{mn} \\
= O_{mn} + \kappa^T F + \zeta^T \Omega + \beta_n^T (\mathbf{H} - E_n) \mathbf{R}_n \\
+ \bar{E}_n (1 - (\mathcal{L}_m^T \mathbf{R}_n))
\]  
(66)

where we have introduced multipliers associated with the different sets of equations, \( \kappa, \zeta \), as well as \( \beta_n \) and \( \bar{E}_n \). We have also introduced the Brillouin condition
\[
(E)_{pq} = \langle \mathbf{H} E_m^p, H(\kappa)|\mathbf{H} \rangle, \quad p > q
\]  
(67)

where
\[
H(\kappa) = \exp(\kappa) H \exp(-\kappa)
\]  
(68)

Furthermore, the similarity transformed the Hamiltonian in \( \Omega \) and \( \mathbf{H} \) is given by
\[
\mathbf{H} = \mathbf{H}(\kappa) = \exp(-T) H(\kappa) \exp(T)
\]  
(69)

and the \( n \)th electronic energy is defined as
\[
E_n = \langle \mathcal{L}_n^0 | \mathbf{H} | \mathbf{R}_n \rangle
\]  
(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 \( \Lambda \) stationarity, eq 60. To keep our notation simple, we will denote the zeroth order terms as \( \gamma \) and \( \lambda(i) \equiv \lambda \), where it should be understood from context when these are \( \gamma \) and \( \lambda \) evaluated at \( x_0 \). Differentiation with respect to the state parameters gives
\[
\frac{\partial \mathcal{L}_{mn}}{\partial \mathbf{R}_n} \bigg|_0 = 0 = \mathcal{L}_m^T + \beta_n^T (\mathbf{H} - E_n I) \\
- (E_n + \beta_n^T \mathbf{R}_n) \mathcal{L}_m^T = 0
\]  
(71)

To solve this equation, we note that if we let
\[
E_n = -E_n \beta_n^T \mathbf{R}_n
\]  
(72)

the equation for \( \beta_n \) becomes
\[
\beta_n^T (\mathbf{H} - E_n I) = -\mathcal{L}_m^T
\]  
(73)

Thus, we have
\[
\beta_n = (E_n - E_m)^{-1} \mathcal{L}_m
\]  
(74)

Next, we consider stationarity with respect to \( t \). This can be expressed as
\[
\frac{\partial \mathcal{L}_{mn}}{\partial t} \bigg|_0 = 0 = \eta^T + \zeta^T A
\]  
(75)

where
\[
\eta_\mu = \langle \mathcal{L}_m | \mathbf{R}_n \rangle + \langle \bar{E}_n | [H, \tau_\mu] | \mathbf{R}_n \rangle
\]  
(76)

and where we have introduced the notation
\[
\mathcal{X} = \exp(T)|\mathcal{X}\rangle
\]  
(77)

\[
\langle \mathcal{X} \rangle = \langle \mathcal{X} | \exp(-T)
\]  
(78)

Finally, we have stationarity with respect to \( \mathbf{K} \), which can be written as
\[
\frac{\partial \mathcal{L}_{mn}}{\partial \mathbf{K}} \bigg|_0 = 0 = \eta^T + \kappa^T A^{HF}
\]  
(79)

where
\[
\eta_\mu = -\langle \mathcal{L}_m | \mathbf{R}_n \rangle + \langle \zeta | [E_n, H] \rangle \mathbf{C}
\]  
(80)

and
\[
A^{HF}_{pq, i} = \langle \mathbf{H} E_m^p, H(\kappa)|\mathbf{H} \rangle
\]  
(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
\[
\langle \mathbf{V}_{mn} | = \langle E_n - E_m^{-1} \rangle \mathcal{L}_m^0 (\mathbf{R}_n) + \langle \zeta | \mathbf{H}^{(i)} | \mathbf{H} \rangle
\]  
(82)

\[
\mathcal{H}^{(i)} = \exp(-T) \mathbf{H}(i) \exp(T)
\]  
(83)

and where quantities at \( x_0 \) 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 \( H_{mn} \) 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, who assumed biorthonormality and used Z-vector substitution on the expression for the vector coupling. Tajti and Szalay identified the same expression indirectly using Z-vector substitution on derivatives of Hamiltonian transition elements. However, they also argued 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
\[
\langle \psi_i | \mathbf{W}_F | \rangle = \delta_{mi} \Rightarrow \mathbf{F}_{mn} = -\mathbf{F}_{mn}^i
\]  
(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 multipliers stationarity conditions. In the case of \( t \), we have
\[
\frac{d \mathbf{K}}{d x_i} \bigg|_0 = 0 = \zeta_{(i)} + A_{(i)}
\]  
(85)

where
\[
\zeta_{(i)} = \langle \mu | \mathbf{H}^{(i)} | \mathbf{H} \rangle + \langle \mu | \exp(-T) \mathbf{K}^{(i)} | \mathbf{H} \rangle \exp(T) \mathbf{H}
\]  
(86)

In the case of \( \mathbf{K} \), we similarly have
where
\[ \kappa_{\xi}^{(i)} = \langle \text{HF}[E_{\xi}^{(i)}, H^{(i)}] \rangle_{\text{HF}} \]
(88)

The biorthonormality condition implies
\[ \frac{d}{dx_i} \left( 1 - \langle L_{\beta}^{(i)} \rangle_{\text{HF}} \right) = - \langle L_{\beta}^{(i)} \rangle_{\text{HF}} \]
while the eigenvalue condition implies
\[ \frac{d}{dx_i} \left( (\mathbf{H} - E_{\xi}) \mathbf{R}_{\xi} \right)_{\text{HF}} = 0 = \mathbf{R}_{\xi}^{(i)} + (\mathbf{H} - E_{\xi}) \mathbf{R}_{\xi}^{(i)} \]
(90)

Here, we have defined
\[ \mathbf{R}_{\xi}^{(i)} = (\mathbf{Y}^{(i)} - L_{\beta}^{(i)} \mathbf{Y}^{(i)} \mathbf{R}_{\xi}) \mathbf{R}_{\xi} \]
(91)

and
\[ \mathbf{Y}_{\mu}^{(i)} = (\mu \mathbf{I} \mathbf{I}^{(i)}) \mathbf{Y}_{\mu} + (\mu \mathbf{I} \mathbf{I}^{(i)}) \mathbf{Y}_{\nu} \]
\[ \mu, \nu \geq 0 \]
(92)

With the derivatives of the parameters determined, let us next consider \( f^{(i)} \) and \( H_{\alpha\beta} \), see eq 64. Recall that the \( \alpha \) and \( \beta \) indices refer to the parameters \( \lambda_\alpha \) and \( \lambda_\beta \). The gradient \( f \) is given by the zeroth order equations for the multipliers, that is, eqs 71, 73, and 79, with \( \lambda = \lambda_0 \) but allowing for \( x \neq x_0 \). Partially differentiating these terms with respect to \( x \) gives \( f^{(i)} \). The blocks of the \( \sum_{\mu=0}^{(i)} \lambda_\mu \) contributions to \( G_{\alpha\beta} \) can be written
\[ \mathbf{R}_{\xi}^{(i)} = \left( \frac{\partial^2 L_{\mu}}{\partial \xi \partial (\mathbf{R}_{\xi})_{\mu}} \right)_{\text{HF}} (\mathbf{R}_{\xi})_{\mu} = (\mathbf{P}_{\beta}^{(i)} H_{\xi}^{(i)} - E_{\xi}^{(i)} \mathbf{R}_{\xi}^{(i)}) \]
(93)

and
\[ t_{\mu}^{(i)} = \left( \frac{\partial^2 L_{\mu}}{\partial \xi \partial (\mathbf{R}_{\xi})_{\mu}} \right)_{\text{HF}} (\mathbf{R}_{\xi})_{\mu} \]
\[ = \langle \zeta \mathbf{I} H^{(i)} \rangle_{\text{HF}} + \langle \mathbf{P}_{\beta}^{(i)} H^{(i)} \rangle_{\text{HF}} \]
\[ \mu \geq 0 \]
(94)

where repeated indices implies summation. For contributions to \( G_{\alpha\beta} \) involving \( H_{\alpha\beta} \) we have, for terms involving \( t \) and \( \kappa \),
\[ t_{\mu}^{(i)} H_{\alpha\beta}^{(i)} t_{\nu}^{(i)} \]
\[ = \left( \frac{\partial^2 L_{\mu}}{\partial \xi \partial (\mathbf{R}_{\xi})_{\mu}} \right)_{\text{HF}} (\mathbf{R}_{\xi})_{\mu} \]
\[ = \langle \zeta \mathbf{I} H^{(i)} \rangle_{\text{HF}} + \langle \mathbf{P}_{\beta}^{(i)} H^{(i)} \rangle_{\text{HF}} \]
(95)

Next, we have terms involving right state and the cluster amplitudes and orbital rotations, i.e.,
\[ t_{\mu}^{(i)} H_{\alpha\beta}^{(i)} \mathbf{R}_{\xi}^{(i)} \]
\[ = \left( \frac{\partial^2 L_{\mu}}{\partial \xi \partial (\mathbf{R}_{\xi})_{\mu}} \right)_{\text{HF}} (\mathbf{R}_{\xi})_{\mu} \]
\[ = \langle \zeta \mathbf{I} H^{(i)} \rangle_{\text{HF}} + \langle \mathbf{P}_{\beta}^{(i)} H^{(i)} \rangle_{\text{HF}} \]
\[ \mu \geq 0 \]
(96)

Finally, we have the partial derivative of the Lagrangian, which can be written as
\[ L_{\alpha\beta}^{(i)} = - \sum_{\mu} \langle \mathbf{L}_{\alpha} \mathbf{P}_{\mu}^{(i)} \rangle^{(i)} \]
\[ + \langle \mathbf{I} H^{(i)} \rangle_{\text{HF}} \]
\[ + \langle \mathbf{P}_{\beta}^{(i)} H^{(i)} \rangle_{\text{HF}} \]
(97)

Written in compact notation, the scalar coupling is
\[ G_{\alpha\beta}^{(i)} = \langle \mathbf{L}_{\alpha} \rangle_{\text{HF}}^{(i)} + \langle \zeta \mathbf{I} H^{(i)} \rangle_{\text{HF}} + \langle \mathbf{P}_{\beta}^{(i)} H^{(i)} \rangle_{\text{HF}} \]
(98)

where we have let
\[ K_{\alpha\beta}^{(i)} = f^{(i)} + 2[f^{(i)}, T^{(i)}] + [\{H^{(i)}, T^{(i)}\}, T^{(i)}] \]
\[ f^{(i)} = H^{(i)} + [\{H^{(i)}, H\}, T^{(i)}] \]
\[ T^{(i)} = 2[H^{(i)}] + [\{H^{(i)}, H\}, T^{(i)}] \]
\[ \{L^{(i)}\}_{\text{HF}} = \langle \mathbf{L}_{\alpha} \rangle_{\text{HF}}^{(i)} \]
\[ f^{(i)} = H^{(i)} + 2[H^{(i)}, H^{(i)}] + [\{H^{(i)}, H\}, T^{(i)}] \]
\[ f^{(i)} = H^{(i)} + 2[H^{(i)}, H^{(i)}] + [\{H^{(i)}, H\}, T^{(i)}] \]
(99)

as well as
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

\[
\mathcal{L}_{mn} = O_{mn} + \gamma^T E_{mn} = O_{mn} + \mathbf{k}^T f + \xi^T \Omega + \beta^T (\mathbf{H} - E_n) \mathcal{R}_n + \tilde{E}_m (1 - \langle \mathcal{L}_m^0 | \mathcal{R}_m^0 \rangle) \tag{109}
\]

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

\[
0 = (1 + \tilde{E}_m - E_m \beta^T \mathcal{R}_n) \mathcal{L}_m^T + \beta^T (\mathbf{H} - E_n) \tag{110}
\]

Here, we again select \( \tilde{E}_m \) to make the first term vanish, giving

\[
\beta^T_n = \mathcal{L}_m^T \tag{111}
\]

Other than this change, the derivation of the scalar coupling is virtually unchanged. Terms involving differentiation of \( O_{mn} \) has the left state \( \mathcal{L}_m^0 \) in the bracket instead of \( \langle \mathcal{L}_m^0 | \mathcal{R}_m^0 \rangle \). In particular, the expression in eq 102 is valid with \( m = n \).

Unlike for the vector coupling, there is no convenient relationship between \( \mathcal{G}_m^{0} \) and \( \mathcal{G}_m^{0} \). To derive the latter quantity, we may consider the Lagrangian

\[
\mathcal{L}_{mn} = O_{mn} + \gamma^T E_{mn} = O_{mn} + \mathbf{k}^T f + \xi^T \Omega + \mathcal{L}_m^T (\mathbf{H} - E_n) \mathcal{R}_n + \tilde{E}_m (1 - \langle \mathcal{L}_m^0 | \mathcal{R}_m^0 \rangle) \tag{109}
\]

where

\[
O_{mn} = \langle \mathcal{L}_m^0 | \exp(-T) \exp(x) | \mathcal{R}_m^0 \rangle \tag{113}
\]

\[
E_m = \mathcal{L}_m^T \mathbf{H} \mathcal{R}_m^0 \tag{114}
\]

The \( \mathcal{L}_m \) stationarity then gives

\[
0 = \mathcal{R}_n + (\mathbf{H} - E_m) \beta_m + (E_m - E_n \mathcal{L}_m^T \beta_m) \mathcal{R}_n \tag{115}
\]

from which we again have \( \tilde{E}_m = E_m \mathcal{L}_m^T \beta_m \) and thus

\[
\beta_m = -(E_m - E_n)^{-1} \mathcal{R}_n \tag{116}
\]

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 \( k^{(i)} \). For the derivative of \( \mathcal{L}_{mn} \), we must solve the equation

\[
\frac{d}{dx} \left[ \mathcal{L}_m^T (\mathbf{H} - E_n) \right]_0 = 0 = \mathcal{L}_m^T \xi^{(i)T} + \mathcal{L}_m^{(i)T} (\mathbf{H} - E_n) \tag{117}
\]

which is analogous to eq 90. In contributions involving \( \langle \beta^T_1 | \mathcal{R}_n \rangle \) in \( \mathcal{G}_{mn} \), we obtain similar expressions involving \( \langle \mathcal{L}_m^0 | \mathcal{R}_m^0 \rangle \) in the case of \( \mathcal{G}_m^{0} \). The end result is

\[
\mathcal{G}_m^{0} = \langle \mathcal{L}_m^0 | \mathcal{R}_n \rangle + \frac{\xi}{\xi} | \mathcal{K}^{(i)} | (CC) + \langle \mathcal{L}_m^0 | \mathcal{K}^{(i)} | \mathcal{R}_m^0 \rangle
\]

\[
+ \langle \text{HF} | \hat{r}_m^{(i)} | \text{HF} \rangle + \langle \mathcal{L}_m^0 | \mathcal{T}_m^{(i)} | - (L^{(i)T})_{nn} \mathcal{R}_m^0 \rangle \tag{118}
\]

with

\[
\langle \mathcal{L}_m^0 | \mathcal{R}_n \rangle = \langle \mathcal{L}_m^0 | (k^{(i)})^2 - 2T^{(i)2} | \mathcal{R}_n \rangle
\]

\[
+ 2 \langle \mathcal{L}_m^0 | k^{(i)} | \mathcal{R}_n \rangle + 2 \langle \mathcal{L}_m^0 | T^{(i)} | \mathcal{R}_n \rangle
\]

\[
- \sum_{pq} \langle \mathcal{L}_m^0 | E_{pq} | \mathcal{R}_n \rangle (\phi_{pq}^T \phi_{pq}^T) \tag{119}
\]

Finally, \( \mathcal{G}_m^{0} \) is obtained in a manner similar to \( \mathcal{G}_m^{0} \) 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.\textsuperscript{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 Christiansen\textsuperscript{13} 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,\textsuperscript{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.\textsuperscript{12}

## 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 \( x \). 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 connection\textsuperscript{31} to describe the orbital basis at neighboring geometries. Our presentation follows closely that given by of Olsen et al.\textsuperscript{31} Using the natural
connection for nonadiabatic coupling elements was also discussed by Christiansen.\textsuperscript{13}

To evaluate derivatives at \( x_0 \) we relate the basis at \( x_0 \) to some basis at \( x = x_0 + \Delta x \). Suppose the molecular orbitals (MOs) at \( x_0 \) are

\[
\phi_i(x) = \sum_\alpha C_{\alpha}^{\prime}(x_0) \chi_{\alpha}(x)
\]

where \( C_{\alpha}^{\prime}(x_0) \) are orbital coefficients and \( \chi_{\alpha}(x) \) are atomic orbitals. The unmodified MOs (UMOs) are defined by freezing the orbital coefficients

\[
\phi_i^m(x) = \sum_\alpha C_{\alpha}^{\prime}(x_0) \chi_{\alpha}(x)
\]

The UMOs are not orthonormal, however

\[
S_{\mu \nu}(x) = \langle \phi_{\mu}^{m}(x) | \phi_{\nu}^{m}(x) \rangle, \quad S_{\mu \nu}(x_0) = \delta_{\mu \nu}
\]

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

\[
\phi_i(x) = \sum_\alpha \phi_i^m(x) T_{\alpha \alpha}(x)
\]

where the connection matrix \( T(x) \) satisfies \( T(x_0) = I \) and \( T(x)S(x)T(x) = I \).

In the natural connection, \( T \) is chosen to be

\[
T(x) = W(x)^{-1}W(x)S(x)W(x)^{1/2} = W(x)^{-1} \Delta(x)
\]

Let us now relate the orbital space at \( x \) to the one at \( x_0 \). In order to do so, we consider a complete orbital basis (denoted by indices \( pq... \)) partitioned into the OMO basis (\( mn... \)) and the orthogonal complement orbitals or OCOs (\( uv... \)). For complete bases, we can write

\[
\phi_i(x) = \sum_q \phi_q^m(x) U_{qp}(x), \quad U_{qp}(x) = \langle \phi_q^m(x_0) | \phi_p^m(x) \rangle
\]

Occupation number states at \( x \) can thus be expressed as

\[
|\Omega(x)\rangle = U(x)|\Omega(x_0)\rangle
\]

with

\[
U(x) = \exp(-b(x)), \quad b(x) = \sum_{pq} b_{pq}^0 a_{pq}^0(x_0) a_{pq}(x_0)
\]

where \( b(x) \) is the anti-Hermitian operator with \( b_{pq}^0(x) \) defined such that \( U(x) = \exp(-b(x)) \). The many-body operators can be expanded as

\[
a_{pq}^i(x) = \sum_q a_{pq}^i(x_0) U_{qp}(x)
\]

To evaluate derivatives with respect to some specific component (denoted \( x \)), we consider the Taylor expansion of a displacement in this direction, \( x = x_0 + \Delta x \), which can be expressed as

\[
a_{pq}^i(x) = a_{pq}^i(x_0) + a_{pq}^i(x_0) \Delta x + \frac{1}{2} a_{pq}^i(x_0) (\Delta x)^2 + ...
\]

\[
b(x) = b(x_0) + b(x_0) \Delta x + \frac{1}{2} b(x_0) (\Delta x)^2 + ...
\]

where \( b(x) = b_{pq}^0 a_{pq}^0(x_0) a_{pq}(x_0) \). Here, we have let \( a_{pq}^i(x_0) \equiv a_{pq}^i(x_0) \) and suppressed the \( x_0 \)-dependence of the derivatives. It is useful to split operator contributions in the OMO (\( \parallel \)) and OCO (\( \perp \)) blocks

\[
a_{pq}^i(x) = \sum_m a_{pq}^m(x_0) U_{mp}(x) + \sum_m a_{pq}^m(x_0) U_{qm}(x)
\]

\[
= a_{pq}^m(x_0) + a_{pq}^m(x_0)
\]

Now, we can evaluate the first derivative contribution

\[
f_{ij} = \langle \Phi_j(x_0) | \frac{\partial}{\partial x} \Phi_i(x_0) \rangle = -\langle \Phi_j(x_0) | b(x_0) \Phi_i(x_0) \rangle
\]

To simplify further, we note that \( U_{mm} = \Delta_{mm} \) is Hermitian in the natural connection. Since the \( U_{mm} \) block can similarly be chosen to be Hermitian, we have\textsuperscript{31}

\[
b_{mm} = b_{mm} = 0 \Rightarrow \hat{b}_{mm}^{(k)} = b_{mm}^{(k)} = 0
\]

and so

\[
f_{ij} = -\sum_{mm} b_{mm}^{(1)}(x_0) a_{mn}^m \Phi_j(x_0) = 0
\]

In general, \( f_{ij} \) is non-zero with connections other than the natural connection.

Next, we evaluate the second derivative contribution

\[
g_{ij} = \left\langle \Phi_j(x_0) \left| \frac{\partial^2}{\partial x^2} \Phi_i(x_0) \right| \right\rangle = \left\langle \Phi_j(x_0) \left| \frac{\partial^2}{\partial x^2} \Phi_i(x_0) \right| \right\rangle
\]

which can be written as

\[
g_{ij} = \langle \Phi_j(x_0) | b^{(2)} + b^{(1)} b^{(1)} \Phi_i(x_0) \rangle
\]

In the final equality, we have used eq\textsuperscript{135}. Now, notice that since

\[
\hat{b}_{mm}^{(1)} = \sum_{m} \hat{b}_{mm}^{(1)} a_{mn}^m + \sum_{m} \hat{b}_{mm}^{(1)} a_{nm}^m a_{nm}^m
\]

the only non-zero \( \hat{b}_{mm}^{(2)} \) contribution is the one that first creates an electron in the complementary space and then destroys it. Thus...
The commutator can be expressed as

\[
[\alpha^{(1)}_{n\downarrow}, \alpha_{n\uparrow}^{(1)}]^\dagger = \sum_u U_{um}^\dagger U_{mu}^{(1)} [\alpha_{u\downarrow}, \alpha_{u\uparrow}^{(1)}] = \sum_u U_{um}^\dagger U_{mu}^{(1)}
\]

The formulas for \( f \) and \( g \) 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

\[
|\psi(x)\rangle = \sum_i c_{i\downarrow}(x) |\Phi_i(x)\rangle
\]

Since \( c_{i\downarrow} \) depends implicitly on \( x \), we have \( \partial c_{i\downarrow}/\partial x = 0 \). Thus

\[
f_{i\downarrow} = \left\langle \psi(x) \left| \frac{\partial}{\partial x} \right| \psi(x) \right\rangle = \sum_i c_{i\downarrow}(x) \left\langle \Phi_i(x) \left| \frac{\partial}{\partial x} \right| \Phi_i(x) \right\rangle = \sum_i c_{i\downarrow}(x) f_{i\downarrow} \psi_{i\downarrow}(x) = 0
\]

and

\[
g_{i\downarrow} = \left\langle \psi(x) \left| \frac{\partial^2}{\partial x^2} \right| \psi(x) \right\rangle = \sum_i c_{i\downarrow}(x) g_{i\downarrow} \psi_{i\downarrow}(x)
\]

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

\[
H = \sum_{pq} h_{pq}(x) E_{pq}(x) + \frac{1}{2} \sum_{pqrs} g_{pqrs}(x) c_{pqrs}(x)
\]

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

\[
\langle \Phi_i(x) | H | \Phi_j(x) \rangle = \langle \Phi_i(x) | U(x) \rangle U(x) | \Phi_j(x) \rangle
\]

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

\[
h_{pq}(x) = \sum_{mn} T_{mp}(x)^\dagger h_{mn}^u(x) T_{qn}(x)
\]

By differentiating \( TW = W^0 T^0 \) and \( I = T^0 ST \), we find that \( T^{(1)} = -W^{(1)} \). Consequently, the partial derivative of the Hamiltonian can be written as

\[
H^{(1)} = H_n^{(1)} - [W^{(1)}, H]
\]

where \( H_n^{(1)} \) is the derivative of the UMO Hamiltonian and

\[
\{W^{(1)}, H\} = \sum_{pq} j_{pq} E_{pq} + \frac{1}{2} \sum_{pqrs} j_{pqrs} g_{pqrs}
\]

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

\[
W^{(1)}_{pq} = \left. \frac{\partial W_{pq}}{\partial x} \right|_0 = \sum_{pqrs} C_{pq}(x_0) C_{pq}(x_0) \int_{x_0}^{x} \frac{\partial \psi_{pq}}{\partial x} \mid_{x_0} dx
\]

is analogous to \( S^{(1)}_{pq} = \partial S_{pq}/\partial x_0 \) 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.

### Appendix B

#### Lagrangian Derivatives

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

\[
\mathcal{L}(\lambda, x, \gamma) = O(\lambda, x) + \gamma^2 E(\lambda, x)
\]

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

\[
\frac{\partial \mathcal{L}}{\partial \lambda_k} = 0, \quad \frac{\partial \mathcal{L}}{\partial \kappa} = 0
\]

Using Einstein notation, we can write the Taylor expansion of \( \mathcal{L} \) about some \( x_0 \) as
where we have ignored terms of order 3 or higher in $\Delta x$. 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.

$$\left. \frac{dL}{dx_i} \right|_0 = \left. \frac{\partial L}{\partial x_i} \right|_0$$

(158)

This is due to the stationarity conditions since they ensure that there are no linear terms in $\Delta x$ and $\Delta \gamma$ 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 $x$. We let

$$a^{(i)} = \frac{\partial a}{\partial x_i}$$

(159)

$$a^{(ij)} = \frac{\partial^2 a}{\partial x_i \partial x_j}$$

(160)

Then, we can write

$$\left. \frac{dL}{dx_i} \right|_0 = \left. \frac{\partial L}{\partial x_i} \right|_0$$

(161)

and

$$\left. \frac{d^2L}{dx_i dx_j} \right|_0 = \left. \left( \frac{\partial L}{\partial x_i} \right)^2 \right|_0 + \left. \frac{\partial L}{\partial x_i} \frac{\partial^2 L}{\partial x_i \partial x_j} \right|_0 + \left. \frac{\partial^2 L}{\partial x_i \partial x_j} \right|_0$$

(162)

Now

$$\gamma^{(i)} \left. \frac{\partial^2 L}{\partial x_i \partial \gamma} \right|_0 + \lambda^{(i)} \left. \frac{\partial^2 L}{\partial x_i \partial \lambda} \right|_0 = \left. \frac{\partial L}{dx_i} \right|_0 = 0$$

(163)

by stationarity, so that

$$\frac{d^2L}{dx_i dx_j} = \left. L^{(i)} + \lambda^{(i)} \frac{\partial^2 L}{\partial \lambda} \right|_0 + \left. \frac{\partial^2 L}{\partial x_i \partial x_j} \right|_0$$

(164)

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

$$f_k = \left. \frac{\partial L}{\partial \lambda_i} \right|_0, \quad H_{ij} = \left. \frac{\partial^2 L}{\partial \lambda_i \partial \lambda_j} \right|_0$$

(165)

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

$$\frac{d^2L}{dx_i dx_j} = \left. L^{(i)} + \lambda^{(i)} H_{ij} \lambda^{(j)} + \lambda^{(i)} f_k + \lambda^{(i)} f^{(i)}_k \right|_0$$

(166)

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