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ABSTRACT

Within the context of fewest-switch surface hopping (FSSH) dynamics, one often wishes to remove the angular component of the derivative coupling between states $|J\rangle$ and $|K\rangle$. In a previous set of papers, Shu *et al.* [J. Phys. Chem. Lett. **11**, 1135–1140 (2020)] posited one approach for such a removal based on direct projection, while we isolated a second approach by constructing and differentiating a rotationally invariant basis. Unfortunately, neither approach was able to demonstrate a *one-electron operator* $\hat{O}$ whose matrix element $\langle J|\hat{O}|K\rangle$ was the angular component of the derivative coupling. Here, we show that a one-electron operator can, in fact, be constructed efficiently in a semi-local fashion. The present results yield physical insight into designing new surface hopping algorithms and are of immediate use for FSSH calculations.

I. INTRODUCTION: SURFACE HOPPING AND LINEAR/ANGULAR MOMENTUM CONSERVATION

Currently, surface hopping is the most popular mixed quantum–classical algorithm for propagating nonadiabatic dynamics,[1,2] offering a reasonable balance between speed and accuracy, while also roughly recovering the correct equilibrium density distribution.[3,4] The essence of the algorithm is to follow dynamics along adiabats, with occasional jumps between adiabats so as to account for electronic relaxation. Importantly, by propagating along adiabats, the algorithm automatically conserves the total energy. That being said, the standard fewest-switch surface hopping (FSSH) algorithm does not conserve linear momentum,[5] a failure that has been addressed before in the literature; angular momentum is also not conserved,[6–8] although this problem is much less well appreciated and discussed (except in the context of exact factorization approaches[9–11] or problems with a Coriolis force[12]).

Momentum conservation fails within FSSH because when a trajectory hops between electronic states, the fundamental ansatz of surface hopping is that the momentum rescaling (between states $|J\rangle$ and $|K\rangle$) should occur along the derivative coupling direction $\boldsymbol{d}_{JK}$ between these two states,

$$d_{JK}^{A\alpha} = \left\langle J \middle| \frac{\partial}{\partial X_{A\alpha}} \middle| K \right\rangle. \tag{1}$$

Here and below, we use A, B, C to index nuclei; I, J, K to index adiabatic electronic states; and α, β, γ to index an x, y, z Cartesian direction. [Although not present in Eq. (1), it should also be noted that three dimensional vectors are written in a **bold** font; $\mu, \nu, \lambda, \sigma$ index atomic orbitals $|\chi_\mu\rangle, |\chi_\nu\rangle, |\chi_\lambda\rangle, |\chi_\sigma\rangle$, respectively.] Now, the nature of the derivative couplings as a function of translation and rotation has been studied in the past.[5] In short, when dealing with the standard electronic Hamiltonian (i.e., without spin-orbital coupling), the usual phase conventions[13] are that the nuclei and electrons are translated together (so that the total wave function is real valued). Mathematically, this means that we choose the phase of state $|K\rangle$ to follow

$$\left(\hat{\boldsymbol{P}}_e + \hat{\boldsymbol{P}}_N\right)|K\rangle = 0, \tag{2}$$

$$\left(\hat{\boldsymbol{L}}_e + \hat{\boldsymbol{L}}_N\right)|K\rangle = 0, \tag{3}$$

where $\hat{\boldsymbol{P}}_e$ and $\hat{\boldsymbol{P}}_N$ are electronic and nuclear linear momentum operators, respectively; $\hat{\boldsymbol{L}}_e$ and $\hat{\boldsymbol{L}}_N$ are electronic and nuclear angular momentum operators, respectively. If one operates by $\langle J|$, we can then automatically find that

$$\langle J|\hat{\boldsymbol{P}}_e|K\rangle + \langle J|\hat{\boldsymbol{P}}_N|K\rangle = 0, \tag{4}$$

$$\langle J|\hat{\boldsymbol{L}}_e|K\rangle + \langle J|\hat{\boldsymbol{L}}_N|K\rangle = 0. \tag{5}$$

These expressions can also be written as

$$\langle J|\hat{\boldsymbol{P}}_e|K\rangle + \frac{\hbar}{i}\sum_A \left\langle J\left|\frac{\partial}{\partial \boldsymbol{X}_A}\right|K\right\rangle = \langle J|\hat{\boldsymbol{P}}_e|K\rangle + \frac{\hbar}{i}\sum_A \boldsymbol{d}^A_{JK} = 0, \tag{6}$$

$$\begin{aligned}\langle J|\hat{\boldsymbol{L}}_e|K\rangle &+ \frac{\hbar}{i}\sum_A \boldsymbol{X}_A \times \left\langle J\left|\frac{\partial}{\partial \boldsymbol{X}_A}\right|K\right\rangle \\ &= \langle J|\hat{\boldsymbol{L}}_e|K\rangle + \frac{\hbar}{i}\sum_A \boldsymbol{X}_A \times \boldsymbol{d}^A_{JK} = 0,\end{aligned} \tag{7}$$

where "×" represents the cross product. Thus, at the end of the day, rescaling the classical nuclear momentum by $\boldsymbol{d}$,

$$\boldsymbol{P}^A_{\text{final}} = \boldsymbol{P}^A_{\text{initial}} + \alpha \boldsymbol{d}^A, \tag{8}$$

must lead to a violation of linear conservation insofar as

$$\sum_A \boldsymbol{P}^A_{\text{final}} = \sum_A \boldsymbol{P}^A_{\text{initial}} + \frac{\alpha\langle J|\hat{\boldsymbol{P}}_e|K\rangle}{i\hbar} \neq \sum_A \boldsymbol{P}^A_{\text{initial}}. \tag{9}$$

At bottom, nuclear displacement drags the electrons (which yield a small change in the total momentum). Similar statements also hold for angular momentum.

For linear and angular momentum conservation, the most natural approach is to modify the rescaling direction by

$$\boldsymbol{P}^A_{\text{final}} = \boldsymbol{P}^A_{\text{initial}} + \alpha(\boldsymbol{d}^A - \boldsymbol{\Gamma}^A), \tag{10}$$

where $\boldsymbol{\Gamma}$ satisfies

$$\sum_A \boldsymbol{\Gamma}^A_{JK} = \frac{\boldsymbol{p}_{JK}}{i\hbar}, \tag{11}$$

$$\sum_A \boldsymbol{X}_A \times \boldsymbol{\Gamma}^A_{JK} = \frac{\boldsymbol{l}_{JK}}{i\hbar}. \tag{12}$$

Here, $\boldsymbol{p}_{JK}$ and $\boldsymbol{l}_{JK}$ are the electronic linear and angular momentum matrix elements between states $|J\rangle$ and $|K\rangle$, respectively. In practice, one often decomposes

$$\boldsymbol{\Gamma} = \boldsymbol{\Gamma}' + \boldsymbol{\Gamma}'',$$

where $\boldsymbol{\Gamma}'$ is the electron translation factor (ETF) and $\boldsymbol{\Gamma}''$ is the electron rotation factor (ERF).

Now, as written above, the $\boldsymbol{\Gamma}'$ and $\boldsymbol{\Gamma}''$ tensors are matrices in a vector space composed of many-body electronic wave functions, $|J\rangle, |K\rangle$, i.e., $\boldsymbol{\Gamma} = \boldsymbol{\Gamma}_{JK}$. In practice, working with such matrices is quite difficult, and it would be much better if one could fashion these matrices as one-electron operators (in an atomic orbital basis) instead. In other words, rather than constructing $\boldsymbol{\Gamma}'_{JK}$ and $\boldsymbol{\Gamma}''_{JK}$ above, it would be extremely convenient if we could define operators $\boldsymbol{\Gamma}'_{\mu\nu}$ and $\boldsymbol{\Gamma}''_{\mu\nu}$ and thereafter evaluate the following matrices:

$$\boldsymbol{\Gamma}'_{JK} = \sum_{\mu\nu} \boldsymbol{\Gamma}'_{\mu\nu} D^{JK}_{\nu\mu}, \tag{13}$$

$$\boldsymbol{\Gamma}''_{JK} = \sum_{\mu\nu} \boldsymbol{\Gamma}''_{\mu\nu} D^{JK}_{\nu\mu}. \tag{14}$$

Here, $D^{JK}_{\mu\nu}$ is the one-electron transition density matrix between states $|J\rangle$ and $|K\rangle$. Since $\boldsymbol{p}_{JK} = \sum_{\mu\nu} \boldsymbol{p}_{\mu\nu} D^{JK}_{\mu\nu}$ and $\boldsymbol{l}_{JK} = \sum_{\mu\nu} \boldsymbol{l}_{\mu\nu} D^{JK}_{\mu\nu}$, the simplest means to satisfy Eqs. (11) and (12) [given the definitions in Eqs. (13) and (14)] is to require

$$\boxed{\sum_A \boldsymbol{\Gamma}^A_{\mu\nu} = \sum_A (\boldsymbol{\Gamma}'^A_{\mu\nu} + \boldsymbol{\Gamma}''^A_{\mu\nu}) = \frac{\boldsymbol{p}_{\mu\nu}}{i\hbar}} \tag{15}$$

$$\boxed{\sum_A \boldsymbol{X}_A \times \boldsymbol{\Gamma}^A_{\mu\nu} = \sum_A \boldsymbol{X}_A \times (\boldsymbol{\Gamma}'^A_{\mu\nu} + \boldsymbol{\Gamma}''^A_{\mu\nu}) = \frac{\boldsymbol{l}_{\mu\nu}}{i\hbar}}. \tag{16}$$

With this background in mind, the goal of this work is to show how to construct such ETF ($\boldsymbol{\Gamma}'$) and ERF ($\boldsymbol{\Gamma}''$) operators. While the study of ETFs is well explored by now, the case of ERFs is quite unexplored, and we will identify it as a new target below. The end result of this work will be a compact expression [Eqs. (45)–(47) and (52)], which can easily be added to the rescaling direction in the future so as to maintain the linear and angular momentum of the nuclei during an FSSH calculation.

II. THEORY: ELECTRON TRANSLATION FACTORS (ETFS) AND ELECTRON ROTATION FACTORS (ERFS)

As stated above, the theory of ETFs is well flushed out in the literature, while the concept of ERFs is far less understood. In order to be as pedagogical as possible, we will now recapitulate the usual prescription for constructing ETFs (whereby one performs an electronic structure calculation in a translating frame) and then discuss how one might extend these ideas to construct ERFs (whereby one performs an electronic structure calculation in a rotating frame). More specifically, an outline of this section is as follows: in Sec. II A, we review the well-studied one-electron ETF term ($\boldsymbol{\Gamma}'$) [see Eq. (18) below]. In Sec. II B, we explore the consequences of Eqs. (15) and (16) (which are constraints on the total $\boldsymbol{\Gamma} = \boldsymbol{\Gamma}' + \boldsymbol{\Gamma}''$), and this exploration leads us to the relevant constraints on $\boldsymbol{\Gamma}''$ [see Eqs. (21) and (25) below]. While Sec. II B 1 reviews our initial approach[7] for constructing one version $\boldsymbol{\Gamma}''$ (which is found to be unstable), Sec. II B 2 offers a new and far more stable ansatz. In Sec. II C, we further investigate these new $\boldsymbol{\Gamma}''$ matrix elements and show that one can achieve size-consistency by demanding the locality of the ERF, which leads to the final expressions for $\boldsymbol{\Gamma}''$ shown in Eqs. (45)–(47). In Sec. II C 2, we briefly demonstrate that the expression we find for $\boldsymbol{\Gamma}''$ is not entirely *ad hoc* but rather can be derived from a general constrained minimization procedure (as show in Appendix C). Finally, the special case of the linear molecule is discussed in Sec. II D.

A. Translation: $\boldsymbol{\Gamma}'$

In the case of translation, the motivation behind ETFs is to perform electronic structure calculations in a translating basis, which leads to so-called ETFs (henceforward, labeled as $\boldsymbol{\Gamma}'$). As shown in several papers,[5,14–20] if one boosts all atomic orbitals by the velocity of their attached nucleus, e.g.,

$$\mu(\boldsymbol{x}) \to \mu(\boldsymbol{x}) \exp\left(i m_e \boldsymbol{v}_B \cdot \boldsymbol{x}/\hbar\right), \tag{17}$$

for orbital μ on atom B, one finds a correction to the derivative couplings of the form

$$\Gamma'^{A\alpha}_{\mu\nu} = \frac{1}{2i\hbar} p^{\alpha}_{\mu\nu}\left(\delta_{BA} + \delta_{CA}\right). \tag{18}$$

Here and below, μ indexes an orbital centered on atom B, ν indexes an orbital centered on atom C, and $p^{\alpha}_{\mu\nu}$ is the α component of the electronic momentum. Intuitively, the electronic momentum operator emerges because we must take into account the fact that any nuclear displacement moves the electrons as well [as highlighted in Eq. (6)].[21–23] It is easy to show from Eq. (18) that

$$\sum_A \boldsymbol{\Gamma}'^{A}_{\mu\nu} = \frac{\boldsymbol{p}_{\mu\nu}}{i\hbar}. \tag{19}$$

As far as angular momentum is considered [i.e., Eq. (16)], Eq. (18) implies that

$$\sum_{A\beta\gamma} \epsilon_{\alpha\beta\gamma} X_{A\beta} \Gamma'^{A\gamma}_{\mu\nu} = \frac{1}{i\hbar} \sum_{\mu\nu} \sum_{\beta\gamma} \left\langle \mu \middle| \frac{1}{2} \epsilon_{\alpha\beta\gamma} \left(X_{B\beta} + X_{C\beta}\right) \hat{p}^{\gamma} \middle| \nu \right\rangle, \tag{20}$$

where we now have used the Levi–Cività symbol, $\epsilon_{\alpha\beta\gamma}$.

B. Rotation: $\boldsymbol{\Gamma}''$

Beyond translation, the much bigger question regards the proper means to restore angular momentum conservation with $\boldsymbol{\Gamma}''$. Given Eq. (19) and the fact that $\boldsymbol{\Gamma} = \boldsymbol{\Gamma}' + \boldsymbol{\Gamma}''$, Eq. (15) requires that $\boldsymbol{\Gamma}''$ must satisfy

$$\boxed{\sum_A \boldsymbol{\Gamma}''^{A}_{\mu\nu} = 0.} \tag{21}$$

Next, according to Eqs. (16) and (20), it follows that $\boldsymbol{\Gamma}''$ must satisfy

$$\sum_{A\beta\gamma} \epsilon_{\alpha\beta\gamma} X_{A\beta} \Gamma''^{A\gamma}_{\mu\nu} = \frac{1}{i\hbar} \left\langle \mu \middle| \frac{1}{2} \left(\hat{l}^{(B)}_{\alpha} + \hat{l}^{(C)}_{\alpha} \right) \middle| \nu \right\rangle. \tag{22}$$

Here, $\hat{l}^{(B)}_{\alpha}$ and $\hat{l}^{(C)}_{\alpha}$ are the α components of the electron angular momentum operators around atoms B and C, respectively,

$$\hat{\boldsymbol{l}}^{(B)} = \left(\hat{\boldsymbol{x}} - \boldsymbol{X}_B\right) \times \hat{\boldsymbol{p}}, \tag{23}$$

$$\hat{\boldsymbol{l}}^{(C)} = \left(\hat{\boldsymbol{x}} - \boldsymbol{X}_C\right) \times \hat{\boldsymbol{p}}. \tag{24}$$

In the compact vector form, Eq. (22) reads

$$\boxed{\sum_A \boldsymbol{X}_A \times \boldsymbol{\Gamma}''^{A}_{\mu\nu} = \frac{1}{i\hbar} \left\langle \mu \middle| \frac{1}{2} \left(\hat{\boldsymbol{l}}^{(B)} + \hat{\boldsymbol{l}}^{(C)} \right) \middle| \nu \right\rangle \equiv \boldsymbol{J}_{\mu\nu}.} \tag{25}$$

Here, we have defined an atom-centered electronic angular momentum $\boldsymbol{J}_{\mu\nu}$; we emphasize that $\boldsymbol{J}_{\mu\nu} \neq \frac{1}{i\hbar} \langle \mu | \hat{\boldsymbol{L}}_e | \nu \rangle$.

Now, in a recent paper,[7] we argued that because one cannot rotate individual basis functions on a single atom without involving other atoms in the course of a rigid rotation, one could not generate a strictly local *one-electron* ERF operator ($\boldsymbol{\Gamma}''^{A}_{\mu\nu}$) directly analogous to the ETF operator ($\boldsymbol{\Gamma}'^{A}_{\mu\nu}$) in Eq. (18). Here, we would define $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$ to be strictly local if $\boldsymbol{\Gamma}''^{A}_{\mu\nu} = 0$ when neither μ nor ν indexes an orbital centered on atom A. To that end, in Ref. 7, we constructed a *many-electron* strictly local ERF operator that rotates atomic orbitals during the course of a rigid rotation. Furthermore, it should be noted that any direct projection of a pre-computed derivative coupling (as in Ref. 6) can also be considered a many-electron operator in some sense. Unfortunately, a many-electron ERF is not desirable—not only because one loses physical meaning but also because one would like to use such an ERF to build a phase space Hamiltonian (see Ref. 24). To that end, in this paper, we will show below that if strict locality is relaxed in favor of semi-locality, we can, in fact, generate a one-electron ERF operator $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$.

1. Review of the approach in Ref. 7

As means of background, imagine a starting geometry $\boldsymbol{X}$ (which is a 3 by N matrix with each column representing the Cartesian coordinate of one atom) and a rotational transformation $\hat{\boldsymbol{R}}$, which rotates both the nuclei and the electrons at an angle $\boldsymbol{\theta}$ (which is a three-dimensional vector as it includes the axis of rotation as well as the magnitude). If one wishes to perform a calculation in the basis of rotating electronic atomic orbitals, the key quantity of interest is the angle at which all orbital shells of the electronic basis functions must be rotated. To that end, if we assume an infinitesimally small pure rotation, we can calculate[7] the angles $d\theta_\alpha$ from the change in nuclear coordinates,

$$d\boldsymbol{X} = \exp\left(-\frac{i}{\hbar} \sum_\alpha d\theta_\alpha \hat{L}^{\alpha}\right) \boldsymbol{X} - \boldsymbol{X} \tag{26}$$

$$\approx -\frac{i}{\hbar} \sum_\alpha d\theta_\alpha \hat{L}^{\alpha} \boldsymbol{X}. \tag{27}$$

Here, $\hat{L}$ is the angular momentum operator with matrix elements $\langle \beta | \hat{L}^{\alpha} | \gamma \rangle = i\hbar \epsilon_{\alpha\beta\gamma}$ in $\mathbb{R}^3$.

Now, in the vicinity of a given geometric configuration $\boldsymbol{X}$, one can always separate the geometries that are strict rotations of $\boldsymbol{X}$ from the geometries that involve moving interior coordinates. If, however, one seeks a general angle $\boldsymbol{\theta}(\boldsymbol{X})$, which is defined for geometries that are not strict rotations of the original configuration $\boldsymbol{X}$, the result is not unique. In Ref. 7, we found an approximate $\boldsymbol{\theta}$ by projecting the $3N$–dimensional problem onto a weighted three-dimensional problem, and the final result was

$$\frac{\partial \theta_\beta}{\partial X_{A\alpha}} = -\frac{1}{2} \sum_{\gamma\sigma} \epsilon_{\alpha\beta\gamma} \Lambda^{-1}_{\gamma\sigma} X_{A\sigma}, \tag{28}$$

where

$$\Lambda_{\alpha\beta} = \sum_B X_{B\alpha} X_{B\beta}. \tag{29}$$

Following the logic in Ref. 7, this finding would lead us to define a one-electron ERF term as

$$\Gamma''^{A\alpha}_{\mu\nu} = -\sum_{\beta} \frac{\partial \theta_\beta}{\partial X_{A\alpha}} J^{\beta}_{\mu\nu}, \tag{30}$$

$$= \frac{1}{2}\sum_{\beta\gamma\sigma} \epsilon_{\alpha\beta\gamma} J^{\beta}_{\mu\nu} \Lambda^{-1}_{\gamma\sigma} X_{A\sigma}. \tag{31}$$

For the definition of $\boldsymbol{\Gamma}''$ in Eq. (31), the constraint in Eq. (25) is automatically satisfied.

2. An improved approach

Unfortunately, the expression $\sum_\sigma \Lambda^{-1}_{\gamma\sigma} X_{A\sigma}$ in Eq. (31) is very unstable when the atoms are nearly co-planar. While the instability for a *linear* molecular might be expected (and be physically meaningful), the instability for a *planar* molecule suggests some defects in the expression. To address this problem here, we propose another way of solving Eq. (27). Note that there are 3 by N variables $(d\mathbf{X}_A)$ but only three angles (θ_α). Thus, a least-squares fit solution would appear to be a strong path forward. Let us define

$$\tilde{\mathbf{X}}^{\alpha} = -\frac{i}{\hbar}\hat{L}^{\alpha}\mathbf{X}, \tag{32}$$

and let us solve for $d\theta_\alpha$ by minimizing the squared norm,

$$\left| d\mathbf{X} - \sum_{\alpha} \tilde{\mathbf{X}}^{\alpha} d\theta_\alpha \right|^2. \tag{33}$$

The solution to this problem is

$$d\theta_\alpha = -\sum_{\beta} K^{-1}_{\alpha\beta} \sum_{A\gamma} \tilde{X}^{\beta}_{A\gamma} dX_{A\gamma}, \tag{34}$$

where

$$K_{\alpha\beta} = -\operatorname{Tr}\left(\tilde{\mathbf{X}}^{\alpha}\tilde{\mathbf{X}}^{\beta\top}\right). \tag{35}$$

In differential form, Eq. (34) reads

$$\frac{\partial \theta_\alpha}{\partial X_{A\gamma}} = -\sum_{\beta} K^{-1}_{\alpha\beta}\tilde{X}^{\beta}_{A\gamma}. \tag{36}$$

Since $L^{\alpha}_{\beta\gamma} = i\hbar\epsilon_{\alpha\beta\gamma}$, the results can then be further simplified as

$$K_{\alpha\beta} = -\sum_{A\gamma} X_{A\gamma}X_{A\gamma}\delta_{\alpha\beta} + \sum_{A} X_{A\alpha}X_{A\beta}, \tag{37}$$

$$\frac{\partial \theta_\alpha}{\partial X_{A\gamma}} = -\sum_{\sigma\beta} K^{-1}_{\alpha\beta}\epsilon_{\sigma\beta\gamma}X_{A\sigma}. \tag{38}$$

Substituting Eq. (38) into Eq. (30) and noting that $K_{\alpha\beta} = K_{\beta\alpha}$, we recover that

$$\Gamma''^{A\gamma}_{\mu\nu} = \sum_{\alpha\beta\sigma} \epsilon_{\gamma\sigma\beta} X_{A\sigma} K^{-1}_{\beta\alpha} J^{\alpha}_{\mu\nu}. \tag{39}$$

The matrix $\boldsymbol{K}$ in Eq. (37) is effectively the negative of a massless moment of inertia and can be written in a simple compact vector form,

$$\boldsymbol{K} = -\sum_{A} \left(\boldsymbol{X}_A^{\top}\boldsymbol{X}_A\right)\mathcal{I} + \sum_{A} \boldsymbol{X}_A\boldsymbol{X}_A^{\top}, \tag{40}$$

where $\boldsymbol{X}_A$ is a column vector representing the Cartesian coordinates of atom A and $\mathcal{I}$ is a 3 × 3 identity matrix. The tensor $\boldsymbol{\Gamma}''$ in Eq. (39) also has a simple compact form,

$$\boldsymbol{\Gamma}''^{A}_{\mu\nu} = \boldsymbol{X}_A \times \left(\boldsymbol{K}^{-1}\boldsymbol{J}_{\mu\nu}\right), \tag{41}$$

which clearly satisfies the constraint in Eq. (25).

C. Locality and size consistency

At this point, we have shown how to satisfy Eq. (25), but we have not addressed the constraint in Eq. (21). That being said, before we address such a constraint, we must first discuss the question of locality. In particular, the ansatz for $\boldsymbol{\Gamma}''$ in Eq. (41) is incredibly delocalized and not size-consistent. Physically, if we have two non-interacting subsystems separated far apart from each other, then if atom A resides on one subsystem, while orbitals χ_μ and χ_ν reside on the other subsystem, we will find that $\boldsymbol{\Gamma}''^{A}_{\mu\nu} \neq 0$, which is unphysical. To have any physical meaning, $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$ must be localized around the atoms where χ_μ, χ_ν are centered. To achieve a measure of locality, we can introduce a weighting factor $\zeta^{A}_{\mu\nu}$ such that

$$\boldsymbol{K} \to \boldsymbol{K}_{\mu\nu} = -\sum_{A} \zeta^{A}_{\mu\nu}\left(\boldsymbol{X}_A^{\top}\boldsymbol{X}_A\right)\mathcal{I} + \sum_{A} \zeta^{A}_{\mu\nu}\boldsymbol{X}_A\boldsymbol{X}_A^{\top}, \tag{42}$$

$$\boldsymbol{\Gamma}''^{A}_{\mu\nu} \to \zeta^{A}_{\mu\nu}\boldsymbol{X}_A \times \left(\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}\right), \tag{43}$$

where $\zeta^{A}_{\mu\nu}$ is maximized when χ_μ or χ_ν are centered on atom A and decays rapidly otherwise. Equations (42) and (43) are almost our desired equations for $\boldsymbol{\Gamma}''$, but we have not yet addressed the constraint in Eq. (21).

In order to satisfy the constraint in Eq. (21), we will need to recenter the position $\boldsymbol{X}_A$ by a quantity $\boldsymbol{X}^{0}_{\mu\nu}$ for each pair of orbitals, χ_μ and χ_ν. According to Eq. (21), we require

$$\sum_{A} \zeta^{A}_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right) = \mathbf{0}, \tag{44}$$

which gives

$$\boldsymbol{X}^{0}_{\mu\nu} = \sum_{A} \zeta^{A}_{\mu\nu}\boldsymbol{X}_A \Big/ \sum_{A} \zeta^{A}_{\mu\nu}. \tag{45}$$

Thus, at the end of the day, a reasonable choice for $\boldsymbol{K}_{\mu\nu}$ and $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$ is

$$\begin{aligned}\boldsymbol{K}_{\mu\nu} = &-\sum_{A} \zeta^{A}_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right)^{\top}\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right)\mathcal{I}\\ &+ \sum_{A} \zeta^{A}_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right)\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right)^{\top},\end{aligned} \tag{46}$$

$$\boldsymbol{\Gamma}''^{A}_{\mu\nu} = \zeta^{A}_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right) \times \left(\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}\right), \tag{47}$$

respectively. Equations (45)–(47) are our final equations for a semi-local one-electron ERF, from which one can verify that $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$ satisfies Eqs. (21) and (25),

$$\sum_{A} \boldsymbol{\Gamma}''^{A}_{\mu\nu} = \sum_{A} \zeta^{A}_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^{0}_{\mu\nu}\right) \times \left(\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}\right) = 0, \tag{48}$$

$$\sum_A \boldsymbol{X}_A \times \boldsymbol{\Gamma}''^A_{\mu\nu} = \sum_A \zeta^A_{\mu\nu} \boldsymbol{X}_A \times \left[\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right) \times \left(\boldsymbol{K}^{-1}_{\mu\nu} \boldsymbol{J}_{\mu\nu}\right)\right], \tag{49}$$

$$= \sum_A \zeta^A_{\mu\nu} \left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right) \times \left[\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right) \times \left(\boldsymbol{K}^{-1}_{\mu\nu} \boldsymbol{J}_{\mu\nu}\right)\right], \tag{50}$$

$$= \boldsymbol{J}_{\mu\nu}. \tag{51}$$

1. The choice of $\zeta^A_{\mu\nu}$

All that remains is to choose a function form for $\zeta^A_{\mu\nu}$ in Eqs. (45)–(47). Below, we investigate a semi-local function of the form

$$\zeta^A_{\mu\nu} = \exp\left(-w \frac{2|(\boldsymbol{X}_A - \boldsymbol{X}_B)|^2 |(\boldsymbol{X}_A - \boldsymbol{X}_C)|^2}{|(\boldsymbol{X}_A - \boldsymbol{X}_B)|^2 + |(\boldsymbol{X}_A - \boldsymbol{X}_C)|^2}\right), \tag{52}$$

where again, we assume that χ_μ is centered on atom B and χ_ν is centered on atom C. The parameter w controls the locality of the final ERF, and below, we will provide insight into how to best optimize and analyze such a function.

2. An alternative approach based on minimization

Interestingly, Eqs. (45)–(47) for $\boldsymbol{\Gamma}''^A_{\mu\nu}$ can be derived from a totally different principle in a more direct fashion. The idea is to compute the minimal $\boldsymbol{\Gamma}''^A_{\mu\nu}$ that are consistent with the constraints in Eqs. (21) and (25). The corresponding Lagrangian is

$$\mathcal{L} = \sum_{A\mu\nu} \frac{1}{\zeta^A_{\mu\nu}} \boldsymbol{\Gamma}''^{A\top}_{\mu\nu} \boldsymbol{\Gamma}''^A_{\mu\nu} - \sum_{\mu\nu} \boldsymbol{\lambda}^\top_{1\mu\nu} \left(\sum_A \boldsymbol{\Gamma}''^A_{\mu\nu}\right) - \sum_{\mu\nu} \boldsymbol{\lambda}^\top_{2\mu\nu} \left(\sum_A \boldsymbol{X}_A \times \boldsymbol{\Gamma}''^A_{\mu\nu} - \boldsymbol{J}_{\mu\nu}\right). \tag{53}$$

Here, $\zeta^A_{\mu\nu}$ is the weighting factor. and the constraints controlled by $\lambda_{1\mu\nu}$ and $\lambda_{2\mu\nu}$ are Eqs. (21) and (25), respectively. As shown in Appendix C, minimizing the Lagrangian in Eq. (53) is identical to Eqs. (45)–(47).

D. Case of linear molecule

Before providing numerical results, one special case must be addressed, for which Eq. (47) needs to be revised, namely, the case of a linear molecule. In such a case, a rotation around the molecular axis is redundant, which leads to troubles for the form that the ERF is calculated in Eq. (47). Specifically, $\boldsymbol{K}_{\mu\nu}$ is not invertible. We can address this issue by assuming that the ERF term should recover $\boldsymbol{J}_{\mu\nu}$ only in the directions perpendicular to the molecular axis. After all, rotating the nuclei along the molecular axis does not change the electron angular momentum.

Mathematically, this assumption allows us to exclude the null space of $\boldsymbol{K}_{\mu\nu}$ when calculating $\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}$ in Eq. (47). Specifically, Let $\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3$ be the complete orthonormal basis of $\mathbb{R}^3$ and $\boldsymbol{u}_3$ is along the molecular axis. Since $\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}$ is parallel to $\boldsymbol{u}_3$, we may write

$$\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu} = x^A_{\mu\nu} \boldsymbol{u}_3 \tag{54}$$

and

$$\boldsymbol{K}_{\mu\nu} = -\sum_A \zeta^A_{\mu\nu} \left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)^\top \left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right) \mathcal{I} + \sum_A \zeta^A_{\mu\nu} \left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right) \left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)^\top \tag{55}$$

$$= -\sum_A \zeta^A_{\mu\nu} \left(x^A_{\mu\nu}\right)^2 \mathcal{I} + \sum_A \zeta^A_{\mu\nu} \left(x^A_{\mu\nu}\right)^2 \boldsymbol{u}_3 \boldsymbol{u}_3^\top \tag{56}$$

$$= -\sum_A \zeta^A_{\mu\nu} \left(x^A_{\mu\nu}\right)^2 \left(\mathcal{I} - \boldsymbol{u}_3 \boldsymbol{u}_3^\top\right). \tag{57}$$

Clearly, $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ are the two degenerate eigenvectors of $\boldsymbol{K}_{\mu\nu}$ with the eigenvalue $-\sum_A \zeta^A_{\mu\nu}\left(x^A_{\mu\nu}\right)^2$, while $\boldsymbol{u}_3$ has the corresponding eigenvalue of zero. Consequently, for a linear molecule, we simply replace $\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}$ in Eq. (47) with

$$\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu} \to -\left(\sum_A \zeta^A_{\mu\nu}\left(x^A_{\mu\nu}\right)^2\right)^{-1} \left(\mathcal{I} - \boldsymbol{u}_3 \boldsymbol{u}_3^\top\right) \boldsymbol{J}_{\mu\nu}. \tag{58}$$

In our developmental version of the Q-Chem electronic structure package,[25] we have implemented two different pieces of code: one which is for the polyatomic case and one for the linear case. Presumably, if an advanced solver with a generalized inversion routine were available that can solve $Ax = b$ for A not invertible, both the cases can be combined into one code.

III. NUMERICAL RESULTS AND DISCUSSION

The choice of w is critical for determining a meaningful ERF. On the one hand, w should not be too small; w controls the locality of the ERF term, and setting w to zero will lead to complete delocalization (which breaks size consistency). On the other hand, an arbitrarily large value is not desirable either as such a choice would force many molecular environments to appear as if they were diatomic (which we argued above is unstable and equivalent to enforcing strict locality). From a numerical perspective, an arbitrarily large w will force the $\boldsymbol{K}_{\mu\nu}$ matrix to become singular, causing numerical instability and a violation of the constraints in Eqs. (21) and (25).

To demonstrate this point, we have applied our algorithm to two systems, namely, the [5]helicene and methanol molecules

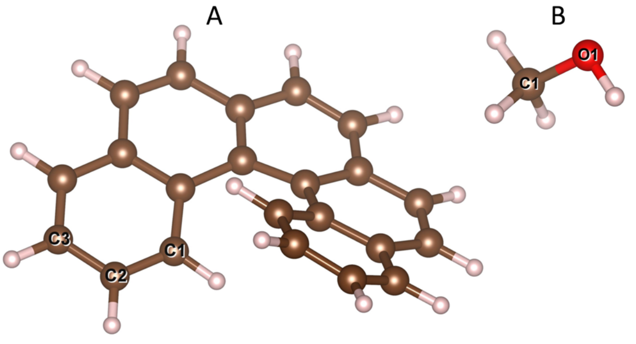

FIG. 1. Systems that the ERF term $\boldsymbol{\Gamma}''$ is calculated for: (a) [5]helicene. (b) methanol. The Cartesian coordinates are provided in Tables I and II in Appendix D.

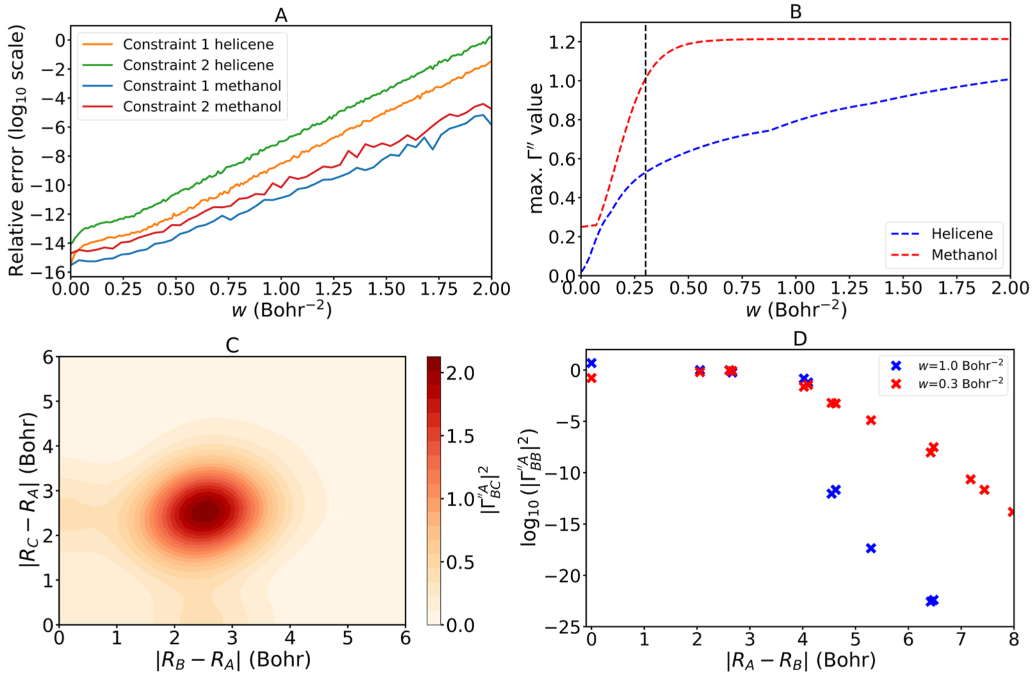

FIG. 2. Numerical stability and locality of $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$. (a) Errors in the constraint in Eq. (21) (marked as constraint 1) and Eq. (25) (marked as constraint 2) as a function of different w values. (b) Maximum value of $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$ (in atomic units) as a function of w. The dashed vertical line represents $w = 0.3$ bohr^{-2}. (c) Heat-map for $\left|\Gamma''^{A}_{BC}\right|^2$ as defined in Eq. (59) with atom A from Eq. (59) fixed as C2 in Fig. 1(a). A Gaussian broadening with $\sigma^2 = \frac{1}{2}$ bohr^2 is applied. (d) Decay of $\left|\Gamma''^{A}_{BB}\right|^2$ as a function of the distance between atom A and atom B.

(shown in Fig. 1). In Fig. 2(a), we plot the errors in the two constraints [Eqs. (21) and (25)] for different w values. We find that the error in the two constraints increases exponentially as w becomes larger, and the deviation to the constraint in Eq. (21) reaches 10^{-7} when w is greater than 1 bohr^{-2}. Next, in Fig. 2(b), we plot the maximum value of $\boldsymbol{\Gamma}''$ vs w. The maximum value of $\boldsymbol{\Gamma}''$ grows rapidly when w changes from 0 to ≈0.3 bohr^{-2} and then slows down. These two characteristics suggest that $w = 0.3$ bohr^{-2} is a safe choice, which balances both the locality and numerical stability. To provide further insights into the locality of the $\boldsymbol{\Gamma}''$ tensor, see Fig. 2(c). Here, we define a quantity

$$\left|\Gamma''^{A}_{BC}\right|^2 = \sum_{\substack{\mu \text{ on B}\\ \nu \text{ on C}}} \left|\boldsymbol{\Gamma}''^{A}_{\mu\nu}\right|^2 \tag{59}$$

and visualize $\boldsymbol{\Gamma}''$ in terms of the distances between atom A and atom B, C. More specifically, we plot a heat map that spans over all possible B, C pairs for [5]helicene with atom A fixed as C2 labeled in Fig. 1(a). The heat map plots $\boldsymbol{\Gamma}''$ calculated with $w = 0.3$ bohr^{-2}; a Gaussian broadening function (with $\sigma^2 = \frac{1}{2}$ bohr^2) is applied for smoothness. In Fig. 2(d), we plot $\left|\Gamma''^{A}_{BC}\right|^2$ with $B = C$ without the Gaussian broadening function, so as to provide the most precise view possible for the decay of $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$.

IV. DISCUSSION: INVARIANCE OF Γ UNDER TRANSLATION AND ROTATION

Before concluding this manuscript, a discussion of translational and rotational invariances is appropriate. Obviously, in order to apply an ETF or ERF in a meaningful fashion, the matrix elements $\boldsymbol{\Gamma}_{JK}$ should not depend on the origin or orientation of the molecule. Unfortunately, establishing such translational and, especially, rotational invariance is complicated by the fact that atomic orbitals come in shells and do not rotate with the molecular frame. For instance, a p_x atomic orbital in one orientation becomes a p_y atomic orbital when rotating the molecule at 90° along the z axis. Now, quite generally, in any quantum chemistry calculation, all calculations depend on the vector space of atomic orbitals (and not on the individual choice of basis functions), which explains why quantum chemical molecular energies are rotationally invariant. This fact can most easily be seen by noting that $h_{\mu\nu}$ transforms as a well-defined tensor operator, and the creation/annihilation operators $a^{\dagger}_{\mu}/a_{\nu}$ transform as vectors. Thus, the one-electronic Hamiltonian,

$$\sum_{\mu\nu} h_{\mu\nu} a^{\dagger}_{\mu} a_{\nu}, \tag{60}$$

is invariant to basis, i.e., we can mix one set of atomic orbitals into any other set of basis functions without changing the overall Hamiltonian. Now, obviously, if considering the operator

$$\sum_{\mu\nu} \boldsymbol{\Gamma}^{A}_{\mu\nu} a^{\dagger}_{\mu} a_{\nu}, \tag{61}$$

mixing basis functions on different atoms does not make much sense because the operator itself depends on a given atom A, but mixing basis functions on the same atom does not change the overall operator. Thus, it should be hoped that such a mixing does not affect any momentum-rescaling results. Indeed, Appendixes A and B present that the rescaling direction $\boldsymbol{\Gamma}_{JK}$ is indeed invariant to translations and rotations of the molecule.

V. CONCLUSIONS AND OUTLOOK

By working on a traveling and rotating basis, we have shown that one can derive physically motivated *one-electron* ETF ($\boldsymbol{\Gamma}'$) and ERF ($\boldsymbol{\Gamma}''$) operators so as to account for electronic motion. While the ETF in Eq. (18) is well-known, the key new equations of this paper are Eqs. (45)–(47). An alternative derivation of the ERF operator (as found by a constrained minimization) is offered in Appendix C as well. Perhaps not surprisingly, while the ETFs involve the electronic linear momentum operator, the ERFs involve the electronic angular momentum operator.

As discussed in Sec. II C, although $\boldsymbol{\Gamma}'^{A}_{\mu\nu}$ can be constructed in a strictly local fashion, the $\boldsymbol{\Gamma}''^{A}_{\mu\nu}$ tensor can be constructed only in a semi-local fashion. This difference is inevitable given the different nature of linear vs angular momentum, but indeed a reasonably semi-localized (not strictly localized) $\boldsymbol{\Gamma}''$ can be achieved by enforcing locality through the ζ weighting factor in Eq. (52). As a practical matter, the data in Fig. 2(b) suggest that $w = 0.3$ bohr^{-2} is a reasonable choice. Note that the one electron operator ERFs derived here should be applicable to just about any excited states, including the time-dependent density functional theory/time-dependent Hartree Fock (TD-DFT/TDHF) states, where the community has established how to interpret the relevant response functions (at least approximately) through the lens of wave functions.[26–29] Interestingly, by enforcing locality (or semi-locality)—which is meaningful as far as achieving size consistency—the matrix elements of the ERFs increase, such that for the molecules presented here, the ERFs between the different configuration interaction singles (CIS) excited states are roughly in the same order of magnitude as the corresponding ETFs (which contrasts with the results in Ref. 7).

Looking forward, it is important to note that the approach above can be easily extended to systems with spin degrees of freedom if we remember that electronic spin is an important form of angular momentum. In such a case, if we wish to conserve the total angular momentum, we need only define

$$J^{\alpha}_{\mu\nu} = \frac{1}{i\hbar}\left\langle \mu \middle| \frac{1}{2}\left(\hat{l}^{(B)}_{\alpha} + \hat{l}^{(C)}_{\alpha}\right) + \hat{s}_{\alpha} \middle| \nu \right\rangle \tag{62}$$

instead of Eq. (25), where we now work with a spin-atomic basis (instead of a spatial orbital basis) and allow for the ERFs to mix spin degrees of freedom.

Finally, in a companion paper,[24] we argue that the ERFs and ETFs proposed in the present paper should have a value far beyond the present context of momentum-rescaling in surface hopping. In particular, as shown in Ref. 8, one can argue that the standard (classical) Born–Oppenheimer dynamics (without a Berry force) ignore the electronic dynamics and, therefore, do not conserve the total angular or linear momentum in general. However, in such a context, Ref. 24 demonstrates that when the dynamics are run along a Hamiltonian parameterized by the nuclear position and momentum, $\hat{H}(\boldsymbol{X},\boldsymbol{P}) = \frac{\boldsymbol{P}^2}{2M} - i\hbar\frac{\boldsymbol{P}}{M}\cdot\boldsymbol{\Gamma} + \hat{H}_{\mathrm{el}}(\boldsymbol{X})$, the resulting dynamics *do* conserve the total linear and angular momentum. Thus, the present derivation of $\boldsymbol{\Gamma}$ may well be extremely important in the future for adiabatic propagation and not just for surface-hopping momentum rescaling. Moreover, Truhlar and co-workers have demonstrated that the Ehrenfest dynamics violate angular momentum conservation, and they have suggested removing the relevant term from the derivative coupling that appears in the Ehrenfest equation of motion. Thus, the present derivation of $\boldsymbol{\Gamma}$ should also be important in the future for non-adiabatic propagation more generally (although we would submit that a better remedy for the Ehrenfest dynamics is to include the non-Abelian Berry curvature[30]). Looking forward, our hope is that the present ERFs will be useful for modeling coupling nuclear–electronic–spin dynamics quite generally, potentially for modeling the chiral-induced spin selectivity (CISS) effect.[31]

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tian Qiu: Conceptualization (equal); Methodology (lead); Writing – original draft (lead); Writing – review & editing (equal). **Mansi Bhati**: Data curation (lead); Writing – review & editing (equal). **Zhen Tao**: Data curation (equal); Writing – review & editing (equal). **Xuezhi Bian**: Data curation (supporting); Writing – review & editing (equal). **Jonathan Rawlinson**: Writing – review & editing (equal). **Robert G. Littlejohn**: Writing – review & editing (equal). **Joseph E. Subotnik**: Conceptualization (equal); Funding acquisition (lead); Supervision (lead); Writing – original draft (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

APPENDIX A: TRANSLATIONAL INVARIANCE

As discussed in Sec. IV, one would like to be sure that within any surface-hopping algorithm, the momentum-rescaling direction does not depend on the orientation or origin of the chemical problem. To that end, let us demonstrate translational invariance here. To begin our discussion, let us emphasize that the one electron Hamiltonian is of course invariant to the translation of the molecule. This fact is clear when we recognize that, upon translation, the atomic orbitals translate with the molecule so that

$$h_{\mu\nu}(\boldsymbol{X} + \delta\boldsymbol{X}) = h_{\mu\nu}(\boldsymbol{X}), \tag{A1}$$

and, therefore, the density matrix between any two electronic states is also unchanged,

$$D^{JK}_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = D^{JK}_{\mu\nu}(\boldsymbol{X}). \tag{A2}$$

Hence, it follows that

$$\left.\left\langle J\middle|\sum_{\mu\nu} h_{\mu\nu}a^\dagger_\mu a_\nu\middle|K\right\rangle\right|_{\boldsymbol{X}_0} = \left.\left\langle J\middle|\sum_{\mu\nu} h_{\mu\nu}a^\dagger_\mu a_\nu\middle|K\right\rangle\right|_{\boldsymbol{X}_0+\delta X}. \tag{A3}$$

Next, consider rescaling the momentum along the proposed $\boldsymbol{\Gamma} = \boldsymbol{\Gamma}' + \boldsymbol{\Gamma}''$ direction, where the ETF is defined in Eq. (18) and the ERF is defined in Eqs. (45)–(47),

$$\left\langle J|\sum_{\mu\nu}\boldsymbol{\Gamma}^A_{\mu\nu}a^\dagger_\mu a_\nu\cdot\boldsymbol{P}|K\right\rangle. \tag{A4}$$

Note that under translation, the following rules hold:

1. $\boldsymbol{P}$ does not change direction.
2. $\boldsymbol{\Gamma}'$ is translational invariant ($\boldsymbol{\Gamma}'^A_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = \boldsymbol{\Gamma}'^A_{\mu\nu}(\boldsymbol{X})$) because $\boldsymbol{p}_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = \boldsymbol{p}_{\mu\nu}(\boldsymbol{X})$.
3. $\boldsymbol{K}_{\mu\nu}$ and $\boldsymbol{J}_{\mu\nu}$ are both invariants under translation, i.e., $\boldsymbol{K}_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = \boldsymbol{K}_{\mu\nu}(\boldsymbol{X})$ and $\boldsymbol{J}_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = \boldsymbol{J}_{\mu\nu}(\boldsymbol{X})$, so that $\boldsymbol{\Gamma}''^A_{\mu\nu}$ is also translationally invariant [$(\boldsymbol{\Gamma}''^A_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = \boldsymbol{\Gamma}''^A_{\mu\nu}(\boldsymbol{X}))$].

These rules prove that

$$\boxed{\boldsymbol{\Gamma}^A_{\mu\nu}(\boldsymbol{X}+\delta\boldsymbol{X}) = \boldsymbol{\Gamma}^A_{\mu\nu}(\boldsymbol{X}).} \tag{A5}$$

APPENDIX B: ROTATIONAL INVARIANCE

The final item that remains to be proven is rotational invariance. Proving rotational invariance is a bit more involved than for translation because, even though a Gaussian basis in a quantum chemistry code translates with the molecule, the basis does not rotate with the molecule. In other words, in practice, the orientation of a given atomic orbital does not depend on the orientation of the molecule. To that end, establishing notation will be essential. Let χ_μ be an atomic orbital centered on atom B with a definitive orientation, e.g., a p_x orbital. If the molecule translates to a new location, we will still index the same orbital by χ_μ (which would still be, e.g., a p_x orbital). Now, if the molecule rotates, let us denote the rotated atomic orbital by $\chi_{\bar{\mu}}, \chi_{\bar{\nu}}$. Let us represent a rotational transformation of $\boldsymbol{X}^A$ by a matrix $\boldsymbol{R}$, i.e.,

$$\boldsymbol{X}^A \to \boldsymbol{R}\boldsymbol{X}^A. \tag{B1}$$

To begin our discussion, consider the one-electron Hamiltonian, $h_{\mu\nu}$. These matrix elements are rotationally invariant,

$$h_{\bar{\mu}\bar{\nu}}(\boldsymbol{R}\boldsymbol{X}) = h_{\mu\nu}(\boldsymbol{X}), \tag{B2}$$

which forces the corresponding transition density matrix to also be invariant,

$$D^{JK}_{\bar{\mu}\bar{\nu}}(\boldsymbol{R}\boldsymbol{X}) = D^{JK}_{\mu\nu}(\boldsymbol{X}). \tag{B3}$$

Equation (B3) reflects the fact that states J and K rotate with the molecule, and the same electronic structure solutions must arise at any geometry in the presence of identical Hamiltonian matrix elements. Altogether, it then follows that

$$\left.\left\langle J\middle|\sum_{\mu\nu} h_{\bar{\mu}\bar{\nu}}a^\dagger_{\bar{\mu}} a_{\bar{\nu}}\middle|K\right\rangle\right|_{\boldsymbol{R}\boldsymbol{X}} = \left.\left\langle J\middle|\sum_{\mu\nu} h_{\mu\nu}a^\dagger_\mu a_\nu\middle|K\right\rangle\right|_{\boldsymbol{X}}. \tag{B4}$$

Next, let us consider the proposed one-electron ETF and ERF terms. We would like to show that these tensors lead to rotationally invariant directions in the sense that

$$\left.\left\langle J\middle|\sum_{\mu\nu} \boldsymbol{\Gamma}'^A_{\bar{\mu}\bar{\nu}}a^\dagger_{\bar{\mu}} a_{\bar{\nu}}\cdot\boldsymbol{R}\boldsymbol{P}\middle|K\right\rangle\right|_{\boldsymbol{R}\boldsymbol{X}} = \left.\left\langle J\middle|\sum_{\mu\nu} \boldsymbol{\Gamma}'^A_{\mu\nu}a^\dagger_\mu a_\nu\cdot\boldsymbol{P}\middle|K\right\rangle\right|_{\boldsymbol{X}}, \tag{B5}$$

$$\left.\left\langle J\middle|\sum_{\mu\nu} \boldsymbol{\Gamma}''^A_{\bar{\mu}\bar{\nu}}a^\dagger_{\bar{\mu}} a_{\bar{\nu}}\cdot\boldsymbol{R}\boldsymbol{P}\middle|K\right\rangle\right|_{\boldsymbol{R}\boldsymbol{X}} = \left.\left\langle J\middle|\sum_{\mu\nu} \boldsymbol{\Gamma}''^A_{\mu\nu}a^\dagger_\mu a_\nu\cdot\boldsymbol{P}\middle|K\right\rangle\right|_{\boldsymbol{X}}. \tag{B6}$$

To that end, note that if we rotate a molecule, it must be true that

$$\boldsymbol{P}^A \to \boldsymbol{R}\boldsymbol{P}^A, \tag{B7}$$

and it is also straightforward to show that

$$\boldsymbol{p}_{\bar{\mu}\bar{\nu}} = \boldsymbol{R}\boldsymbol{p}_{\mu\nu}, \tag{B8}$$

$$\boldsymbol{J}_{\bar{\mu}\bar{\nu}} = \boldsymbol{R}\boldsymbol{J}_{\mu\nu}. \tag{B9}$$

This equality is also proved explicitly in the Appendix of Ref. 24. At this point, Eq. (B5) follows from the definition in Eq. (18) and the rotational transformations in Eqs. (B3), (B7), and (B8).

Furthermore, from Eqs. (45) and (46), it follows that

$$\boldsymbol{X}^0_{\bar{\mu}\bar{\nu}} = \sum_A \zeta^A_{\mu\nu}\boldsymbol{R}\boldsymbol{X}_A \Big/ \sum_A \zeta^A_{\mu\nu}, \tag{B10}$$

$$= \boldsymbol{R}\boldsymbol{X}^0_{\mu\nu}, \tag{B11}$$

$$\boldsymbol{K}_{\bar{\mu}\bar{\nu}} = -\sum_A \zeta^A_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)^\top\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\mathcal{I} + \sum_A \zeta^A_{\mu\nu}\boldsymbol{R}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)^\top\boldsymbol{R}^\top \tag{B12}$$

$$= \boldsymbol{R}\boldsymbol{K}_{\mu\nu}\boldsymbol{R}^\top. \tag{B13}$$

Substituting the above-mentioned equations into Eq. (47), we find

$$\boldsymbol{\Gamma}''^A_{\bar{\mu}\bar{\nu}} = \zeta^A_{\mu\nu}\left(\boldsymbol{R}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\right)\times\left(\boldsymbol{R}\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{R}^\top\boldsymbol{R}\boldsymbol{J}_{\mu\nu}\right) \tag{B14}$$

$$= \zeta^A_{\mu\nu}\left(\boldsymbol{R}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\right)\times\left(\boldsymbol{R}\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}\right) \tag{B15}$$

$$= \zeta^A_{\mu\nu}\boldsymbol{R}\left(\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\times\left(\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}\right)\right) \tag{B16}$$

$$= \boldsymbol{R}\boldsymbol{\Gamma}''^A_{\mu\nu}. \tag{B17}$$

Therefore, in the end, we can prove Eq. (B6) using Eqs. (B3), (B7), and (B17). Indeed, the rescaling direction for the momentum will be the same (relative to the molecular frame) for any molecular orientation. Note that, according to Eqs. (18), (B8), and (B17),

$$\boxed{\boldsymbol{\Gamma}^A_{\bar{\mu}\bar{\nu}}(\boldsymbol{R}\boldsymbol{X}) = \boldsymbol{R}\boldsymbol{\Gamma}^A_{\mu\nu}(\boldsymbol{X}).} \tag{B18}$$

APPENDIX C: EQUIVALENCE OF A LAGRANGIAN APPROACH AND THE APPROACH BASED ON A ROTATING BASIS

Here, we will show that the results above in Eqs. (45)–(47) (which were found by calculating the derivative coupling in a rotating basis) can also be achieved by minimizing a constrained Lagrangian, whereby we seek the smallest ERFs that satisfy Eqs. (21) and (25). The relevant Lagrangian is of the form

$$\mathcal{L} = \sum_{A\mu\nu}\frac{1}{\zeta^A_{\mu\nu}}\boldsymbol{\Gamma}''^{A\top}_{\mu\nu}\boldsymbol{\Gamma}''^{A}_{\mu\nu} - \sum_{\mu\nu}\boldsymbol{\lambda}^\top_{1\mu\nu}\left(\sum_A \boldsymbol{\Gamma}''^A_{\mu\nu}\right) - \sum_{\mu\nu}\boldsymbol{\lambda}^\top_{2\mu\nu}\left(\sum_A \boldsymbol{X}_A\times\boldsymbol{\Gamma}''^A_{\mu\nu} - \boldsymbol{J}_{\mu\nu}\right). \tag{C1}$$

We will now show that the solution to this constrained problem is

$$\boldsymbol{X}^0_{\mu\nu} = \sum_A \zeta^A_{\mu\nu}\boldsymbol{X}_A \Big/ \sum_A \zeta^A_{\mu\nu}, \tag{C2}$$

$$\boldsymbol{K}_{\mu\nu} = -\sum_A \zeta^A_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)^\top\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\mathcal{I} + \sum_A \zeta^A_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)^\top, \tag{C3}$$

$$\boldsymbol{\Gamma}''^A_{\mu\nu} = \zeta^A_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\times\left(\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}\right). \tag{C4}$$

To begin our derivation, note that the gradient of $\mathcal{L}$ in Eq. (C1) w.r.t. $\boldsymbol{\Gamma}''^A_{\mu\nu}$ is zero, which reads

$$\frac{2}{\zeta^A_{\mu\nu}}\boldsymbol{\Gamma}''^A_{\mu\nu} - \boldsymbol{\lambda}_{1\mu\nu} - \boldsymbol{\lambda}_{2\mu\nu}\times\boldsymbol{X}_A = \boldsymbol{0}. \tag{C5}$$

For the simplicity of the notation, we may absorb factor 2 into the Lagrangian multipliers and neglect the μ, ν indices,

$$\boldsymbol{\Gamma}''^A = \zeta^A\boldsymbol{\lambda}_1 + \zeta^A\boldsymbol{\lambda}_2\times\boldsymbol{X}_A. \tag{C6}$$

From the first constraint,

$$\sum_A \boldsymbol{\Gamma}''^A = \boldsymbol{0}, \tag{C7}$$

we have

$$\boldsymbol{\lambda}_1 = -\boldsymbol{\lambda}_2\times\frac{\sum_A\zeta^A\boldsymbol{X}_A}{\sum_A\zeta^A} = -\boldsymbol{\lambda}_2\times\boldsymbol{X}^0, \tag{C8}$$

where $\boldsymbol{X}^0$ is defined in Eq. (C2). Then,

$$\boldsymbol{\Gamma}''^A = \zeta^A\boldsymbol{\lambda}_2\times\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right). \tag{C9}$$

Substituting the equation above with the second constraint,

$$\sum_A \boldsymbol{X}_A\times\boldsymbol{\Gamma}''^A = \boldsymbol{J}, \tag{C10}$$

we have

$$\sum_A \boldsymbol{X}_A\times\left(\zeta^A\boldsymbol{\lambda}_2\times\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right) = \boldsymbol{J}, \tag{C11}$$

and the double cross product is

$$\sum_A \boldsymbol{X}_A\times\left(\zeta^A\boldsymbol{\lambda}_2\times\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right) = \sum_A \zeta^A\boldsymbol{X}^\top_A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\boldsymbol{\lambda}_2 - \sum_A \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\boldsymbol{X}^\top_A\boldsymbol{\lambda}_2 \tag{C12}$$

$$= \left(\left(\sum_A \zeta^A\boldsymbol{X}^\top_A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right)\mathcal{I} - \sum_A \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\boldsymbol{X}^\top_A\right)\boldsymbol{\lambda}_2. \tag{C13}$$

Let

$$\boldsymbol{K} = -\left(\sum_A \zeta^A\boldsymbol{X}^\top_A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right)\mathcal{I} + \sum_A \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\boldsymbol{X}^\top_A. \tag{C14}$$

We compute

$$\lambda_2 = -\boldsymbol{K}^{-1}\boldsymbol{J} \tag{C15}$$

and, therefore,

$$\boldsymbol{\Gamma}''^A = \zeta^A(-\boldsymbol{K}^{-1}\boldsymbol{J})\times\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right) \tag{C16}$$

$$= \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\times(\boldsymbol{K}^{-1}\boldsymbol{J}). \tag{C17}$$

When recovering the μ, ν indices, we have found

$$\boldsymbol{\Gamma}''^A_{\mu\nu} = \zeta^A_{\mu\nu}\left(\boldsymbol{X}_A - \boldsymbol{X}^0_{\mu\nu}\right)\times(\boldsymbol{K}^{-1}_{\mu\nu}\boldsymbol{J}_{\mu\nu}). \tag{C18}$$

The only thing left is to show that $\boldsymbol{K}$ defined in Eq. (C14) is equivalent to Eq. (C3). Note that since

$$\sum_A \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right) = \boldsymbol{0}, \tag{C19}$$

we can add $\boldsymbol{X}^{0\top}\left(\sum_A\zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right)$ and $-\left(\sum_A\zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right)\boldsymbol{X}^{0\top}$ to the first and second terms of Eq. (C14), respectively, which yields

$$\boldsymbol{K} = -\left(\sum_A \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)^\top\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\right)\mathcal{I} + \sum_A \zeta^A\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)\left(\boldsymbol{X}_A - \boldsymbol{X}^0\right)^\top, \tag{C20}$$

which is exactly Eq. (C3). As a result, the solution to minimizing the Lagrangian in Eq. (C1) is equivalent to Eqs. (C2)–(C4).

APPENDIX D: GEOMETRIES FOR [5]HELICENE AND METHANOL

Table I shows Cartesian coordinates of [5]helicene in the unit of angstrom. Table II shows Cartesian coordinates of methanol in the unit of angstrom.

TABLE I. Cartesian coordinates of [5]helicene in the unit of angstrom.

C	1.169 858	1.521 282	−0.904 004
C	2.022 419	2.582 079	−1.139 007
C	3.350 247	2.551 820	−0.667 900
C	3.812 404	1.422 047	−0.027 389
C	2.968 889	0.303 892	0.186 737
C	1.588 966	0.370 167	−0.186 999
C	0.723 707	−0.781 432	0.054 863
C	1.367 883	−2.020 903	0.328 544
C	0.650 443	−3.244 646	0.207 739
C	−0.649 875	−3.244 715	−0.207 773
C	−1.367 520	−2.021 066	−0.328 413
C	−0.723 558	−0.781 522	−0.054 646
C	−1.588 946	0.369 996	0.187 169
C	−2.968 796	0.303 559	−0.187 008
C	−3.812 463	1.421 610	0.026 694
C	−3.350 702	2.551 392	0.667 510
C	−2.023 164	2.581 731	1.139 337
C	−1.170 460	1.520 877	0.904 963
H	−0.162 572	1.562 077	1.297 426
H	−1.666 948	3.440 348	1.702 121
H	−4.012 124	3.396 249	0.838 907
H	−4.849 376	1.355 036	−0.294 565
C	−3.509 600	−0.921 295	−0.687 867
C	−2.752 239	−2.052 082	−0.689 718
H	−3.185 559	−3.009 065	−0.970 220
H	−4.554 636	−0.948 962	−0.986 370
H	−1.176 808	−4.177 601	−0.391 862
H	1.177 529	−4.177 477	0.391 646
C	2.752 651	−2.051 731	0.689 672
C	3.509 962	−0.920 863	0.687 562
H	4.554 976	−0.948 444	0.986 120
H	3.186 120	−3.008 619	0.970 309
H	4.849 493	1.355 555	0.293 303
H	4.011 573	3.396 656	−0.839 828
H	0.161 740	1.562 284	−1.295 880
H	1.665 954	3.440 783	−1.701 508

TABLE II. Cartesian coordinates of methanol in the unit of angstrom.

C	−0.652 998	0.022 929	−0.000 032
O	0.736 526	−0.133 385	0.000 018
H	−0.980 477	0.560 041	−0.916 513
H	−0.980 097	0.564 936	0.913 717
H	−1.127 527	−0.979 878	0.002 897
H	1.113 883	0.784 406	−0.000 055

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