

Derivative Couplings with Built-In Electron-Translation Factors: Application to Benzene

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ABSTRACT: Derivative couplings are the essential quantities at the interface between electronic-structure calculations and nonadiabatic dynamics. Unfortunately, standard approaches for calculating these couplings usually neglect electronic motion, which can lead to spurious electronic transitions. Here we provide a general framework for correcting these anomalies by incorporating perturbative electron-translation factors (ETFs) into the atomic-orbital basis. For a range of representative organic molecules, we find that our ETF correction is often small but *can* be qualitatively important, especially for few-atom systems or highly symmetric molecules. Our method entails no additional computational cost, such that ETFs are “built-in,” and it is equivalent to a simple rule of thumb: We should set the antisymmetrized version of the nuclear overlap-matrix derivative to zero wherever it appears. Thus, we expect that built-in ETFs will be regularly incorporated into future studies of nonadiabatic dynamics.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory

H $\xrightarrow{V(t) = V}$
Estimated timescale for 2p-to-1s transition without ETFs is 686 fs.
With ETFs, there is no transition.

Derivative (nonadiabatic) couplings switch on transitions between the adiabatic states obtained from electronic-structure theory. They are crucial ingredients for treatments of nonadiabatic dynamics,¹ and they have been studied extensively in the context of multireference configuration-interaction theory (MR-CI)^{2–4} and time-dependent density-functional theory (TD-DFT).^{5–7}

In a recent article,⁸ we presented a self-contained treatment of the analytic-gradient theory for configuration-interaction singles (CIS) derivative couplings. While preparing ref 8, we became acquainted with a long-standing problem:^{9–12} Standard derivative couplings exhibit many anomalous properties; for example, they disrespect translational symmetry, such that constant-velocity motion of the entire system can nevertheless induce an electronic transition. To illustrate this fact, consider the familiar case of a molecular system initially described by an arbitrary electronic wave function, $|\Psi(0)\rangle$, and governed by electronic Hamiltonian H . This Hamiltonian gives rise to adiabatic states and potential energy surfaces, $\{|\Psi_j\rangle \equiv |\Psi_j(\mathbf{R})\rangle\}$ and $\{E_j \equiv E_j(\mathbf{R})\}$, that depend parametrically on the nuclear configuration, \mathbf{R} . If each nucleus, Q , follows a classical trajectory given by $\{\mathbf{R}_Q(t), \mathbf{P}_Q(t)\}$, as in surface-hopping approaches,^{1,13–16} the equations of motion for the wave function may be determined¹ by substituting its adiabatic expansion, $|\Psi(t)\rangle = \sum_j c_j(t) |\Psi_j\rangle$, into the time-dependent Schrödinger equation, $i\hbar(\partial/\partial t)|\Psi(t)\rangle = H|\Psi(t)\rangle$. We obtain

$$i\hbar\dot{c}_I = c_I E_I - i\hbar \sum_J c_J \sum_Q \mathbf{d}_{IJ}^{[Q]} \cdot \mathbf{v}_Q \quad (1)$$

where $\mathbf{v}_Q = \dot{\mathbf{R}}_Q$ is the nuclear velocity, and we have defined the Cartesian derivative coupling between states I and J due to the motion of Q

$$\mathbf{d}_{IJ}^{[Q]} \equiv \langle \Psi_I | \nabla_Q | \Psi_J \rangle \quad (2)$$

The form of eq 1 admits the following interpretation: At any moment in time, nuclear motion perturbs the electronic dynamics away from purely adiabatic evolution. Because the individual derivative-coupling terms can differ in sign, the size of this perturbation for a specific state pair is bounded from above by

$$\varepsilon_{IJ} = \hbar c_J \sum_Q \mathbf{d}_{IJ}^{[Q]} \cdot \mathbf{v}_Q \quad (3)$$

$$\lesssim \hbar \sum_Q d_{IJ}^{[Q]} v_Q |\cos \theta_Q| \quad (4)$$

with the magnitude of the derivative couplings given by $d_{IJ}^{[Q]} = (\mathbf{d}_{IJ}^{[Q]} \cdot \mathbf{d}_{IJ}^{[Q]})^{1/2}$. Suppose that the relative orientations of the couplings and nuclear momenta are random, such that we can replace $|\cos \theta_Q|$ with its average, $(2/\pi)$. Setting v_Q to the root-mean-square speed drawn from the Maxwell–Boltzmann distribution for a particle of mass m_Q , $v_Q^{\text{rms}} = (3kT/m_Q)^{1/2}$, yields the estimate

$$\varepsilon_{IJ} \lesssim \frac{2\hbar}{\pi} \sqrt{3kT} \sum_Q \tilde{d}_{IJ}^{[Q]} \quad (5)$$

where we define mass-weighted derivative couplings $\tilde{d}_{IJ}^{[Q]} \equiv (\mathbf{d}_{IJ}^{[Q]} / m_Q)^{1/2}$. We can now use the energy-time uncertainty relation, $\Delta E \Delta t \gtrsim \hbar$, to determine an instantaneous time scale for transitions between states I and J at room temperature ($T = 300$ K):

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$$\tau_{IJ} \gtrsim \frac{191 \text{ fs}}{\sum_Q (d_{IJ}^{[Q]}/a_0^{-1})(\sqrt{\text{amu}}/\sqrt{A_Q})} \quad (6)$$

where A_Q is the atomic mass. Transitions occur more frequently when couplings are large and the temperature is high, such that atoms move quickly.

Imagine that the initial electronic wave function is given by one of the adiabatic states, $|\Psi(0)\rangle = |\Psi_J\rangle$, and that the entire system translates through space at constant velocity, $\{\mathbf{V}_Q(t) = \mathbf{V}\}$. The system cannot “know” that it is moving, because an inertial reference frame exists in which it is motionless. If electronic transitions are to be excluded, eq 1 requires that the derivative couplings satisfy the putative sum rule

$$\sum_Q \mathbf{d}_{IJ}^{[Q]} \stackrel{?}{=} 0 \quad (7)$$

Equation 7 implies that the electronic wave function should be insensitive to motion of the nuclear center of mass, $\mathbf{P}_N = -i\hbar \sum_Q \nabla_Q$, as would be true in the infinite-mass limit implied by the Born–Oppenheimer approximation.¹² We know, however, that the total (nuclear and electronic) center-of-mass momentum is a conserved quantity:

$$[\mathbf{P}, H] = [(\mathbf{P}_N + \mathbf{P}_e), H] = 0 \quad (8)$$

where $\mathbf{P}_e = -i\hbar \sum_e \nabla_e$. Because the Hamiltonian and the total momentum commute, \mathbf{P} and H share a common set of eigenstates, and we can infer $\langle \Psi_I | \mathbf{P} | \Psi_J \rangle = 0$. Thus, the proper sum rule for the derivative couplings is given not by eq 7, but by

$$\sum_Q \mathbf{d}_{IJ}^{[Q]} = -\sum_e \langle \Psi_I | \nabla_e | \Psi_J \rangle \quad (9)$$

Equation 9 shows that there is no guarantee that mixed (quantum/classical) nonadiabatic dynamics will respect the simple principle of translational invariance, irrespective of the level of theory at which one obtains the adiabatic states, potential energy surfaces, and derivative couplings, and even whether the electronic-structure calculations are performed in an atomic-orbital or plane-wave basis.

As a concrete example, consider an excited (2p) hydrogen atom translating through space. There are nonvanishing, *analytical* derivative couplings between the 2p and 1s states of magnitude⁷ $\langle 1s | \nabla_H | 2p \rangle = (16\sqrt{2}/81)a_0^{-1}$. The implication of eqs 1 and 9 is that the excited electron can be quenched spontaneously to the 1s state on a time scale as short as 686 fs at 300 K. The hydrogen nucleus speeds up concurrently, with its translational kinetic energy increasing by 10.2 eV (i.e., the energy separating the electronic states).^{17,18} This prediction involves a blatant violation of momentum conservation.

Electron-Translation Factors. The scenario just described is ultimately a consequence of having neglected electronic motion in the Born–Oppenheimer wave function *Ansatz*. Indeed, it was recognized very early on that spurious components of the derivative couplings can be removed by modifying the wave function to include electron-translation factors (ETFs), i.e., by assigning the electrons a time-dependent phase factor consistent with the velocity of at least one nucleus.^{11,19–21} These modifications have frequently been made at the molecular-orbital level, requiring interpolation between sets of orbitals corresponding to distinct asymptotic nuclear geometries.^{11,20} At the atomic-orbital level, by contrast, there is an

unambiguous association between a basis function centered at a given nucleus and an ETF, yielding traveling atomic orbitals (TAOs),

$$\chi_\mu(\mathbf{r}; \mathbf{R}_{Q_\mu}) \rightarrow \chi_\mu(\mathbf{r}; \mathbf{R}_{Q_\mu}) e^{(i/\hbar)m_e \mathbf{V}_{Q_\mu} \cdot \mathbf{r}} \quad (10)$$

Use of TAOs significantly complicates self-consistent-field calculations for the adiabatic states and their propagation in time.²¹ Micha and co-workers have nevertheless employed a full treatment of ETFs in their Born–Oppenheimer molecular dynamics studies of excitation-energy and electron transfer processes.^{22,23}

In this Letter, we obtain a simple analytical expression, applicable within any wave function theory based on linear combinations of atomic orbitals (LCAOs), that incorporates the effects of ETFs to first order in the nuclear velocities, $\{\mathbf{V}_Q \approx 0\}$. This treatment is in the spirit of Helgaker and Jørgensen, who derived perturbative corrections to the Hamiltonian for the calculation of magnetic properties.²⁴ In the low-velocity limit, the modification given by eq 10 is equivalent to applying an electronic boost operator $W(\mathbf{r})$ to the adiabatic states, which we express in terms of localized, orthonormal LCAOs, $\phi_n(\mathbf{r}; \mathbf{R}) = \sum_\mu C_{\mu n} \chi_\mu(\mathbf{r}; \mathbf{R}_{Q_\mu})$. (The symmetrically orthogonalized atomic orbitals are one such set.²⁵) We may then write

$$W(\mathbf{r}) \phi_n(\mathbf{r}; \mathbf{R}) = \frac{i}{\hbar} \sum_\mu C_{\mu n} (m_e \mathbf{V}_{Q_\mu} \cdot \mathbf{r}) \chi_\mu(\mathbf{r}; \mathbf{R}_{Q_\mu}) \quad (11)$$

The corresponding second-quantized operator yields the modified wave function, $|\tilde{\Psi}_I\rangle \approx (1 + W)|\Psi_I\rangle$; it is

$$W \equiv \frac{i}{\hbar} \sum_{qt} C_{\nu t} (m_e \mathbf{V}_{Q_\nu} \cdot \langle q | \mathbf{r} | t \rangle) a_q^\dagger a_t \quad (12)$$

$$\approx \frac{i}{\hbar} \sum_{qt} (m_e \mathbf{V}_{qt} \cdot \mathbf{r}_{qt}) a_q^\dagger a_t = -W^\dagger \quad (13)$$

In obtaining the second equality, we have made two additional approximations: First, we treat the localized orbitals as though they were strictly atom-centered. Second, we note that the position operator is local, too, and we assume that \mathbf{r}_{qt} will be small, effectively vanishing unless orbitals q and t lie on the same atom. The physical implication is that boosting to a moving frame causes mild distortions in the electronic structure around each atom but *not* a transfer of density between them; this assumption is effectively the same as that in the original TAO *Ansatz* of eq 10.

Within these approximations, the modified matrix elements of some electronic operator O are given by

$$\langle \tilde{\Psi}_I | O | \tilde{\Psi}_J \rangle = \langle \Psi_I | O | \Psi_J \rangle + \langle \Psi_I | W^\dagger O + O W | \Psi_J \rangle \quad (14)$$

$$\approx O_{IJ} + \langle \Psi_I | [O, W] | \Psi_J \rangle \quad (15)$$

with the commutator $[O, W]$ functioning as a correction operator that incorporates the effect of the ETFs. (Note that the associated correction will be anti-Hermitian if O is Hermitian, and vice versa.) As a practical matter, O is usually separable into one- and two-electron parts, such that we can rewrite $[O, W]$ as

$$[O, W] = \sum_{qt} O_{qt}^{(1)} [a_q^\dagger a_t, W] + \sum_{qstv} O_{qstv}^{(2)} [a_q^\dagger a_s^\dagger a_t a_v, W] \quad (16)$$

Focusing on the one-electron part of eq 16 and invoking the same atom-centering and locality approximations as before, we obtain (with q, t on the same atom)

$$\sum_{qt} O_{qt}^{(1)} [a_q^\dagger a_t, W] \approx \frac{i}{\hbar} \sum_{qst} m_e \mathbf{V}_{qt} \cdot (O_{qs}^{(1)} \mathbf{r}_{st} - \mathbf{r}_{qs} O_{st}^{(1)}) a_q^\dagger a_t \quad (17)$$

$$\approx \frac{i}{\hbar} \sum_{qt} m_e \mathbf{V}_{qt} \cdot [O^{(1)}, \mathbf{r}]_{qt} a_q^\dagger a_t \quad (18)$$

The last equality requires that we also treat our local-orbital basis as complete (or nearly so). Similar reasoning about the two-electron part of eq 16 yields (with q, s, t , and v on the same atom)

$$[O, W] \approx \frac{i}{\hbar} \sum_{qt} m_e \mathbf{V}_{qt} \cdot [O^{(1)}, \mathbf{r}]_{qt} a_q^\dagger a_t + \frac{i}{\hbar} \sum_{qstv} m_e \mathbf{V}_{qsvt} \cdot [O^{(2)}, \mathbf{r}]_{qsvt} a_q^\dagger a_s^\dagger a_t a_v \quad (19)$$

Equations 15 and 19 are the fundamental results of our analysis, and they imply that position-dependent operators $O(\mathbf{r})$ are not affected by adopting a traveling basis, at least to first order. Only quantities involving the electronic momentum change. For example, the Born–Oppenheimer adiabatic wave functions carry no electronic momentum at all, $\langle \Psi_I | \mathbf{p}_e | \Psi_I \rangle = 0$. In the traveling basis, by contrast, each electron in the wave function is imparted with some momentum, and $\langle \tilde{\Psi}_I | \mathbf{p}_e | \tilde{\Psi}_I \rangle = \sum_q m_e \mathbf{V}_{qq} \langle \Psi_I | a_q^\dagger a_q | \Psi_I \rangle$ is equal to the sum. Similarly, kinetic-energy terms of form $(\mathbf{p}^2/2m_e)$ provide an ETF correction for H . Applying the canonical commutation relation $[\mathbf{r}, \mathbf{p}] = i\hbar$, we find that

$$\langle \tilde{\Psi}_I | H | \tilde{\Psi}_J \rangle \approx H_{IJ} + \sum_{qt} \mathbf{V}_{qt} \cdot \mathbf{p}_{qt} \langle \Psi_I | a_q^\dagger a_t | \Psi_J \rangle \quad (20)$$

$$\approx E_I \delta_{IJ} + i\hbar \sum_Q \left[\sum_{qt} S_{qt}^{A[Q]} \langle \Psi_I | a_q^\dagger a_t | \Psi_J \rangle \right] \cdot \mathbf{V}_Q \quad (21)$$

$$\equiv E_I \delta_{IJ} + i\hbar \sum_Q \Delta d_{IJ}^{[Q]} \cdot \mathbf{V}_Q \quad (22)$$

In the second equality, we evaluated \mathbf{p}_{qt} using the same atom-centering approximation as above, plus the atomic-orbital identity $\nabla_e |v\rangle = -\nabla_Q |v\rangle$, thereby obtaining an antisymmetric version of the overlap-matrix derivative,⁸ $S_{\mu\nu}^{A[Q]} = [(\langle \mu | \nabla_Q | \nu \rangle - \langle \nu | \nabla_Q | \mu \rangle)/2]$.

Our ultimate goal is to describe the electronic dynamics in the moving frame. To do so, we obtain new equations of motion in the traveling basis by expanding the electronic wave function in the ETF-corrected states, $|\tilde{\Psi}(t)\rangle = \sum_j c_j(t) |\tilde{\Psi}_j\rangle$, and evaluating the time-dependent Schrödinger equation. If we assume that the nuclear velocities vary slowly, we find that the only first-order modification to eq 1 comes from eq 21. The full set of corrected couplings takes the form

$$\mathbf{d}_{IJ}^{\text{ETF}} = \mathbf{d}_{IJ} - \Delta \mathbf{d}_{IJ} \quad (23)$$

The ETF correction $\Delta \mathbf{d}_{IJ}^{[Q]}$ is actually well-known in the CI derivative-coupling literature. In fact, it is equal and opposite to

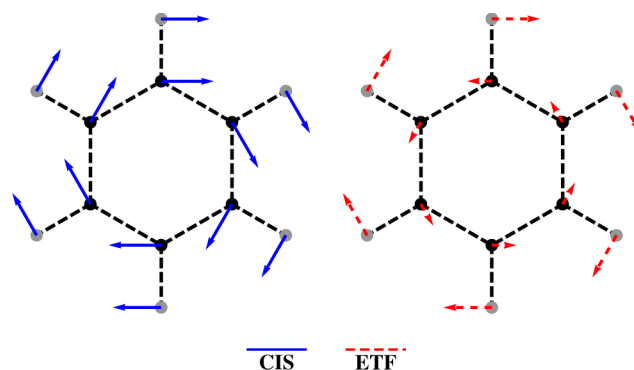


Figure 1. Mass-weighted derivative couplings $\tilde{\mathbf{d}}_{12}$ for benzene at the S_1 minimum, as computed using analytical theory (solid blue arrows at left, CIS) and corrected using built-in ETFs (dashed red arrows at right, ETF). Black and gray points represent carbons and hydrogens, respectively; dashed black lines indicate bond edges. C–C (C–H) bonds are 1.413 (1.074) Å long.

Table 1. Magnitudes of the Atomic Derivative Couplings for Benzene at the S_1 Minimum, As Computed Using Analytical Theory (CIS) and Corrected Using Built-in ETF, and the Associated Transition-Lifetime Estimate at 300 K

theory	$d_{12}^{[C]} (a_0^{-1})$	$d_{12}^{[H]} (a_0^{-1})$	τ_{12} (fs)
CIS	0.104598	0.027844	549
ETFs	0.048727	0.027676	764

the “orbital configuration-state function (CSF)” contribution to the couplings, and this term is known to be the sole source of translational variance.^{4,8} Thus, the corrections $\Delta \mathbf{d}_{IJ}$ in eq 23 and the orbital CSF terms cancel. $S^{A[Q]}$ does not appear in other contexts, so we can propose the following rule of thumb: To incorporate electronic motion into quantum-chemistry calculations in an atom-centered basis, simply set $S^{A[Q]} \rightarrow 0$. Because this replacement requires no computational effort, ETFs can be “built in.”

Benzene: A Case Study. We showed previously that the corrections given by eq 23 are large for lithium hydride but small for naphthalene.⁸ To help understand the practical conditions under which ETF corrections will be important for larger systems, we studied a set of 20 planar molecules, including conjugated hydrocarbons (e.g., *trans*-butadiene), polycyclic aromatic hydrocarbons (e.g., azulene), heterocycles (e.g., thiophene), and the “inorganic benzene” borazine. We optimized the geometry of each molecule in the first singlet excited state (S_1) at the CIS/6-31G** level using Q-Chem,²⁶ then computed the couplings to S_2 by the method of ref 8. Qualitatively important corrections were identified by checking whether $d_{12} \leq \Delta d_{12}$. Only two of the 20 molecules (ethylene and benzene) ever satisfied this condition; we chose to focus our attention on benzene.

Examining the left panel of Figure 1 shows that the standard couplings already satisfy the naive translational sum rule of eq 7. Even though the symmetry of the system causes the right-hand side of eq 9 to vanish, there are visible effects from the built-in ETFs in the right panel of Figure 1: The correction reduces the strength of the carbon couplings by more than a factor of 2 and flips their sign (cf. Table 1), while the hydrogen couplings are largely unchanged. The aggregate effect of these modifications is an increase in estimated transition lifetime of 39%. Note that we have depicted the mass-weighted couplings

Table 2. Symmetries and Excitation Energies of the First Three CIS/6-31G Singlet States of Benzene at the S_1 Minimum^a**

state	symmetry	$E_{\text{CIS}} - E$ (eV)
S_1	B_{2u}	6.1175
S_2	B_{1u}	6.2969
S_3	E_{1u}	8.3275

^aNote that S_3 is energetically well-separated from the lower-lying states; the Hartree-Fock ground-state energy is $E = -230.704236 E_h$.

\tilde{d}_{12} in Figure 1; in doing so, we have visually encoded the contribution of each atom to ϵ_{12} and, thus, its relative importance for the nonadiabatic transition. While the standard derivative couplings suggest that carbon and hydrogen motions are roughly equally important, the corrected couplings indicate that hydrogen motions are twice as important as those of the carbons.

Now, benzene belongs to the D_{6h} symmetry group, and the first three excited singlets have symmetries corresponding to $\pi \rightarrow \pi^*$ transitions^{27,28} (cf. Table 2). The direct product of S_1 and S_2 state symmetries is $B_{2u} \otimes B_{1u} = A_{2g}$; as such, the collective motions predicted to couple the states are overall rotation and in-plane counterrotation of the carbons and hydrogens (“twist”).^{29,30} In fact, Figure 1 shows that the standard derivative couplings look like a rotation around the central axis, and their ETF-corrected counterparts are arranged as a twist. More quantitatively, we find that the mixture of these motions in the standard couplings is 3:2, as compared with 1:3 in the corrected couplings. This result suggests that ETFs may be important for understanding whether rotations can lead to nonadiabatic transitions in larger molecules.

Finally, a few words about the practical role of symmetry in nonadiabatic dynamics seem appropriate. Our test set of 20 planar molecules varied widely in symmetry (from C_s to D_{6h}), and only two highly symmetric molecules (D_{2h} ethylene and D_{6h} benzene) exhibited qualitative corrections. To establish the importance of symmetry in our observations for benzene, we computed couplings for a large number of plausible finite-temperature geometries. We used the all-atom OPLS force field³¹ and the TINKER molecular dynamics package³² to sample benzene at three choices of temperature: 5000 structures at liquid-hydrogen temperature (14 K), such that symmetry was very weakly broken; 5000 at room temperature (300 K); and 10 000 at a very high temperature (12 000 K), for which symmetry-breaking was severe. The magnitudes of the full set of standard couplings and the associated ETF corrections are plotted with respect to the energy gap for each geometry, ΔE_{21} . At liquid-hydrogen temperature, three-fifths of the structures exhibited corrections larger than the couplings. At room temperature, by contrast, only one of the sampled structures does.

It is well-known that the derivative couplings contain several terms inversely proportional to the energy gap between the states,^{4,8} while the “orbital CSF” term (and, thus, the ETF correction) is functionally independent of ΔE_{21} (cf. eq 23). One might imagine, then, that there are regions of configuration space characterized by energy gaps so large that $d_{12} \approx \Delta d_{12}$. Our high-temperature results did not include even one such instance, and our preliminary conclusion is that symmetry is a key requirement for qualitative ETF corrections. Additional research into the typical behavior of Δd_{12} could prove very enlightening.

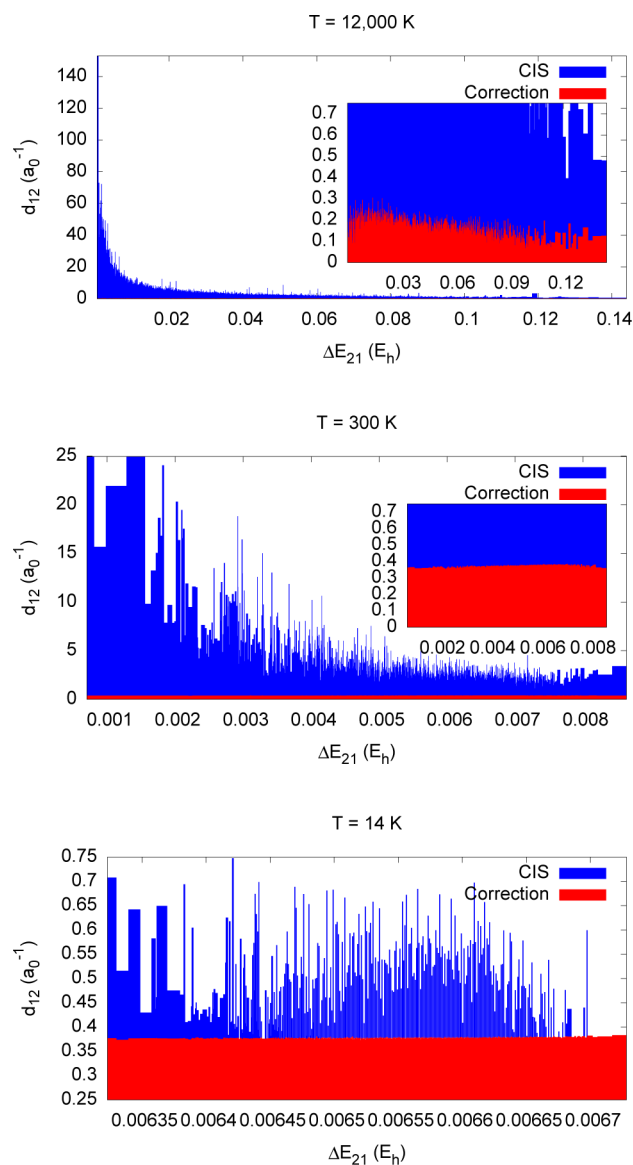


Figure 2. d_{12} and Δd_{12} for structures generated from molecular dynamics simulations at 12 000 K (top), 300 K (middle), and 14 K (bottom). Insets in the top and middle panel demonstrate that Δd_{12} is functionally independent of the energy gap and the temperature. Note that these plots are not histograms, and multiple data points are generally overlaid for a given value of ΔE_{21} ; in fact, nearly 3000 of 5000 total structures are represented by the region of largest gap for $T = 14$ K.

Conclusions. We have presented a general approach to incorporating ETFs into quantum-chemistry calculations in an atom-centered basis, as well as an equivalent rule of thumb: $S^{A[Q]} \rightarrow 0$. This rule is a simple prescription in the context of electronic-structure theory that achieves a useful dynamical result, namely, the reintroduction of electronic momentum into mixed quantum/classical dynamics. Our findings for benzene suggest that qualitative effects of correcting for electronic motion will be observed primarily in small or highly symmetric systems. Some uncertainty remains, however, largely because we have not been able to obtain an explicit analytical bound on the size of these corrections (and not for lack of effort). Even so, our perturbative treatment guarantees translational symmetry and center-of-mass momentum conservation without incurring *any* computational

cost, and we believe that it will find broad application in future studies of nonadiabatic phenomena.

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Notes

The authors declare no competing financial interest.

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