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

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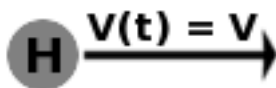
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Abstract

Flaws in the Born-Oppenheimer approximation and the adiabatic wavefunction *Ansatz* can lead to spurious transitions in nonadiabatic dynamics simulations, even when analytical derivative couplings are used as input. We showed recently that some of these anomalies can be corrected by the inclusion of electron-translation factors (ETFs) in the atomic-orbital basis. In the perturbative limit, these ETFs can be “built into” configuration-interaction theories: Including them actually reduces the cost of the derivative-coupling calculation. Here we explore the properties of the associated correction in the context of configuration-interaction singles. We conclude that built-in ETFs will be of greatest importance for very small systems; for highly-symmetric molecules like benzene, which we discuss in depth; at low temperature; and away from conical intersections. Even so, the intuitive physics and reduced computational cost associated with built-in ETFs support their general use.

TOC Graphic



**Estimated timescale
for 1s-to-2p transition
without ETFs is 686 fs.**

**With ETFs, there is no
transition.**

Keywords: derivative coupling, nonadiabatic dynamics, electron-translation factor, benzene

Derivative (or nonadiabatic) couplings are the crucial ingredients for studies of nonadiabatic dynamics.¹ As such, there is a rich literature devoted to computing these couplings, especially in the context of multi-reference configuration-interaction theory (MR-CI).²⁻⁴ Interest in the community is trending toward the study of nonadiabatic dynamics in ever more complicated systems,^{5,6} and so there has also been some work on this problem within time-dependent density-functional theory (TD-DFT).⁷⁻⁹ Research in our group, by contrast, has focused on working toward a unified framework for studying nonadiabatic dynamics within the context of the simple and affordable wavefunction theory of configuration-interaction singles (CIS);¹⁰ as a step in this direction, we recently presented a self-contained treatment of an analytic-gradient theory for CIS derivative couplings.¹¹

In the course of that work, we became acquainted with a long-standing problem:^{9,12-14} Among other strange properties, the couplings disrespect translational symmetry, such that constant-velocity motion of the entire system can nevertheless induce an electronic transition. To see that this is so, we consider a molecular system initially described by some arbitrary electronic wavefunction $|\Psi(0)\rangle$ and governed by Hamiltonian H , which gives rise to adiabatic states $\{|\Psi_J\rangle \equiv |\Psi_J(\mathbf{R})\rangle\}$ and potential energy surfaces $\{E_J \equiv E_J(\mathbf{R})\}$ that depend parametrically on the nuclear configuration \mathbf{R} . If each nucleus Q follows a classical trajectory given by $\{\mathbf{X}_Q(t), \mathbf{P}_Q(t)\}$, it is straightforward to use the time-dependent Schrödinger equation to determine the equations of motion for the wavefunction expanded in the adiabatic basis, $|\Psi(t)\rangle = \sum_J c_J(t) |\Psi_J\rangle$. Suppressing the time and configuration dependence of the various quantities involved, 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 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 have opposite signs, the size of this perturbation for a specific state pair, ϵ_{IJ} , is bounded from above by

$$\epsilon_{IJ} \leq \sum_Q \hbar d_{IJ}^{[Q]} V_Q |\cos \theta|, \quad (3)$$

We can estimate this quantity by making two simple approximations: First, we suppose that the relative orientations of the derivative couplings and nuclear momenta are random, such that we can replace $|\cos \theta|$ with its average. Second, we set V_Q to the root-mean-square speed drawn from the Maxwell-Boltzmann distribution. Making these substitutions, we obtain

$$\epsilon_{IJ} \lesssim \frac{2\hbar}{\pi} \sqrt{3kT} \sum_Q \tilde{d}_{IJ}^{[Q]}, \quad (4)$$

where we have implicitly defined the mass-weighted derivative coupling $\tilde{\mathbf{d}}_{IJ}^{[Q]} \equiv (\mathbf{d}_{IJ}^{[Q]} / \sqrt{m_Q})$. We can now use the energy-time uncertainty relation $\Delta E \Delta t \gtrsim \hbar$ to determine an instantaneous internal-conversion lifetime for states I and J ; at room temperature ($T = 300$ K) and in units appropriate to our calculations, it is

$$\tau_{IJ} \gtrsim \frac{191 \text{ fs} \cdot (a_0^{-1} / \sqrt{\text{amu}})}{\sum_Q (d_{IJ}^{[Q]} / \sqrt{A_Q})} \quad (5)$$

where A_Q is the atomic mass. This relation is quite sensible — transitions should occur more frequently when couplings are large and the temperature is high (such that atoms are fast).

Now, imagine that the initial wavefunction is one of the adiabats, $|\Psi(0)\rangle = |\Psi_J\rangle$, and that the entire system translates through space at constant velocity, $\{\mathbf{V}_Q(t) = \mathbf{V}\}$. Under these assumptions,

the initial form of Eq. (1) is

$$i\hbar\dot{c}_J = E_J \quad (6a)$$

$$\dot{c}_I = -\mathbf{v} \cdot \sum_Q \mathbf{d}_{IJ}^{[Q]} \quad (6b)$$

Intuition suggests that the system cannot “know” that it is moving, because an inertial reference frame exists in which it is motionless. But if these equations are to admit a stationary solution, such that the wavefunction simply accumulates a phase and τ_{IJ} diverges, the derivative couplings must satisfy the sum rule

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

This expression implies that the electronic wavefunction should not be affected by the operator corresponding to motion of the nuclear center of mass, $\mathbf{P}_N = -i\hbar\sum_Q \nabla_Q$.

Here we have the crux of the problem: The Born-Oppenheimer approximation can be understood to apply in the limit of infinite nuclear mass — that is, when the nuclear center of mass coincides with that of the full system.¹⁵ But nuclei are not infinitely heavy, and the total center-of-mass identity involving the nuclear *and* electronic momenta ($\mathbf{P}_e = -i\hbar\sum_e \nabla_e$) is the one that holds. Thus, the proper sum rule for the derivative couplings is

$$\sum_Q \mathbf{d}_{IJ}^{[Q]} = -\sum_e \langle \Psi_I | \nabla_e | \Psi_J \rangle. \quad (8)$$

The electronic matrix element in Eq. (8) can vanish for specific systems, rendering Eq. (7) valid as a special case, but there is in general no guarantee that the nonadiabatic dynamics will respect the simple principle of translational invariance, even if the states, energies, and derivative couplings are exact. As a concrete example, consider the non-vanishing couplings between the 1s and 2p states of hydrogen, $\langle 2p | \nabla_H | 1s \rangle = (16\sqrt{2}/81)$,⁹ which suggest a finite timescale for transitions of 686 fs.

These and other anomalous couplings have been attributed to the neglect of electronic motion in

the adiabatic *Ansatz* for the wavefunction; because the electronic states describe only bound-state motion, any displacement of the electrons in tandem with the nuclei takes place because they are forcibly dragged along. These center-of-mass-type motions contribute to the derivative couplings *in addition to* “real” effects like distortion and polarization of the states.¹⁴ It was recognized very early on that the former contributions could be removed by modifying the wavefunction to include electron-translation factors (ETFs) — plane-waves that assign the electrons a time-dependent momentum and phase consistent with the velocity of at least one nucleus.^{14,16–18} These modifications were frequently made at the molecular-orbital level, which introduced significant complications related to interpolation between the orbitals appropriate to various asymptotic configurations.^{14,17} Similar modifications at the atomic-orbital level, though simpler because of the unambiguous association between a given nucleus and an ETF, have typically been limited to the use of traveling-atomic-orbital (TAO) basis functions

$$\chi_{\mu}(\mathbf{r}; \mathbf{X}_{Q_{\mu}}) e^{i\frac{m_e}{\hbar} \mathbf{V}_{Q_{\mu}} \cdot \mathbf{r}}, \quad (9)$$

which complicates the self-consistent field (SCF) calculations for the diabats.¹⁸ Note, however, that Micha and co-workers incorporated a full treatment of ETFs into their Born-Oppenheimer molecular dynamics approach to excitation-energy and electron transfer.^{19,20}

Our contribution in this area was to develop a perturbative (low-nuclear-velocity) treatment of the ETFs in their guise as TAOs, yielding a correction operator for the derivative couplings.¹¹ (This approach is similar in spirit to that of Helgaker and Jørgensen, who derived perturbative corrections to the Hamiltonian for the calculation of magnetic properties.²¹) The resulting correction can be applied to couplings obtained from *any* theory based on linear combinations of atomic orbitals; does not affect the energies and orthonormality of the diabats, such that no complex SCF is required; takes the form of a commutator between the Hamiltonian and an electronic boost operator, $[H, W]$, such that it can be extended trivially to systems in fields and other environments; and can be shown to eliminate all translational invariance from couplings in CI-based theories, from CIS

all the way up to MR-CI. The last property stems from the fact that the sole source of translational invariance in the CI coupling due to atom Q is a term equal and opposite to that given by our correction,

$$\mathbf{Corr}_{IJ}^{[Q]} = -\text{Tr} \left[\mathbf{S}^{\text{A}[Q]} \mathbf{D}^{IJ} \right], \quad (10)$$

where \mathbf{D}^{IJ} is the one-particle transition density matrix for the IJ state pair and $\mathbf{S}^{\text{A}[Q]}$ is an antisymmetric counterpart to the derivative of the overlap matrix. Consequently, the corrected couplings

$$\mathbf{d}_{IJ}^{\text{ETF}} = \mathbf{d}_{IJ}^{\text{CI}} + \mathbf{Corr}_{IJ} \quad (11)$$

can also be obtained by the replacement $\mathbf{S}^{\text{A}[Q]} \rightarrow 0$, which we postulate as a general rule for building ETFs into CI-based theories. And because our correction obviates the construction and further manipulation of these $3N$ non-standard matrices, the ETF-corrected couplings will always be cheaper to compute than their analytical counterparts.

One question raised by our previous work was whether molecules larger than diatomics can exhibit ETF corrections of qualitative importance — that is, corrections comparable to or larger than the analytical couplings themselves. In order to address this question, we developed a set of 20 planar molecules, including conjugated hydrocarbons (e.g., *trans*-butadiene), polycyclic aromatic hydrocarbons (e.g., azulene), and heterocycles (e.g., thiophene), as well as the “inorganic benzene” borazine. For each molecule, we optimized geometries (\mathbf{R}_1 and \mathbf{R}_2) for the two lowest-lying singlet excited states (S_1 and S_2) at the CIS/6-31G** level, then computed the couplings ($\mathbf{d}_{12}^{\text{CIS}}$) between them, identifying qualitatively-important corrections by checking whether $d_{12} \leq \text{Corr}_{12}$. (These calculations were performed in a development version of Q-Chem.²²) Only two molecules, ethylene and benzene, ever satisfied this condition — ethylene at the first-excited-state minimum and benzene at both. We therefore focused our attention on benzene.

As described in Table 1, benzene structures \mathbf{R}_1 and \mathbf{R}_2 are nearly identical to each other and to the optimum ground-state geometry \mathbf{R}_0 ; bond lengths differ by no more than a few percent. It is not surprising, then, that the associated couplings and corrections are very similar, or that analyzing

them should lead to similar conclusions. For brevity’s sake, we will discuss our findings for the \mathbf{R}_1 geometry in detail.

Table 1: Bond lengths for benzene optimized at the HF/6-31G (\mathbf{R}_0) and CIS/6-31G** ($\mathbf{R}_{1,2}$) levels of theory. All structures are regular hexagons with C–H bonds bisecting the angle formed by any three adjacent carbons, as shown in Figure 1.**

structure	C–C length (Å)	C–H length (Å)
\mathbf{R}_0	1.385910	1.075982
\mathbf{R}_1	1.413337	1.073835
\mathbf{R}_2	1.414175	1.074068

Benzene belongs to the D_{6h} symmetry group. The ground state is totally symmetric (A_{1g}), while the first three singlets have symmetries corresponding to $\pi \rightarrow \pi^*$ transitions,^{23,24} as listed in Table 2. Because CIS does not provide a balanced description of the ground and excited states,²⁵ we do not consider couplings between them here. And because the lower-lying excited states are well-separated energetically from the S_3 pair, we do not consider those couplings either.

Table 2: Symmetries and excitation energies of the first three CIS singlet states of benzene at \mathbf{R}_1 . The ground-state Hartree-Fock energy is $E = -230.704236 E_h$.

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

We are left, then, with the problem of characterizing \mathbf{d}_{12} before and after the ETF correction. Comparison of the raw magnitudes (Table 3) shows that the correction reduces the strength of the carbon couplings by more than a factor of two; inspection of Figure 1 shows that they also flip sign. The hydrogen couplings, by contrast, are almost identical, and the total effect of our correction is a change in internal-conversion lifetime of 39%. Note that both analytical and corrected couplings satisfy the looser translational sum rule of Eq. (7); benzene exhibits sufficient symmetry in its molecular-orbital coefficients and CIS transition amplitudes for the electronic matrix element in Eq. (8) to vanish.

The collective motions most likely to induce a transition between the states can be “read off” quite straightforwardly from Figure 1: The analytical couplings look like an overall rotation around

Table 3: Magnitudes of the atomic derivative couplings for benzene at \mathbf{R}_1 , as computed using analytical theory (CIS) and corrected using built-in electron-translation factors (ETF), and the associated estimated instantaneous internal-conversion lifetimes τ_{12} 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
ETF	0.048727	0.027676	764

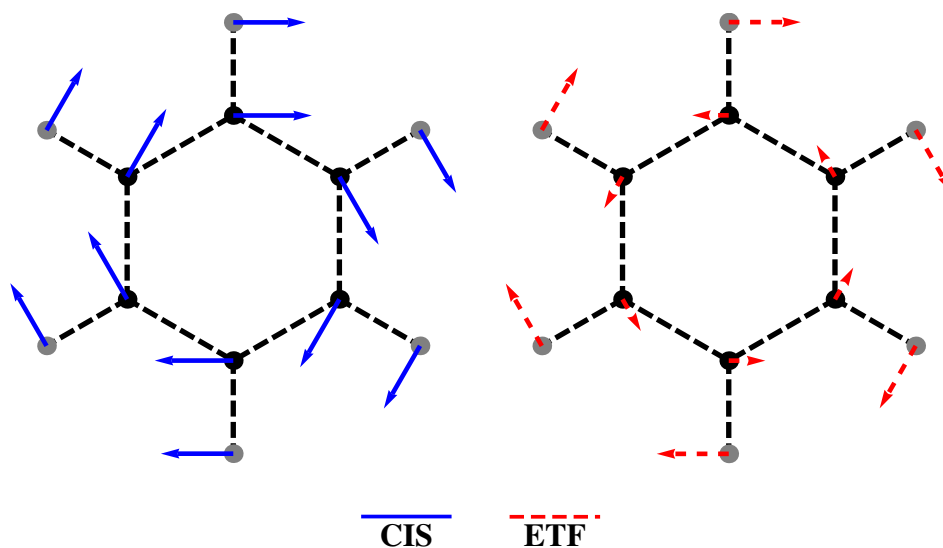


Figure 1: Mass-weighted derivative couplings $\tilde{\mathbf{d}}_{12}$ for benzene at \mathbf{R}_1 , computed using analytical theory (solid blue arrows at left, CIS) and corrected using built-in electron-translation factors (dashed red arrows at right, ETF). Black and grey points represent carbons and hydrogens, respectively; dashed black lines indicate bond edges.

the central axis, while their ETF-corrected counterparts involve in-plane counterrotation of the carbons and hydrogens (“twist”). These motions correspond to the direct product of the S_1 and S_2 state symmetries, $B_{2u} \otimes B_{1u} = A_{2g}$ — in other words, both sets of couplings are completely consistent with simple group theory.^{26,27} Of course, because rotation and twist have the same symmetry, they can be mixed. We quantified this mixing by evaluating the projection and rejection of the mass-weighted couplings $\tilde{\mathbf{d}}_{12}$ with the mass-weighted and normalized twisting-mode vectors $\hat{\mathbf{t}}$ obtained from a ground-state frequency calculation,

$$\text{projection} = (\tilde{\mathbf{d}}_{12} \cdot \hat{\mathbf{t}})\hat{\mathbf{t}} \tag{12}$$

$$\text{rejection} = \tilde{\mathbf{d}}_{12} - (\tilde{\mathbf{d}}_{12} \cdot \hat{\mathbf{t}})\hat{\mathbf{t}}. \tag{13}$$

Because the rejection consists entirely of rotation, the rejection:projection ratio corresponds to the relative mixing. We found that rotation and twist were mixed 3:2 for the analytical couplings, while the ETF-corrected couplings were formed from a 1:3 mix.

Note that we have depicted $\tilde{\mathbf{d}}_{12}$ in Figure 1; in doing so, we have visually encoded the relative contribution of each atom to ϵ_{12} and, thus, its relative importance to the process of internal conversion. It is clear to see that the analytical couplings suggest that carbon and hydrogen motions are roughly equally important, while the ETF-corrected couplings indicate that hydrogen motions are twice as important than those of the carbons. Given the severity of the approximations we have made in obtaining τ_{12} — not least that we consider values of the couplings for only one configuration — it is encouraging to see that our estimates for the internal-conversion lifetime are within roughly an order of magnitude of the experimental lifetime (48 ± 4 fs).²⁸

We found that large corrections to the couplings are not unique to the minimum geometries \mathbf{R}_0 , \mathbf{R}_1 , and \mathbf{R}_2 : The line in configuration space connecting the two excited-state minima can be understood as defining a crude reaction coordinate for internal conversion. Adopting a linear interpolation with parameter $\lambda = \mathbf{R}_2 - \mathbf{R}_1$, we computed couplings for 50 additional structures in the interval $\mathbf{R}_1 \pm 625\lambda$. Qualitative corrections were observed over the range $[\mathbf{R}_1 - 450\lambda, \mathbf{R}_1 + 250\lambda]$,

which corresponds to a 57% (16%) increase in C–C (C–H) bond lengths. The ETF correction is clearly significant for a variety of structures — or, at least, for those that maintain D_{6h} symmetry.

The extent to which D_{6h} symmetry is crucial to our observations so far can be established by computing couplings for plausible finite-temperature geometries of benzene. We used the all-atom OPLS force field²⁹ and the TINKER molecular dynamics package³⁰ to generate structures at three choices of temperature: 5000 at liquid-hydrogen temperature (14 K), for which symmetry will be very weakly broken; 5000 at room temperature (300 K); and 10,000 structures at a very high temperature (12,000 K), for which symmetry-breaking will be severe. The magnitudes of the analytical couplings and the associated corrections are plotted with respect to the energy gap in Figure 2. (Note that these plots are not histograms, and multiple data points can coincide for a given value of the energy gap.) At liquid-hydrogen temperature, two-thirds of the structures exhibit corrections larger than the couplings. At room temperature, by contrast, only one of the structures does, and none do at 12,000 K. The symmetry of the benzene molecule is a key requirement for qualitative corrections.

Because \mathbf{d}_{12} is inversely proportional to the energy gap $\Delta E_{21} = E_2 - E_1$, we know that d_{12} and Corr_{12} must converge as the gap widens. We do see this trend in the higher-temperature panels of Figure 2, but the magnitudes never actually meet. It appears unlikely that any thermally-accessible region of benzene’s configuration space can be characterized by an energy gap sufficiently large to force such a convergence, which implies that qualitative corrections will appear exclusively at low temperature. Note also that certain geometries at higher temperature have very large derivative couplings to begin with, indicating proximity to a conical intersection; because Corr_{12} is independent of the energy gap, the ETF correction will be progressively less important for these configurations (and, thus, have only a very minor effect on the estimated internal-conversion lifetime).

We must conclude, therefore, that qualitative effects of the ETF correction will be observed primarily in small, highly symmetric systems and at cryogenic temperatures. Even so, built-in electron-translation factors will *always* repair any anomalous translational variance in the analytical derivative couplings obtained from configuration-interaction theories, rendering the associated

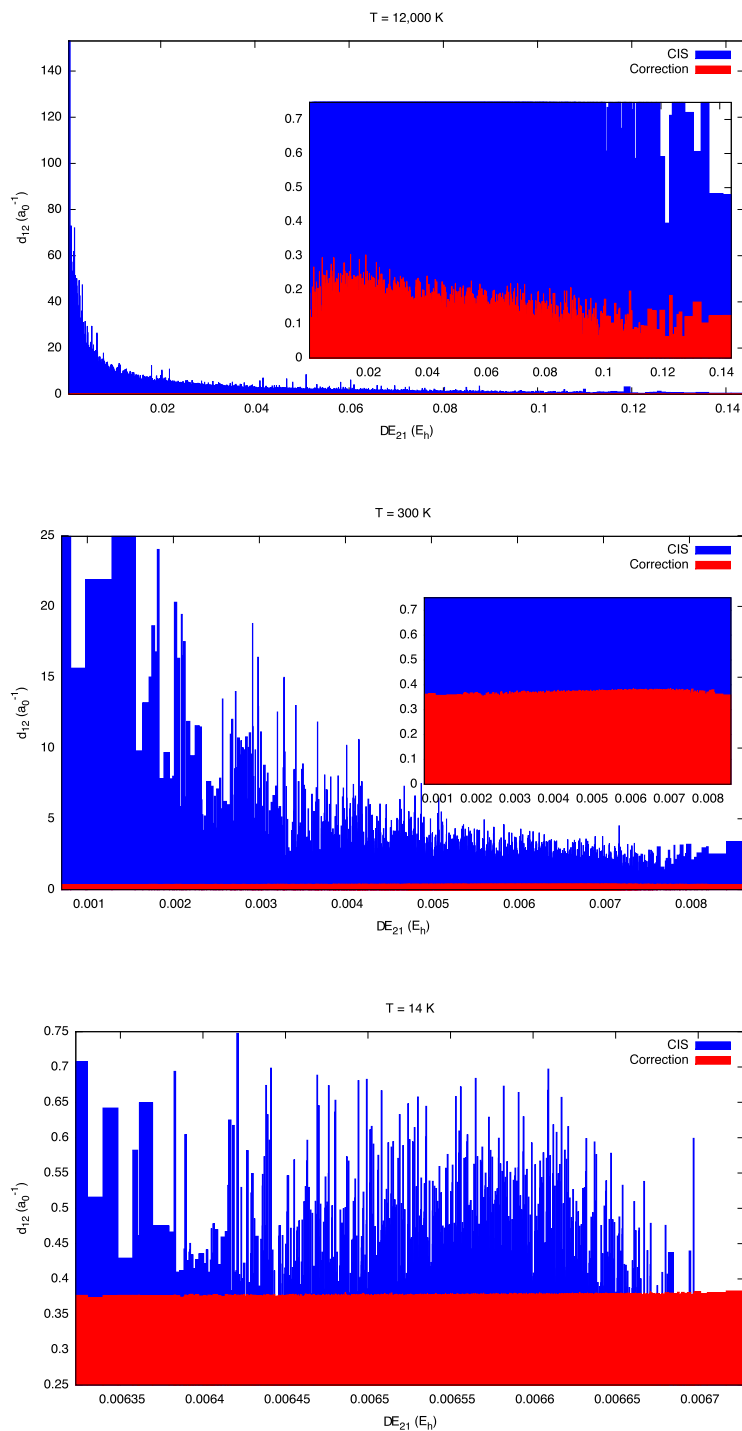


Figure 2: d_{12} and $Corr_{12}$ for structures generated from molecular dynamics simulations at 12,000 K (top), 300 K (middle), and 14 K (bottom). Insets in the top and middle panel demonstrate that $Corr_{12}$ is functionally independent of the energy gap (as it should be) and also the temperature.

nonadiabatic dynamics consistent with physical intuition. Further, they save the effort involved in constructing the $3N$ non-standard overlap-matrix derivatives $\mathbf{S}^{A[Q]}$, which will become ever more time-consuming as applications turn to truly large systems. These attractive qualities of our method argue in favor of its general use.

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