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Letter

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Fast Numerical Evaluation of Time-Derivative Nonadiabatic Couplings for Mixed Quantum−Classical Methods

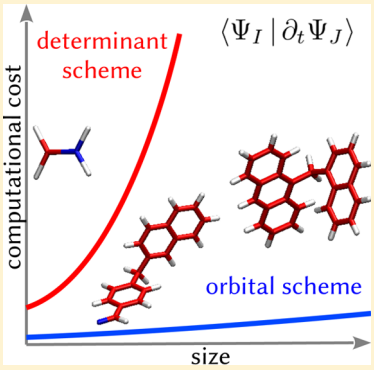
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Supporting Information

ABSTRACT: We have developed a numerical differentiation scheme that eliminates evaluation of overlap determinants in calculating the time-derivative nonadiabatic couplings (TDNACs). Evaluation of these determinants was the bottleneck in previous implementations of mixed quantum−classical methods using numerical differentiation of electronic wave functions in the Slater determinant representation. The central idea of our approach is, first, to reduce the analytic time derivatives of Slater determinants to time derivatives of molecular orbitals and then to apply a finite-difference formula. Benchmark calculations prove the efficiency of the proposed scheme showing impressive several-order-of-magnitude speedups of the TDNAC calculation step for midsize molecules.



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Simple quantum−classical methods for simulating nonadiabatic dynamics, Ehrenfest and fewest-switches surface hopping (FSSH),[1,2] often provide accurate and efficient ways to investigate chemical processes involving several electronic states. The simplicity of these methods stems from restricting quantum mechanical consideration to the electronic part and treating the nuclear part classically with minimal intervention of quantum mechanics. For describing the quantum evolution of the electronic subsystem, its nonstationary electronic wave function is written in terms of the adiabatic eigenfunctions $\{\Psi_J(\mathbf{r}; \mathbf{R})\}$ of the electronic Hamiltonian $\hat{H}_e$ as

$$\psi(t, \mathbf{r}; \mathbf{R}(t)) = \sum_J c_J(t)\Psi_J(\mathbf{r}; \mathbf{R}(t)) \tag{1}$$

The time-dependent coefficients $c_J(t)$ then can be obtained via projecting the time-dependent electronic Schrödinger equation onto the orthonormal basis of $\{\Psi_J(\mathbf{r}; \mathbf{R})\}$ (atomic units are assumed hereinafter)

$$\mathrm{i}\frac{\mathrm{d}c_K}{\mathrm{d}t} = \sum_J c_J(\delta_{KJ}E_J(\mathbf{R}) - \mathrm{i}\tau_{KJ}) \tag{2}$$

where δ_{KJ} is the Kronecker delta, $E_J(\mathbf{R})$ are the adiabatic potential energy surfaces (PESs), and

$$\tau_{KJ} = \langle \Psi_K | \partial_t \Psi_J \rangle \qquad K \neq J \tag{3}$$

are the time-derivative nonadiabatic couplings (TDNACs). Using the chain rule, one can further decompose $\tau_{KJ} = \dot{\mathbf{R}}\cdot\mathbf{d}_{KJ}$, where $\mathbf{d}_{KJ} = \langle \Psi_K | \nabla_{\mathbf{R}} \Psi_J \rangle$ is the $3M$-dimensional (M is the number of nuclei in the system) derivative couplings vector, and $\dot{\mathbf{R}}$ is the $3M$-dimensional nuclear velocity vector. $\mathbf{d}_{KJ}$ are implemented analytically for some electronic structure methods, such as multiconfigurational self-consistent field (MCSCF),[3,4] configuration interaction singles (CIS),[5,6] and multireference configuration interaction (MR-CI).[7,8] However, many electronic structure methods either lack the analytic implementation (e.g., XMCQDPT[9]) or have intrinsic problems in their definition.[10−15] Of course, numerical differentiation is always an option for evaluation of $\mathbf{d}_{KJ}$'s, but it is also quite computationally expensive considering the dimensionality of these quantities.

On the other hand, it has been recognized that it is more efficient to apply numerical differentiation to TDNACs directly.[16] For example, any of the following formulas can be employed

$$\tau_{KJ} = \frac{1}{\Delta t}\langle \Psi_K(t) | \Psi_J(t + \Delta t) \rangle + o(\Delta t) \tag{4}$$

$$\tau_{KJ} = \frac{1}{4\Delta t}(\langle \Psi_K(t - \Delta t) | \Psi_J(t + \Delta t) \rangle - \langle \Psi_K(t + \Delta t) | \Psi_J(t - \Delta t) \rangle) + o(\Delta t^2) \tag{5}$$

giving rise to the first-order forward and the second-order central finite difference schemes, respectively. Moreover, as was shown in ref 17, use of numerical TDNACs can be advantageous close to surface crossings. However, in the conventional FSSH method, $\mathbf{d}_{KJ}$ quantities are also needed to rescale nuclear velocities if a hop between electronic surfaces $E_K(\mathbf{R})$ and $E_J(\mathbf{R})$ occurs.

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Recently, to avoid numerical evaluation of $\mathbf{d}_{KJ}$, a simpler version of the FSSH method has been suggested.[18] In this simplified version, nuclear velocities are rescaled uniformly after a surface hop. It was shown that this simplified scheme can adequately model nonadiabatic dynamics and deviates from the regular FSSH algorithm only in regions where $\mathbf{d}_{KJ}$'s change rapidly, but these deviations have only a minor effect on overall dynamics.[19] Thus, if we focus on the simplified FSSH method, the only required nonadiabatic coupling terms will be TDNACs.

In commonly used numerical formulations (eq 4 or 5), TDNACs are obtained from an electronic overlap matrix

$$\Sigma_{KJ}(t, t + \Delta t) = \langle \Psi_K(t) | \Psi_J(t + \Delta t) \rangle \tag{6}$$

whose matrix elements require Slater determinant pair overlaps for electronic wave functions in the Slater determinant representation[19]

$$\Sigma_{KJ}(t, t + \Delta t) = \sum_{\{p,q\}} C^K_{\{p\}}(t) C^J_{\{q\}}(t + \Delta t) \times \langle \Phi_{\{p\}}(t) | \Phi_{\{q\}}(t + \Delta t) \rangle \tag{7}$$

where $C^K_{\{p\}}$ and $C^J_{\{q\}}$ are coefficients of the $|\Phi_{\{p\}}(t)\rangle$ and $|\Phi_{\{q\}}(t + \Delta t)\rangle$ Slater determinants. Here, we use collective indices $\{p\}$ and $\{q\}$ denoting sets of orbitals present in the Slater determinants $|\Phi_{\{p\}}(t)\rangle$ and $|\Phi_{\{q\}}(t + \Delta t)\rangle$. This scheme quickly becomes computationally expensive with the system size because it requires evaluation of many Slater determinant pair overlaps $\langle \Phi_{\{p\}}(t) | \Phi_{\{q\}}(t + \Delta t) \rangle$ given by the Löwdin formula[20,21]

$$\langle \Phi_{\{p\}}(t) | \Phi_{\{q\}}(t + \Delta t) \rangle = \det \mathbf{S}[\{p\}\{q\}] \tag{8}$$

where $\mathbf{S}[\{p\}\{q\}]$ is the overlap matrix of molecular orbitals comprising the determinants $|\Phi_{\{p\}}(t)\rangle$ and $|\Phi_{\{q\}}(t + \Delta t)\rangle$. The Löwdin formula appears as a result of nonorthogonality between sets of orbitals at different times. The computational cost of $\det \mathbf{S}[\{p\}\{q\}]$ calculation grows cubically with the number of electrons in the system, N_e.[22] Considering that all pairs of determinants in eq 7 need to be evaluated, use of eq 7 in large systems makes the evaluation of TDNACs the bottleneck of mixed quantum−classical simulations.

In this Letter, we show how computing of the determinant overlaps can be avoided in numerical evaluation of TDNACs without introducing any approximations and by making the procedure faster by at least a factor of $\sim N^3_{\mathrm{occ}}$ for each determinant pair ($N_{\mathrm{occ}} = N_e/2$ for the closed-shell case). We illustrate the performance of our approach by computing TDNACs at the CIS level of theory, which is one of the simplest methods for treating excited states. Our developments can be straightforwardly applied to any other method presenting wave functions as linear combinations of Slater determinants (e.g., MR-CI or MCSCF).

In the CIS method, excited-state wave functions are written as linear combinations of singly excited Slater determinants $|\Phi^a_i\rangle = \hat{a}^\dagger_a \hat{a}_i |\Phi_0\rangle$ obtained from the ground-state Hartree−Fock determinant $|\Phi_0\rangle$

$$|\Psi_K\rangle = \sum_{ia} C^K_{ia} |\Phi^a_i\rangle \tag{9}$$

with coefficients C^K_{ia} defined by the secular matrix problem $\hat{\mathbf{H}}_e\mathbf{C} = \mathbf{EC}$. Here, we follow the common convention where subscripts $a,b,c,\ldots$ denote virtual orbitals, $i,j,k,\ldots$ label occupied orbitals, and $p,q,r,\ldots$ are used for any type of orbitals.

To avoid computational difficulties associated with overlap determinants (eq 8), we will start with the formal definition of TDNACs as time derivatives (eq 3) and postpone applying a finite difference scheme until we account for the antisymmetric structure of Slater determinants. Assuming real-valued molecular orbitals and CIS coefficients, TDNACs can be written as

$$\tau_{KJ} = \sum_{ijab} \left(C^K_{ia} \partial_t C^J_{jb} \langle \Phi^a_i | \Phi^b_j \rangle + C^K_{ia} C^J_{jb} \langle \Phi^a_i | \partial_t \Phi^b_j \rangle \right) \tag{10}$$

All terms in eq 10 refer to the same t; hence, there are no complications with orbital nonorthogonality as in eq 7. One may apply the Slater−Condon rules to the first term but not to the second one because the time derivative ∂_t is *not* an operator in the space of electronic variables. Instead, we differentiate determinants $|\Phi^b_j\rangle$ directly

$$\partial_t |\Phi^b_j\rangle = \sum_{k \neq j} |\Phi^{bk'}_{jk}\rangle + |\Phi^{b'}_j\rangle \tag{11}$$

where the notation $|\Phi^{q'}_p\rangle$ means that a molecular orbital ϕ_p is replaced with the time derivative $\partial_t \phi_q$. Therefore, TDNACs between determinants become

$$\langle \Phi^a_i | \partial_t \Phi^b_j \rangle = \sum_{k \neq j} \langle \Phi^a_i | \Phi^{bk'}_{jk} \rangle + \langle \Phi^a_i | \Phi^{b'}_j \rangle \tag{12}$$

The last term in eq 12 is reduced to $\delta_{ij} \langle \phi_a | \partial_t \phi_b \rangle$, while only one term with $k = i$ and $a = b$ from the sum over k survives because of orthogonality conditions, $\langle \phi_p | \partial_t \phi_p \rangle = 0$ (for real orbitals) and $\langle \phi_p | \phi_q \rangle = \delta_{pq}$. Finally, we have

$$\langle \Phi^a_i | \partial_t \Phi^b_j \rangle = \delta_{ij} \langle \phi_a | \partial_t \phi_b \rangle - P_{ij} \delta_{ab} \langle \phi_j | \partial_t \phi_i \rangle \tag{13}$$

where P_{ij} is an additional phase factor that depends on the ordering convention for the orbitals in the Slater determinants. There are two common choices that result in different P_{ij} values

$$|\Phi^a_i\rangle = \det\{\ldots, \phi_{i-1}, \phi_a, \phi_{i+1}, \ldots\} \qquad P_{ij} = 1 \tag{14a}$$

$$|\Phi^a_i\rangle = \det\{\ldots, \phi_{i-1}, \phi_{i+1}, \ldots, \phi_a\} \qquad P_{ij} = (-1)^{|j-i|} \tag{14b}$$

Use of eq 13 leads to substantial reduction of TDNAC computation scaling because eq 10 is simplified to

$$\tau_{KJ} = \sum_{ia} C^K_{ia} \partial_t C^J_{ia} + \sum_{iab} C^K_{ia} C^J_{ib} \langle \phi_a | \partial_t \phi_b \rangle - \sum_{ija} P_{ij} C^K_{ia} C^J_{ja} \langle \phi_j | \partial_t \phi_i \rangle \tag{15}$$

Each term in eq 15 scales as $N_{\mathrm{occ}}N_{\mathrm{virt}}$, $N_{\mathrm{occ}}N^2_{\mathrm{virt}}$, and $N^2_{\mathrm{occ}}N_{\mathrm{virt}}$, respectively, where N_{occ} and N_{virt} are the numbers of occupied and virtual orbitals. In typical calculations, $N_{\mathrm{virt}} > N_{\mathrm{occ}}$, and the second term (eq 15) is dominating in the overall computational cost, providing the overall cubic scaling with the size of the system. This scaling should be compared with the $N^5_{\mathrm{occ}}N^2_{\mathrm{virt}}$ scaling of eq 7 for the CIS method with the determinant scheme. Note that evaluation of all terms in eq 15 can be reformulated as highly efficient matrix−matrix multiplications.

The possibility of reducing time derivatives of determinants to time derivatives of orbitals has been already mentioned in several works.[23,24] However, eq 13 has never been derived explicitly; our treatment, therefore, provides a rigorous

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foundation for the orbital formulation and for its extension to multi-Slater determinant wave functions.

To apply eq 13, one has to convert it into a corresponding finite-difference expression. Any finite-difference expression requires continuity of orbitals at different times. However, orbital phases at different times are arbitrary, reflecting the existence of the wave function gauge (phase) degree of freedom. Thus an appropriate orbital phase matching and tracking procedure is necessary.

The finite-difference counterpart of eq 13 is obtained by substituting

$$\langle \phi_p | \partial_t \phi_q \rangle \rightarrow \frac{1}{\Delta t} S_{pq}(t, t + \Delta t) \qquad p \neq q \tag{16}$$

where

$$S_{pq}(t, t + \Delta t) = \langle \phi_p(t) | \phi_q(t + \Delta t) \rangle \tag{17}$$

is the orbital overlap matrix. To keep track of relative signs of orbitals at t and $t + \Delta t$, we introduce an integer-valued matrix $\mathbf{O}$, which is obtained from $\mathbf{S}(t,t + \Delta t)$ by rounding off its matrix elements to ± 1 or 0. $\mathbf{O}$ has a structure of the signed permutation matrix as long as Δt is sufficiently small.[25] Performing the permutation and sign changes of molecular orbital coefficients in $\mathbf{C}(t + \Delta t)$ according to $\mathbf{O}$, we obtain matrix $\tilde{\mathbf{C}}(t + \Delta t)$. The set of orbitals $\tilde{\mathbf{C}}(t + \Delta t)$ is subsequently used to calculate the CIS coefficients at the moment $t + \Delta t$. Tracking and phase matching for the CIS states remain the same as those for the determinant-based procedure.[19] Computational overhead for the orbital tracking and phase matching scales as $(N_{occ} + N_{virt})^2$ and is negligible compare to other components of the algorithm.

To test the accuracy and efficiency of the proposed scheme, we benchmark it against the conventional scheme based on eqs 7 and 8 as implemented by Pittner and co-workers in the Newton-X program.[26,27] Table 1 shows that accuracies of the orbital- and determinant-based schemes are very similar, as could be expected from numerical schemes of the same order. For the efficiency comparison, it is worth noting that the Newton-X scheme has been used with a screening threshold of 5×10^{-5} for the products of CIS coefficients to reduce the number of determinant overlaps in eq 7. Our implementation uses matrix−matrix multiplication and thus does not employ a screening procedure. Table 2 illustrates speedups achieved by the current scheme for two midsize organic molecules and various basis sets. The speedups are especially prominent for small basis sets, where N_{occ} is comparable to the total number of basis functions. Increase of the basis set size makes the CIS coefficient product screening more productive, but the orbital-based scheme still outperforms the conventional scheme by more than two orders of magnitude.

Table 1. Errors of Numerical Differentiation for Representative TDNACs in $CH_2NH_2^+$ Using the 3-21G Basis[28a]

	step size, fs	determinant	orbital
$\Delta\tau_{31}$	0.1	-1.4×10^{-6}	-1.6×10^{-6}
	0.2	-7.5×10^{-6}	-8.1×10^{-6}
	0.5	-5.3×10^{-5}	-5.7×10^{-5}
$\Delta\tau_{21}$	0.1	-2.0×10^{-7}	$<1.0 \times 10^{-7}$
	0.2	-7.0×10^{-7}	-2.0×10^{-7}
	0.5	-5.0×10^{-6}	-2.5×10^{-6}

[a]TDNAC values converged up to 1×10^{-7}, $\tau_{31} = -1.170 \times 10^{-3}$, and $\tau_{21} = -2.375 \times 10^{-4}$ are obtained with a 0.05 fs time step.

Table 2. Relative Speedups for a Single Time Step Evaluation of TDNACs as Compared to the Newton-X Procedure[a]

molecule	basis set	N_{occ}[b]	N_{virt}	speedup
$C_{18}H_{14}O$[c]	STO-3G	46	44	400
	6-31G**	46	290	248
	cc-pVTZ	46	701	172
$C_{25}H_{18}$[d]	STO-3G	59	59	1372
	6-31G**	59	381	292

[a]In all calculations, TDNACs between the first three lowest electronic states were evaluated. [b]Excluding 1s core orbitals of C and O. [c]4-(2-Naphthylmethyl)-benzaldehyde. [d]9-((1-Naphthyl)-methyl)-anthracene.

In practical applications, one is more concerned with the total simulation time. Apart from TDNACs calculations, mixed quantum−classical nonadiabatic simulations include also the electronic structure and classical dynamics steps. For the electronic structure CIS calculations, we have used the Gaussian program.[4] To give an idea of the overall speedup, we consider the first 50 fs of a single FSSH trajectory for the $C_{18}H_{14}O$ molecule using the 6-31G** basis set and the 0.2 fs time step. The electronic structure part involved evaluation of characteristics for the three lowest electronic states. On a single Intel Xeon X5650 @ 2.67 GHz CPU, it took 99 h in total to complete this trajectory for the original NEWTON-X procedure, with 54 h[29] spent on the TDNAC calculations; the corresponding numbers for our algorithm are only 45 h and 12 min.

In conclusion, we have developed a numerical procedure that eliminates evaluation of overlap determinants in TDNACs calculations. This elimination produces tremendous speedup in quantum−classical nonadiabatic simulations where evaluation of TDNACs was the bottleneck. The central idea of our approach is to postpone introducing a finite-difference scheme (eqs 4 or 5) and to convert the expression for TDNACs given in terms of many-electron wave functions (eq 10) into the corresponding orbital-based formula (eq 15). This alternation of steps allows us to manipulate with orthogonal molecular orbitals and thus to avoid overlap determinants that arose as a result of orbital nonorthogonality in the determinant formulation. Benchmark calculations have proven the efficiency of the proposed scheme and illustrated its potential for mixed quantum−classical studies of medium and large molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b02062.

Geometric configuration data (TXT)

■ AUTHOR INFORMATION

Author Contributions

[‖]I.G.R. and J.N. contributed equally to this study.

Notes

The authors declare no competing financial interest.

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(28) The geometric configuration is provided in the Supporting Information
(29) In fact, NEWTON-X spent twice as much time as that (108 h) at TDNACs calculations because it repeated the same calculations for both α and β sets of molecular orbitals assuming the spin-unrestricted formalism. Here, we accounted only for a single set of calculations necessary in the spin-restricted formulation.

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