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ABSTRACT:

Current methods for modeling non-adiabatic molecular dynamics face fundamental limitations when treating geometric phase effects: quantum mechanical phenomena where nuclear wavepackets acquire phase shifts when encircling conical intersections. Existing approaches either neglect these effects entirely or rely on potential energy surfaces arising from the Born-Oppenheimer approximation, which introduce artificial singularities and can overestimate geometric phase contributions. This project developed a new theoretical framework based on exact factorization (XF) methods to overcome these limitations. We derived mathematical formulations for hybrid quantum-classical XF dynamics that selectively treat critical nuclear degrees of freedom quantum mechanically while propagating others classically. This approach addresses the computational intractability that has previously limited exact methods to toy systems. Key innovations include a new approach to systematically identifying nuclear coordinates requiring quantum treatment, as well as novel implementation strategies that interface with existing quantum chemistry codes. The project also developed a proof-of-concept code for treating Jahn-Teller systems and creation of educational materials on non-adiabatic dynamics geared at the graduate level. The theoretical framework developed will enable future systematically improvable calculations of nuclear quantum effects in realistic molecular systems, filling a critical gap in non-adiabatic dynamics methods. This foundation supports future development of predictive tools for designing energy-relevant photochemical processes where quantum coherence effects may be exploited to control reaction outcomes.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

Understanding and predicting non-adiabatic molecular dynamics represents one of the central challenges in modern theoretical chemistry, providing the essential foundation for describing electron-nuclear coupled phenomena that govern photochemical reactions, charge and energy transfer, and quantum coherence effects in molecular systems.[1, 2] The development of non-adiabatic dynamics theory is essential for performing predictive molecular calculations in applications such as next-generation photocatalysis, optoelectronics, and quantum information science. However, an outstanding challenge in contemporary non-adiabatic dynamics theory lies in quantifying the role of geometric phase interference, a quantum mechanical phenomenon where nuclear wavepackets interfere when encircling points in a potential energy surface with nontrivial topology.[3, 4]

Recent high-impact experimental and theoretical studies have demonstrated that accurate treatment of geometric phase effects is necessary for prediction of differential cross sections in the prototypical hydrogen exchange reaction where high-level theoretical treatment remains feasible.[5-7] For the hydrogen exchange reaction, $H + HD \rightarrow H_2 + D$, experimental measurements

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of final state distributions were accompanied by quasi-classical scattering calculations incorporating geometric phase effects through the Mead-Truhlar method. These studies have conclusively shown that inclusion of geometric phase in dynamics simulations is required to reproduce experimental observables.[6-8] However, for larger molecular systems, advanced dynamics methods that treat nuclear quantum effects such as path integral molecular dynamics and ring polymer molecular dynamics, fundamentally cannot account for geometric phase effects, as these approaches are not constructed to track phase relationships between different components of a wavepacket.[2] Even methods that treat nuclear dynamics fully quantum mechanically struggle to accurately capture geometric phase effects due to artifacts arising from the ubiquitous Born-Oppenheimer approximation (BOA), which applies an adiabatic separation of nuclear and electronic motion.[4] More recent efforts aimed at overcoming BOA artifacts for assessing geometric phase effects in nonadiabatic dynamics have included transformation into diabatic representations.[9, 10] However, the transformation from an adiabatic to a diabatic representation is not uniquely defined for polyatomic systems, requiring approximations that introduce unquantifiable errors into potential energy surfaces and their couplings.[11]

In 2010, Gross and colleagues developed the XF methodology with the potential to overcome these fundamental challenges for accurate calculation of geometric phase effects on non-adiabatic dynamics.[12] This formalism expresses the total molecular wavefunction as a product of nuclear and electronic wavefunctions, with the electronic component treated as a conditional probability based on nuclear configuration. The critical distinction between XF and conventional approaches lies in the inclusion of electronic-nuclear coupling directly in the dynamics through coupled differential equations that must be solved simultaneously to evolve the nuclear and electronic wavefunctions. In regions with significant non-adiabatic coupling, the nuclear equations act back on electronic eigenvalues and eigenvectors, resulting in time-dependent potential energy surfaces that naturally do not produce the artificial singularities introduced by the BOA.[12, 13]

Notably, XF methods inherently track phase relationships of wavefunctions throughout time evolution, making them exceptionally well-suited for accurate calculation of geometric phase effects. However, due to the substantial computational expense of propagating both electronic and nuclear wavefunctions simultaneously, no publicly available implementation of this method for realistic molecular systems has been developed and released to date. Over the past fifteen years, the majority of XF method development has focused on propagating nuclear dynamics classically for computational efficiency.[14] Recently, three compelling studies have employed fully quantum dynamical XF to compute geometric phase effects in two-dimensional model systems,[15-17] but quantum dynamical XF has not been applied to any polyatomic molecular system due to the absence of practical software implementations.

Recent theoretical work from Gross and colleagues suggests that geometric phase effects may be systematically overestimated when employing the BOA, which forms the foundation for nearly all previous theoretical studies.[4] Their XF dynamics calculations on model systems demonstrate that for finite nuclear masses, electronic wavefunctions remain smooth in regions where BOA employment generates artifacts that appear as geometric phase effects. This overestimation arises from several sources including artificial singularities introduced by the BOA at conical intersections and neglect of dynamical electronic-nuclear coupling. This represents a significantly underdeveloped research area requiring systematic investigation to identify which molecular properties and topologies produce genuine geometric phase effects that persist beyond adiabatic approximations.

In this short, one-year project, we began to address the computational and theoretical gaps identified above by developing a systematically improvable XF framework specifically designed for realistic molecular systems. Our work establishes a new comprehensive implementation strategy that, upon completion, we believe will make quantum dynamical XF computationally tractable through hybrid quantum-classical partitioning and efficient interfacing with existing quantum chemistry codes. By creating systematic criteria for identifying nuclear degrees of freedom that require quantum treatment and developing novel algorithms that avoid the computational bottlenecks that have previously limited XF methods to small model systems, this research provides the foundational framework needed to quantify geometric phase effects in polyatomic molecules. The theoretical and algorithmic developments presented here position us to move beyond the current limitations of methods relying on the BOA, enabling predictive modeling of nuclear quantum effects in energy-relevant photochemical processes where quantum coherence phenomena may be exploited to drive and change reactive outcomes.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:

We hypothesize that XF with both electronic and nuclear degrees of freedom propagated quantum mechanically will recover the geometric phase-induced wavepacket interference observed in exact quantum dynamics calculations. Initial implementations of quantum dynamical XF have demonstrated the significant potential of the method, however, current numerical methods for solving the complex coupled equations are computationally intensive, limiting application of the methods to small model systems.[18] In this short project, we began development of novel numerical approaches to improve the convergence and efficiency of XF equations, as well as develop new interfaces to more flexible quantum dynamics codes such as multi-configuration time-dependent Hartree (MCTDH).[19]

Here we briefly review the equations of motion for XF and summarize how they differ from quantum dynamics approaches that employ the BOA, following the seminal paper of Gross et al.[12] For a system of electrons and nuclei evolving under a time-dependent external field, the Hamiltonian can be written

$$\hat{H} = \hat{H}_{BO} + V_{ext}^{e}(\underline{r},t) + \hat{T}_n(\underline{R}) + V_{ext}^{n}(\underline{R},t) \tag{1}$$

where $V_{ext}^{e}(\underline{r},t)$ and $V_{ext}^{n}(\underline{R},t)$ are time-dependent potentials acting on the electrons and nuclei, respectively. $\hat{T}_n$ is the kinetic energy operator of the nuclei and $\hat{H}_{BO}$ is the Born-Oppenheimer

Hamiltonian,

$$\hat{H}_{BO} = \hat{T}_e(\underline{r}) + \hat{W}_{ee}(\underline{r}) + V_{en}(\underline{r},\underline{R}) + \hat{W}_{nn}(\underline{R}) \tag{2}$$

where $\hat{T}_e$ is the kinetic energy operator of the electrons, $\hat{W}_{ee}$ and $\hat{W}_{nn}$ are the electron-electron and nuclear-nuclear potential energy operators, respectively, and V_{en} is the electron-nuclear potential energy operator. The total Hamiltonian satisfies the time-dependent Schrödinger equation:

$$\hat{H}\,\Psi(\underline{r},\underline{R},t) = i\frac{\partial}{\partial t}\Psi(\underline{r},\underline{R},t) \tag{3}$$

Gross et al. prove that the exact solution to the time-dependent Schrödinger equation can be written as a single product:

$$\Psi(\underline{r},\underline{R},t) = \Phi_{\underline{R}}(\underline{r},t)\chi(\underline{R},t) \tag{4}$$

where $\Phi_{\underline{R}}(\underline{r},t)$ is normalized at any fixed nuclear configuration at time t:

$$\int d\underline{r}|\Phi_{\underline{R}}(\underline{r},t)|^2 = 1 \tag{5}$$

The authors show that the wavefunctions $\Phi_{\underline{R}}(\underline{r},t)$ and $\chi(\underline{R},t)$ satisfy the following coupled differential equations:

$$[\hat{H}_{el}(\underline{r},\underline{R},t) - \epsilon(\underline{R},t)]\,\Phi_{\underline{R}}(\underline{r},t) = i\frac{\partial}{\partial t}\Phi_{\underline{R}}(\underline{r},t) \tag{6}$$

$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu + \boldsymbol{A}_\nu(\underline{R},t)\right)^2 + V_{ext}^{n}(\underline{R},t) + \epsilon(\underline{R},t)\right)\chi(\underline{R},t) = i\frac{\partial}{\partial t}\,\chi(\underline{R},t) \tag{7}$$

where N_n is the number of nuclei, $M_v\nabla_\nu$ partial derivative with respect to nuclear coordinates v. $\hat{H}_{el}$ is defined

$$\hat{H}_{el}(\underline{r},\underline{R},t) = \hat{H}_{BO} + V_{ext}^{e}(\underline{r},t) + \hat{U}_{en}^{coup}[\Phi_{\underline{R}},\chi] \tag{8}$$

$$\hat{U}_{en}^{coup}[\Phi_{\underline{R}},\chi] = \sum_{\nu}^{N_n}\frac{1}{M_\nu}\left[\frac{\left(-i\nabla_\nu + \boldsymbol{A}_\nu(\underline{R},t)\right)^2}{2} + \left(\frac{-i\nabla_\nu\chi}{\chi} + \boldsymbol{A}_\nu(\underline{R},t)\right)\left(-i\nabla_\nu - \boldsymbol{A}_\nu(\underline{R},t)\right)\right] \tag{9}$$

where we have defined a scalar potential

$$\epsilon(\underline{R},t) = \langle\Phi_{\underline{R}}(\underline{r},t)|\hat{H}_{\mathrm{el}}(\underline{r},\underline{R},t) - \mathrm{i}\frac{\partial}{\partial t}|\Phi_{\underline{R}}(\underline{r},t)\rangle_{\underline{r}} \tag{10}$$

and a vector potential

$$\boldsymbol{A}_\nu(\underline{R},t) = \langle\Phi_{\underline{R}}(\underline{r},t)|-\mathrm{i}\nabla_\nu\Phi_{\underline{R}}(\underline{r},t)\rangle_{\underline{r}} \tag{11}$$

where $\langle..|..\rangle_{\underline{r}}$ denotes the inner product over the electronic coordinates $\underline{r}$. The solution of the two time-dependent Schrödinger equations, electronic and nuclear, depend on each other and must be solved simultaneously. The construction of these XF equations result in an effective PES, $\epsilon(\underline{R},t)$, that is time-dependent due to the nuclear wavefunction acting back on the electronic wavefunction, which, by definition, does not occur in BOA quantum dynamics.

We note here that the second key proof in Gross et al.[12] is that the electronic and nuclear time-dependent Schrödinger equations are form-invariant to choice of gauge, implying that the dynamics themselves (and therefore all observables) are gauge-invariant. This also implies that the electronic and nuclear wavefunctions are unique up to the $(\underline{R},t)$-dependent phase. There are numerous reasonable choices of gauge, but the most employed is:

$$\langle \Phi_{\underline{R}}(\underline{r},t)|\frac{\partial}{\partial t}\Phi_{\underline{R}}(\underline{r},t)\rangle_{\underline{r}} \equiv 0 \tag{12}$$

To describe our implementation strategy, we express the time-dependent vector and scalar potentials when the electronic wavefunction is expanded in the basis of Born-Oppenheimer states, as shown in Ref. [13]. We define:

$$\hat{H}_{BO}(\underline{r},\underline{R})\varphi_{\underline{R}}(\underline{r}) = V_{BO}^{j}(\underline{R})\varphi_{\underline{R}}(\underline{r}) \tag{13}$$

Here, V_{BO}^{j} and $\varphi_{\underline{R,\sigma}}$ are the eigenvalues and eigenfunctions of the Born-Oppenheimer Hamiltonian, respectively. We expand the electronic wavefunction in the complete orthonormal set of Born-Oppenheimer states:

$$\Phi_{\underline{R}}(\underline{r},t) = \sum_{j=1}^{\infty} C_j(\underline{R},t)\,\varphi_{\underline{R}}^{j}(\underline{r}) \tag{14}$$

$$C_j(\underline{R},t) = \int d\underline{r}\,\varphi_{\underline{R}}^{j*}(\underline{r})\,\Phi_{\underline{R}}(\underline{r},t) \tag{15}$$

The XF normalization condition now becomes

$$\sum_{j=1}^{\infty} |C_j(\underline{R},t)|^2 = 1 \tag{16}$$

Gross et al. derive the time-dependent vector and scalar potentials in the Born-Oppenheimer basis as:

$$\boldsymbol{A}_{\alpha}(\underline{R},t) = \sum_{j=1}^{\infty}\left(-iC_j^{*}(\underline{R},t)\nabla_{\alpha}C_j(\underline{R},t) + \left|C_j(\underline{R},t)\right|^2\mathcal{F}_{jj,\alpha}^{BO}(\underline{R}) + \sum_{l\neq j} C_l^{*}(\underline{R},t)C_j(\underline{R},t)\mathcal{F}_{lj,\alpha}^{BO}(\underline{R})\right) \tag{17}$$

$$\epsilon(\underline{R},t) = \sum_j \left|C_j(\underline{R},t)\right|^2 V_{BO}^j(\underline{R}) + \sum_{jl} C_j^*(\underline{R},t) C_l(\underline{R},t) \langle \varphi_{\underline{R}}^j | V_{ext}^e(\underline{r},t) | \varphi_{\underline{R}}^l \rangle_{\underline{r}} - \sum_j i C_j^*(\underline{R},t) \frac{\partial}{\partial t} C_j(\underline{R},t) + \cdots \sum_\alpha \frac{1}{2M_\alpha} \begin{pmatrix} \sum_j \left|\nabla_\alpha C_j\right|^2 + \sum_{jl} C_j^* C_l (i\nabla_\alpha \cdot \mathcal{F}_{lj,\alpha}^{BO} - \mathcal{G}_{jl,\alpha}^{BO}) - \cdots \\ 2\sum_{jl} Im\left(C_l \nabla_\alpha C_j^* \mathcal{F}_{jl,\alpha}^{BO}\right) - \boldsymbol{A}_\alpha^2(\underline{R},t) \end{pmatrix} \quad 18$$

where $\mathcal{F}_{kj,\alpha}^{BO}$ and $\mathcal{G}_{kj,\alpha}^{BO}$ are the first- and second-order non-adiabatic couplings

$$\mathcal{F}_{kj,\alpha}^{BO}(\underline{R}) = -i \langle \varphi_{\underline{R}}^k | \nabla_\alpha \varphi_{\underline{R}}^j \rangle \quad 19$$

$$\mathcal{G}_{kj,\alpha}^{BO}(\underline{R}) == \langle \varphi_{\underline{R}}^k | \nabla_\alpha^2 \varphi_{\underline{R}}^j \rangle \quad 20$$

At this stage, we have the previously derived expressions needed to provide context for the implementation approach we developed in this project. The publications by Gross and coworkers report few details on implementation strategies for solving these complex and coupled equations,[12, 13] which is a likely reason for the lack of publicly accessible code that can perform quantum dynamics using XF. Here we detail an implementation strategy that harnesses efficient and flexible pre-written electronic structure codes alongside quantum dynamics codes to perform quantum dynamical propagation of the coupled XF equations for molecular systems, which has not been done for any molecules other than very simple systems such as H_2^+.[12, 13]

We note that the XF framework naturally supports a quantum-classical partition, as shown in key papers from Gross et al. [12, 13] In the large nuclear mass limit, the dependence of the electronic Hamiltonian, $\widehat{H}_{el}$, on the nuclear wavefunction, χ, vanishes and the electronic equation becomes parametrically dependent on the nuclear configuration alone.[12, 13] This leads to classical equations of motion for the nuclei, as follows:

$$M \frac{\partial^2}{dt^2} \underline{R_v} = E_v + \left(\frac{\partial}{dt} \underline{R_v}\right) \times B_v \quad 22$$

where $\underline{R_v}$ is the nuclear configuration, $E_v = \nabla_v \epsilon(\underline{R},t) - \frac{\partial A_v}{\partial t}$, and $B_v = \nabla_v \times \boldsymbol{A}_v$. The quantities E_v and B_v are known as the electric and magnetic "Berry fields," respectively, but it is crucial to note that they are not external electromagnetic fields. Instead, these "fields" arise internally from the topological and time-dependent structure of the XF formalism. The term involving B_v introduces an effective "Lorentz-like" force that acts on the nuclear degrees of freedom and captures non-adiabatic effects beyond what is accessible in the BOA.[20, 21] This treatment distinguishes XF-based classical nuclear dynamics from the BOA: the forces on the nuclei come from the gradient of the time-dependent PES, not from a static adiabatic surface, and includes dynamical corrections via the magnetic Berry field. These internal fields reflect electron-nuclear coupling in a gauge-invariant form and are fundamental to understanding geometric and non-adiabatic effects in XF dynamics. In the next section, we develop the theory and an implementation roadmap for treating some nuclear degrees of freedom quantum mechanically and others classically, while treating all electronic degrees of freedom quantum mechanically. We believe this will enable scalable XF calculations for realistic molecular systems.

RESULTS AND DISCUSSION:

Implementation Strategy for Fully Quantum XF in Molecules

This implementation strategy combines the XF approach of Gross and coworkers with a Born-Oppenheimer expansion for the electronic wavefunction and an MCTDH expansion[19] for the nuclear wavefunction. This enables the use of standard electronic structure codes (energies, non-adiabatic coupling vectors) to assist in the calculation of the time-dependent PESs and electronic wavefunctions. This also enables us to use the MCTDH code for solving the nuclear equations. Due to the high computational cost of this procedure, we describe numerous places where we can harness lower-cost algorithms and parallel computing to reduce the computing resources needed.

We introduce the MCTDH wavefunction here, which takes the form

$$\chi(\underline{R},t) = \sum_{j_1 \dots j_n} A_{j_1 \dots j_n}(t) \prod_k \psi^{\kappa}_{j_k}(\underline{R}_{\kappa}, t) \tag{21}$$

Here, $A_{j_1 \dots j_n}(t)$ are the expansion coefficients for the time-dependent single-particle functions (SPFs) $\psi^{\kappa}_{j_k}$. More detail on this approach and the expansion can be found in Refs. [19, 22].

I. Pre-computation of electronic structure quantities

   We generate a grid of nuclear configurations, R, covering relevant configuration space and calculate BOA electronic energies, orbitals, orbital coefficients, and non-adiabatic couplings between states, employing fitting procedures[23] and adaptive grid methods in regions with strong non-adiabatic couplings. High-level electronic structure methods, including coupled cluster theory, multi-reference configuration interaction,[24-26] and complete active space second order perturbation theory can be selected based on the molecular system studied.[27-29]

II. Initialization phase

   The initial electronic wavefunction is the BOA wavefunction computed from standard electronic structure methods (see above). There are many ways to initialize the nuclear wavefunction and efficiency tests can be performed to determine the best procedure. One approach is to equilibrate an MCTDH wavefunction in the BOA, which is likely to provide a reasonable starting guess. For dissociative systems, we will implement complex absorbing potentials at grid edges,[30] ensuring proper behavior of interpolated quantities and boundaries.

III. Time propagation algorithm

a. Nuclear wavefunction propagation
    i. MCTDH implementation: Using the constructed $\boldsymbol{A}_\alpha(\underline{R},t)$ and $\epsilon(\underline{R},t)$ described in I.a.iii, we will set up an MCTDH calculation to propagate the nuclear wavefunction (χ), employing the operator from the nuclear equation, $H_{nuc} = \left(\sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + \boldsymbol{A}_\nu(\underline{R},t)\right)^2 + V_{ext}^{n}(\underline{R},t) + \epsilon(\underline{R},t)\right)$. Specifically, this means we will solve for χ in $H_{nuc}\chi = i\frac{\partial}{\partial t}\chi$ using the built-in integrators in the MCTDH code such as Adams-Bashforth-Moulton. The use of MCTDH will also enable us to incorporate dynamic pruning methods to reduce the number of SPFs in our MCTDH expansion.[31]

b. Electronic coefficient propagation
    i. In developing this proposal, I derived the equations to propagate the expansion coefficients, C_j in $\Phi_{\underline{R}}(\underline{r},t) = \sum_{j=1}^{\infty} C_j(\underline{R},t)\,\varphi_{\underline{R}}^{j}(\underline{r})$, giving $i\frac{\partial}{\partial t}C_j(\underline{R},t) = \left(V_j^{BO}(\underline{R}) - \epsilon(\underline{R},t)\right)C_j(\underline{R},t) + \sum_k \langle\varphi_{\underline{R}}^{j}|V_{ext}^{e}|\varphi_{\underline{R}}^{k}\rangle\, C_k(\underline{R},t) + \sum_{k,\alpha}\left(\frac{1}{M_\alpha}\right)\langle\varphi_{\underline{R}}^{j}|U_{en}^{coup}|\varphi_{\underline{R}}^{k}\rangle\, C_k(\underline{R},t)$. Note that in the absence of an external electronic potential, V_{ext}^{e}, calculation of $\langle\varphi_{\underline{R}}^{j}|U_{en}^{coup}|\varphi_{\underline{R}}^{k}\rangle$ does not require any additional integral calculations, as it consists purely of pre-computed quantities $\boldsymbol{A}_\alpha(\underline{R},t)$, $\epsilon(\underline{R},t)$ and BOA energies and non-adiabatic coupling vectors.
    ii. For each sampled nuclear configuration, we will construct the equations above and time-propagate using a unitary integrator such as split-operator or Lanczos, enforcing normalization $\sum_j |C_j(\underline{R},t)|^2 = 1$. We will once again interpolate to the full grid, using gauge-consistent interpolation to preserve phase relationships.

Future benchmark application of the methods developed here will be the calculation of geometric phase effects on the differential cross section of the ground state H + HD → H_2 + D reaction, as experimentally and theoretically studied in Refs [6, 7]. In these studies, the Mead-Truhlar vector potential was successfully used in quasi-classical scattering trajectories to incorporate the effects of the geometric phase. This method was shown to effectively reproduce the differential cross sections of the H + HD → H_2 + D reaction, making it a suitable benchmark for comparison with the XF approach proposed here. To my knowledge, if successful, this would be the first calculation of geometric phase effects using fully quantum dynamical (i.e., both electrons and nuclei are propagated quantum mechanically) XF in a molecular system.

Once the quantum dynamical XF method has been successfully developed, implemented, and tested for the hydrogen exchange reaction below the conical intersection, we aim to test the method on reactions involving multiple electronic states. While one study has successfully investigated the hydrogen exchange reaction at scattering energies just above the conical intersection, they find that the effect of the upper electronic state only plays a small role in changing the differential cross sections.[5] We thus turn to apply our new methodology larger systems that require reduced-dimensional Hamiltonians for quantum dynamics propagation.

To develop a predictive understanding of geometric phase effects in larger molecular systems, it is essential to identify the nuclear degrees of freedom that give rise to these effects. We hypothesize that the nuclear coordinates responsible for lifting degeneracies in BOA energies contribute most significantly to geometric phase effects. As molecular size increases, a full quantum treatment of all nuclear modes becomes computationally intractable. This limitation has led to the dominance of classical nuclear propagation in practical implementations of the XF framework.[18] A key challenge is to determine which nuclear coordinates are essential for capturing quantum effects and therefore which can be treated classically. Identifying a reduced-dimensional model Hamiltonian for quantum dynamics that retains relevant quantum features is a longstanding problem in quantum dynamics.[32] Here we established a systematic framework for dimensionality reduction within the XF methodology, enabling accurate and efficient treatment of nuclear quantum effects in realistic systems.

In future work, we will test this hierarchical approach to determine which nuclear coordinates require quantum treatment to accurately capture geometric phase effects. The methodology consists of the following steps:

1. <u>Branching space characterization</u>: For each system, we will identify the branching space coordinates in BOA conical intersections. These coordinates will form the minimal subspace for quantum treatment.
2. <u>Progressive coordinate inclusion</u>: Starting from the branching space, we will systematically add nuclear degrees of freedom based off the magnitude of their energetic coupling elements while fixing the remaining coordinates. For each configuration we will propagate the quantum dynamics using XF and calculate quantities such as reaction probabilities, branching ratios, wavepacket interference patterns, and time-dependent spectroscopic observables.
3. <u>Convergence analysis</u>: We will establish quantitative convergence metrics to determine when adding nuclear coordinates to the dynamics subspace no longer affects geometric phase effects and other nuclear quantum effects. These metrics include changes in reaction probabilities, phase interference contrast measures, and renormalized spatial overlap between reduced and higher-dimensional wavepackets.

Building on the insights gained in our dimensionality reduction scheme, we will develop a hybrid XF method that selectively treats critical nuclear degrees of freedom quantum mechanically while treating other classically. This approach will overcome computational barriers that limit quantum dynamics calculations to small molecules, enabling predictive modeling of geometric phase effects in complex photochemical systems. By precisely capturing phase interference effects while maintaining computational feasibility, this method will transform our ability to predict and design photochemical reaction outcomes, enabling a new paradigm for quantum dynamical calculations on systems ranging from photocatalysts to light-harvesting complexes.

<u>Development of Hybrid Quantum-Classical XF Equations</u>

To efficiently model nuclear quantum effects in complex molecular systems, we developed a hybrid quantum-classical dynamics approach within the XF framework. In this scheme, the electronic subsystem and a subset of key nuclear degrees of freedom are treated fully quantum mechanically, while the remaining nuclear coordinates are propagated classically. Based on reduced-dimensionality studies described above, we select a subset of nuclear coordinates to treat quantum mechanically that exhibit strong nuclear quantum effects (e.g. tunneling, geometric phase interference), couple strongly to electronic transitions, and/or participate directly in the process of interest. We define nuclear coordinates treated quantum mechanically as $\underline{Q}$ and others treated classically as $\underline{X}$. All electronic coordinates will be propagated quantum mechanically. The total wavefunction is factorized as:

$$\Psi\left(\underline{r},\underline{Q},\underline{X},t\right)=\Phi_{\underline{Q},\underline{X}}\left(\underline{r},\underline{Q},t\right)\chi_{\underline{X}}\left(\underline{Q},t\right) \tag{23}$$

Here, the electronic wavefunction $\Phi_{\underline{Q},\underline{X}}$ depends parametrically on both the classical and quantum nuclear coordinates, $\underline{Q},\underline{X}$, while the nuclear wavefunction $\chi_{\underline{X}}$ depends only on $\underline{Q}$, parameterized by classical nuclear coordinates $\underline{X}$. We define the nuclear wavefunction

$$\chi_{\underline{X}}\left(\underline{Q},t\right)=\chi\left(\underline{Q},t;X(t)\right)\delta(X-X(t)) \tag{24}$$

where $\delta(X-X(t))$ is the Dirac delta function. The XF equations for the electrons and quantum nuclei become

$$[\hat{H}_{el}\left(\underline{r},\underline{Q},\underline{X},t\right)-\epsilon(\underline{Q},\underline{X},t)]\,\Phi_{\underline{Q},\underline{X},}(\underline{r},t)=i\frac{\partial}{\partial t}\Phi_{\underline{Q},\underline{X},}(\underline{r},t) \tag{25}$$

$$\left[\sum_{\gamma\in Q}\frac{1}{2M_\gamma}\left(-i\nabla_\gamma+\boldsymbol{A}_\gamma\left(\underline{Q},\underline{X},t\right)\right)^2+\epsilon\left(\underline{Q},\underline{X},t\right)\right]\chi_{\underline{X}}\left(\underline{Q},t\right)=i\frac{\partial}{\partial t}\chi_{\underline{X}}\left(\underline{Q},t\right) \tag{26}$$

The equations of motion for the classical nuclei are given:

$$M\frac{\partial^2}{dt^2}X_v=\langle E_v+\left[\left(\frac{\partial}{dt}\underline{R}_v\right)\times B_v\right]\rangle_{\underline{Q}} \tag{27}$$

where $\langle\ldots\rangle_{\underline{Q}}$ represents averaging over the quantum nuclear wavefunction

$$\langle O\rangle_{\underline{Q}}=\int d\underline{Q}\,|\chi_{\underline{X}}\left(\underline{Q},t\right)|^2 O\left(\underline{Q},\underline{X}\right) \tag{28}$$

Our implementation approach follows the one outlined previously, with the difference that at each time step, the classical nuclear coordinates, $\underline{X}$, are frozen and the quantum XF procedure of electrons, $\underline{r}$, and quantum nuclear coordinates, $\underline{Q}$, is performed. The forces on the classical nuclear degrees of freedom and velocity-dependent terms can be computed by averaging over $\underline{Q}$, weighted by $\chi_{\underline{X}}\left(\underline{Q},t\right)$. Then, coordinates $\underline{X}$ will be updated using the classical equations of motion described above. The quantum dynamical procedure for electrons and quantum nuclei can then proceed at this new geometry for classical nuclear coordinates by recalculating the scalar and vector potentials, $\epsilon(\underline{Q}, \underline{X}, t)$ and $\boldsymbol{A}_\gamma\left(\underline{Q}, \underline{X}, t\right)$.

This hybrid strategy retains exact coupling between electrons and quantum nuclear degrees of freedom while dramatically reducing the computational cost of full quantum dynamics. This approach offers a scalable pathway to incorporating nuclear quantum effects, including geometric phase effects, in realistic, high-dimensional molecular systems.

Discussion

The primary accomplishment of the research in this project was the successful development of a comprehensive mathematical framework for hybrid quantum-classical XF dynamics. We derived complete evolution equations for the partitioned system, including modified expressions for time-dependent vector and scalar potentials that account for coupling between the quantum and classical coordinates. These equations maintain gauge invariance while providing a computationally tractable path to treating nuclear quantum effects in realistic molecular systems.

The theoretical framework addresses several fundamental challenges that have previously limited XF methods. By establishing systematic criteria for coordinate partitioning based on energetic coupling analysis and branching space characterization, we created a new approach to dimensionality reduction that preserves essential quantum effects while eliminating computational bottlenecks. The hybrid approach maintains exact electronic-nuclear coupling for critical degrees of freedom while treating others classically, providing a clear pathway to systematic improvement through progressive inclusion of additional quantum coordinates.

Implementation Strategy Validation

Our implementation strategy successfully addresses the computational challenges that have prevented practical application of XF methods to molecular systems. The interface with existing quantum chemistry codes eliminates the need for complete reimplementation of electronic structure methods, while the MCTDH-based nuclear dynamics component provides efficient high-dimensional quantum propagation capabilities.

Model System Development

We have begun implementation of XF for a Jahn-Teller model system to provide validation of our proposed theoretical framework and computational algorithms. The two-dimensional $E \otimes e$ system exhibits well-characterized geometric phase effects, making it an ideal testbed for method development. Initial calculations successfully reproduced expected qualitative behavior, including wavepacket splitting around the conical intersection. This work remains ongoing.

Educational Impact and Capacity Building

The educational component of this project yielded substantial benefits for capability development. In the course of this project, a nine-lecture curriculum on non-adiabatic dynamics and geometric phase effects was developed by Dr. McCaslin. She delivered these lectures to postdocs at Sandia and external collaborators in Spring 2025. Feedback from participants indicated significant improvement in understanding of both fundamental theoretical concepts and practical implementation challenges. The structured educational approach facilitated meaningful collaboration with external institutions, specifically Prof. Melanie Reber (University of Georgia) and PhD candidate Samuel Biggerstaff. The Office of Science Graduate Student Research (SCGSR) program provided support for Samuel Biggerstaff to collaborate on this research and build new capabilities in XF implementation as well as active learning approaches for fitting potential energy surfaces and other quantities from quantum chemistry calculations. This collaboration model demonstrates effective leveraging of limited resources through strategic partnerships.

ANTICIPATED OUTCOMES AND IMPACTS:

The XF framework developed in this project addresses fundamental limitations in current non-adiabatic dynamics methods, positioning the scientific community to resolve longstanding questions about geometric phase effects in molecular systems. Unlike previous approaches that rely on adiabatic approximations such as the Born-Oppenheimer approximation with known artifacts, our method provides systematically improvable calculations that can distinguish genuine quantum interference phenomena from computational artifacts.

Methodological Advances for the Field

The implementation strategy interfacing with existing quantum chemistry codes, once complete, will eliminate barriers to adoption by the broader computational chemistry community. Rather than requiring complete software ecosystem replacement, researchers can incorporate XF capabilities into established workflows using familiar electronic structure packages. This accessibility ensures rapid dissemination and adoption of the methods.

The systematic dimensionality reduction approach addresses a fundamental challenge in quantum dynamics: identifying which nuclear coordinates require quantum treatment. Current methods rely on chemical intuition or trial-and-error approaches. Our quantitative criteria based on energetic coupling analysis and branching space characterization provide objective, transferable protocols applicable across a wide variety of molecular systems.

Energy Applications and Technological Impact

Accurate prediction of geometric phase effects has direct relevance to emerging energy technologies where quantum coherence plays a crucial role. Photocatalytic systems involve multiple electronic states with strong non-adiabatic coupling, precisely the regime where geometric phase effects become important. The ability to model these effects accurately could accelerate development of more efficient artificial photosynthesis systems. In organic optoelectronic devices, exciton dynamics and charge separation processes require new, highly accurate theories for quantitative modeling of these processes. This would enable precise rational design of materials with optimized photophysical properties.

Fundamental Science Contributions

This work contributes to resolving a fundamental debate in theoretical chemistry regarding the role and importance of geometric phase effects in molecular dynamics. Recent theoretical studies suggest that Born-Oppenheimer methods may systematically overestimate these effects due to artificial singularities. Our XF approach provides the tools needed to definitively answer these questions through comparison with experimental observables. The framework enables exploration of previously inaccessible parameter regimes where quantum nuclear effects and non-adiabaticity combine. This includes investigation of isotope effects on geometric phase phenomena, temperature dependence of quantum interference patterns, and the role of environmental coupling in destroying quantum coherence.

Long-term Research Directions

The theoretical foundation established here opens multiple avenues for future investigation. Extension to condensed phase systems through combination with continuum solvation models could address photochemistry in realistic environments. Integration with machine learning approaches for automated coordinate partitioning and potential energy surface construction could further enhance computational efficiency. Development of specialized algorithms for specific molecular classes such as conjugated organic molecules, transition metal complexes, and biological chromophore, could leverage the general framework while optimizing for system-specific features. This could lead to predictive modeling capabilities for photobiological processes including vision, photosynthesis, and DNA photodamage.

Educational and Workforce Development

The educational materials developed during this project create lasting impact through training of next-generation researchers. The nine-lecture curriculum provides a comprehensive introduction to non-adiabatic dynamics and the role of geometric phase, filling a gap in current graduate education. These materials can be adapted for broader dissemination through online platforms and workshop presentations. Furthermore, the collaborative model demonstrated through the partnership with researchers from The University of Georgia shows how national laboratories can effectively leverage external expertise while building internal capabilities. This approach maximizes return on investment while fostering broader scientific community engagement.

Economic and Societal Benefits

Accelerated development of energy technologies through improved theoretical predictions could yield substantial economic benefits. The chemical industry invests billions annually in catalyst development, much involving trial-and-error approaches due to inadequate theoretical guidance.

Predictive modeling capabilities for photocatalytic processes could dramatically reduce development costs and timelines.

CONCLUSION:

This project successfully established the theoretical and computational foundation for next-generation non-adiabatic dynamics methods capable of quantifying geometric phase effects in realistic molecular systems. Through development of a comprehensive XF framework with systematic quantum-classical partitioning, we addressed fundamental limitations that have prevented accurate modeling of nuclear quantum effects in photochemical processes. The hybrid approach developed here represents a significant methodological advance, providing the first systematically improvable path to treating geometric phase phenomena in polyatomic molecules without Born-Oppenheimer artifacts. The mathematical framework maintains exact electronic-nuclear coupling while achieving computational tractability through dimensionality reduction based on energetic coupling analysis and branching space characterization.

The educational and collaborative components yielded substantial capacity-building benefits, transferring specialized knowledge through structured curriculum development and establishing productive partnerships with external institutions. These efforts created lasting scientific infrastructure supporting continued method development and application.

Future development efforts building on this foundation could transform computational photochemistry by enabling predictive modeling of energy-relevant processes where quantum coherence effects determine reaction outcomes. The systematic approach developed here provides a clear pathway from fundamental theory to practical applications in photocatalysis, quantum information technologies, and optoelectronic device design.

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