

NEXMD v2.0 Software Package for Nonadiabatic Excited State Molecular Dynamics Simulations

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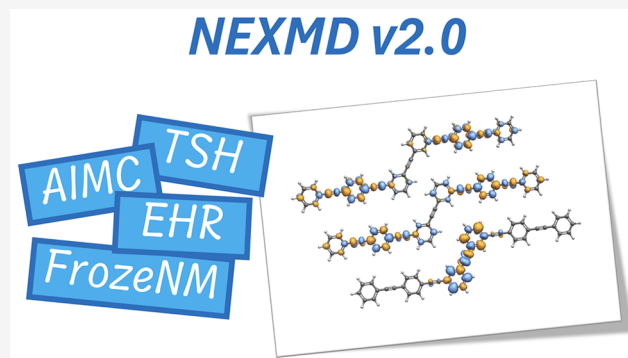


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ABSTRACT: We present NEXMD version 2.0, the second release of the NEXMD (Nonadiabatic EXcited-state Molecular Dynamics) software package. Across a variety of new features, NEXMD v2.0 incorporates new implementations of two hybrid quantum-classical dynamics methods, namely, Ehrenfest dynamics (EHR) and the Ab-Initio Multiple Cloning sampling technique for Multiconfigurational Ehrenfest quantum dynamics (MCE-AIMC or simply AIMC), which are alternative options to the previously implemented trajectory surface hopping (TSH) method. To illustrate these methodologies, we outline a direct comparison of these three hybrid quantum-classical dynamics methods as implemented in the same NEXMD framework, discussing their weaknesses and strengths, using the modeled photodynamics of a polyphenylene ethylene dendrimer building block as a representative example. We also describe the expanded normal-mode analysis and constraints for both the ground and excited states, newly implemented in the NEXMD v2.0 framework, which allow for a deeper analysis of the main vibrational motions involved in vibronic dynamics. Overall, NEXMD v2.0 expands the range of applications of NEXMD to a larger variety of multichromophore organic molecules and photophysical processes involving quantum coherences and persistent couplings between electronic excited states and nuclear velocity.



1. INTRODUCTION

In the last few decades, a great volume of research has focused on the discovery and design of new materials with desired photoactive properties. Inspiring examples in nature, such as vision¹ and photosynthesis,^{2–4} have brought to the spotlight organic conjugated materials ranging from small molecules and donor–acceptor systems to polymers and molecular crystals.^{5,6} These systems feature complex excited state electronic structure arising from strong electronic correlations and low dimensionality,⁷ combined with delocalized and polarizable π -electrons that are key for the generation of mobile charge carriers.⁶ Such systems typically undergo an efficient non-radiative relaxation⁸ that can take place through several nonadiabatic pathways leading to overall dissipation of an excess of electronic energy into heat. Many physical processes, such as internal conversion,⁹ energy transfer,¹⁰ charge separation,^{11,12} exciton self-trapping,¹³ or vibronic coherences,^{14–16} can be important. While the development of novel synthesis procedures has opened a wide range of materials design possibilities, computational methods have arisen alongside as an essential tool to facilitate such explorations by lowering the cost of the experimental trial-and-error

approach. These computational methods provide atomistic insights and the electronic structure features responsible for the functionality of various devices, such as organic light emitting diodes,¹⁷ photovoltaics,^{18–20} field-effect transistors,^{21,22} sensors,^{23–27} photocatalysts,²⁸ or solar cells.^{29,30} Consequently, multiple software packages have been developed for performing nonadiabatic molecular dynamics (NAMD) simulations, such as Q-Chem,³¹ SHARC,^{32–34} COBRAMM,³⁵ Newton-X,^{36,37} PYXAID,^{38,39} NWChem,^{40–42} TURBOMOLE,^{43,44} Libra,⁴⁵ PyUNIxMD,⁴⁶ DynEmol,⁴⁷ JADE,⁴⁸ Hefei-NAMD,⁴⁹ and NEXMD.^{50,51}

In particular, NEXMD⁵⁰ (Nonadiabatic EXcited-state Molecular Dynamics) has been aimed to describe photo-induced phenomena in relatively large conjugated molecular

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60 systems. In this paper, we present the next release of the
 61 package, NEXMD v2.0, which incorporates implementations of
 62 additional methods that enable computational modeling of a
 63 larger variety of multichromophore organic molecules and
 64 photophysical processes involving quantum coherences or
 65 persistent couplings between electronic excited states.
 66 NEXMD can perform both Born–Oppenheimer Molecular
 67 Dynamics (BOMD) and nonadiabatic Molecular Dynamics
 68 (NAMD). The original NEXMD release was limited to using
 69 only the Fewest Switches Trajectory Surface Hopping
 70 (TSH)⁵² algorithm for NAMD, with an adiabatic basis set to
 71 represent quantum transitions through the manifold of excited
 72 states. NEXMD v2.0 now also incorporates alternative NAMD
 73 methods, namely, Ehrenfest dynamics (EHR)⁵³ and the Ab-
 74 Initio Multiple Cloning (AIMC)⁵⁴ sampling technique for
 75 Multiconfigurational Ehrenfest quantum dynamics (MCE).⁵⁵
 76 As implemented in NEXMD v2.0, all three methods (i.e., TSH,
 77 EHR, AIMC) share the same level of electronic structure
 78 implementation consisting of Configuration Interaction Singles
 79 (CIS)⁵⁶ or Time-Dependent Hartree–Fock (TDHF)^{57,58}
 80 combined with semiempirical Hamiltonian models. The latter
 81 provides a fast and sufficiently accurate description of the
 82 excited state manifold for molecules in the range of one-three
 83 hundred atoms and including up to a few dozen excited states.
 84 Furthermore, analytical routines allow on-the-fly calculation of
 85 excited states nonadiabatic couplings^{59,60} and gradients.^{61–63}
 86 The combination of these features has allowed the application
 87 of NEXMD to study a broad range of materials including
 88 polymers,^{64–70} dendrimers,^{16,71–77} nanorings and nano-
 89 belts,^{78–83} light harvesting complexes,^{2,3,84} and energetic
 90 materials.^{85–87}
 91 The paper is organized as follows. Section 2 covers the new
 92 features released in NEXMD v2.0, highlighting in particular the
 93 theory behind the new available nonadiabatic molecular
 94 dynamics methods, i.e., EHR and AIMC. In Section 3, we
 95 present exemplary simulations of the photoinduced dynamics
 96 of a polyphenylene ethylene (PPE) dendrimer building block
 97 emphasizing the effects of different new features implemented
 98 in NEXMD v2.0. Finally, in Section 4, we present our
 99 concluding remarks and perspectives for future implementa-
 100 tions.

2. NEXMD/NEXMD V2.0 FEATURES

101 NEXMD/NEXMD v2.0 has been developed to perform on-
 102 the-fly ground-state and adiabatic or nonadiabatic excited state
 103 molecular dynamics simulations at Hartree–Fock (HF),
 104 TDHF, or CIS levels of electronic structure using semi-
 105 empirical Hamiltonians. The abbreviated list of features
 106 released in NEXMD v2.0 compared to NEXMD is given in
 107 Table 1. All of them have been tested in previous
 108 articles,^{14–16,76,88–90} and they are finally getting released in
 109 NEXMD v2.0.

110 **2.1. Electronic Structure Calculation Overview.** While
 111 the detailed NEXMD electronic structure calculation back-
 112 ground can be found elsewhere,⁵⁰ we briefly summarize it here
 113 for the sake of completeness. The ground state density matrix
 114 is calculated with the means of the Hartree–Fock (HF) self-
 115 consistent field iterative procedure.⁵⁶ NEXMD utilizes semi-
 116 empirical quantum mechanics methods,⁹¹ including several
 117 semiempirical Hamiltonians including the Austin Model
 118 (AM1),⁹² the Parametrized Model 3 (PM3),⁹³ and the
 119 Parametrized Model 6 (PM6),⁹⁴ among others.

Table 1. Features Present in NEXMD/NEXMD v2.0

Features	NEXMD	NEXMD v2.0
Semiempirical Hamiltonian models (AM1, MNDO, PM3, PM6)	×	×
Hartree–Fock ground state	×	×
TDHF or CIS excited states	×	×
Continuum solvation models	×	×
Analytical ground and excited-state gradients	×	×
Analytical nonadiabatic couplings	×	×
Geometry optimization of ground or excited states	×	×
Langevin thermostat	×	×
Adiabatic dynamics of ground or excited states	×	×
Trajectory Surface Hopping NAMD	×	×
Empirical decoherence methods	×	×
Trivial unavoided crossings	×	×
On-the-fly elimination of unnecessary states		×
Ehrenfest NAMD		×
Ab-Initio Multiple Cloning sampling technique for Multiconfigurational Ehrenfest NAMD		×
Hessian and vibrational normal modes calculations		×
Distance constraints (RATTLE) for dynamics		×
Normal mode constraints (FrozeNM) for dynamics		×
Orbital analysis of transition density	×	×
Analysis of transition density flux	×	×
Real space analysis of transition density matrix	×	×

The time-dependent Hartree–Fock (TDHF) equation is
 120 solved for the single electron transition density matrix⁹⁵ using
 121 the Collective Electronic Oscillator (CEO) approach.^{96,97} A
 122 single electron transition density matrix element, representing
 123 a transition from the ground state (denoted as 0) to an excited
 124 state I , is given by
 125

$$(\rho_{0I})_{nm} = \langle \phi_0 | c_m^\dagger c_n | \phi_I \rangle \quad (1)$$

where $c_m^\dagger$ and c_n are the electronic creation and annihilation
 127 operators acting over the atomic orbitals m and n , respectively.
 128 These transition density matrices are the eigenfunctions of the
 129 Liouville superoperator L ⁹⁸ or in tetradic notation
 130

$$L\xi_I = \Omega_I \xi_I \quad (2)$$

where ξ_I is the transition density matrix ρ_{0I} spanned as a
 132 column vector, and Ω_I is the transition energy from the ground
 133 state to excited state I . In the molecular orbital basis, this
 134 equation can be recast in the form⁶³
 135

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \Omega \begin{bmatrix} X \\ Y \end{bmatrix} \quad (3)$$

which is also known as the Random Phase Approximation
 137 (RPA) eigenvalue equation.⁵⁶ In this representation, transition
 138 density matrices $\xi = \begin{bmatrix} X \\ Y \end{bmatrix}$ consist of particle-hole X and hole-
 139 particle Y subparts.⁹⁶ Neglecting the nondiagonal blocks B is
 140 equivalent to the CIS approximation,⁹⁹ analogue to the Tamm-
 141 Dancoff approximation,¹⁰⁰ leading to
 142

$$AX = \Omega X \quad (4)$$

where A is the Hermitian CIS matrix. TDHF includes
 144 calculation of B , making it computationally more expensive.
 145 For both cases, solving for every eigenfunction is too
 146 expensive. Instead, the Davidson diagonalization algo-
 147 rithm^{99,101–103} is used to find numerically converging solutions
 148 for the requested number of the lowest energy excited states.
 149

For practical purpose, two additional states beyond the requested number are always computed with the Davidson algorithm, since the algorithm is empirically known to occasionally energetically misorder two states in the iterative diagonalization procedure leading to “skipped” states. The number of eigenfunctions requested determines the size of the adiabatic electronic basis for NAMD.

2.2. Nonadiabatic Molecular Dynamics Methods. NEXMD v2.0 has three different methods to perform nonadiabatic excited-state molecular dynamics on-the-fly: TSH, EHR, and MCE were coupled with AIMC. TSH dynamics has already been extensively explored¹⁰⁴ and applied to a wide range of photophysical processes.^{105–107} In general, EHR dynamics is adequate for homogeneous dynamic processes involving weak, but persistent, couplings between electronic excited states.^{15,108} However, in contrast to TSH, the EHR cannot describe branching relaxation pathways, transient population trapping on specific electronic states, or electronic relaxations involving state-specific driving forces. Furthermore, both TSH and EHR dynamics suffer from the improper treatment of decoherence in the electronic system. MCE treats decoherence in a natural way beyond mean-field Born–Oppenheimer dynamics on several excited states, expanding the range of practical applications.^{14,16,42,109} The implementation of these three methods within the NEXMD framework allows for a direct comparison of their weaknesses and strengths,⁸⁸ as well as their relative efficiencies. Taking TSH as reference, which is the numerically fastest approach, EHR dynamics can be approximately n times fold slower, where n is the number of excited states considered, typically from 2 to 10. For a larger number of states, EHR dynamics becomes impractical because all gradients for states and coupling between pairs of states are required. While being a controlled approximation, AIMC adds an extra numerical cost: each bifurcation augments the nuclear basis set, with a new configuration coming with its own electronic structure. Depending on the number of clones, AIMC dynamics can be approximately 1 order of magnitude slower than EHR dynamics.

2.2.1. Ehrenfest (EHR) Dynamics. In the NEXMD v2.0 implementation of EHR dynamics, nuclei are treated classically, while the electronic wave function is expanded over N_I adiabatic states, ϕ_I :

$$\varphi = \sum_I^{N_I} a_I \phi_I \quad (5)$$

The coefficients a_I evolve in time according to¹¹⁰

$$\dot{a}_I = -\frac{i}{\hbar} V_I - \sum_J a_J \dot{\mathbf{R}} \cdot \mathbf{d}_{IJ} \quad (6)$$

where V_I is the electronic potential energy of excited state I , $\dot{\mathbf{R}}$ is the nuclear velocity, and $\mathbf{d}_{IJ}$ is the nonadiabatic coupling vector

$$\mathbf{d}_{IJ} = \langle \phi_I | \nabla_{\mathbf{R}} | \phi_J \rangle \quad (7)$$

with $\nabla_{\mathbf{R}}$ being the gradient with respect to nuclear coordinates $\mathbf{R}$. In this context, the force $\mathbf{F}$ acting over the nuclei is given by

$$\mathbf{F} = -\sum_I |a_I|^2 \nabla_{\mathbf{R}} V_I - \sum_{I,J} (a_J)^* a_I \mathbf{d}_{IJ} (V_I - V_J) \quad (8)$$

such that $\mathbf{F}$ includes two terms: the first term corresponds to a sum of gradients for all electronic states weighted by their Ehrenfest populations $|a_I|^2$, and the second term represents the nonadiabatic contribution. The quantities V_I , $\nabla_{\mathbf{R}} V_I$, and $\mathbf{d}_{IJ}$ ($I, J \leq N_I$) are calculated analytically on-the-fly at the electronic structure level described in Section 2.1.

2.2.2. Trajectory Surface Hopping (TSH) Dynamics. The TSH implementation also involves equations 5–7, but the nuclei evolve on a potential energy surface that is defined by a single electronic state at a given time. That is, the force acting over nuclei is reduced to

$$\mathbf{F} = -\nabla_{\mathbf{R}} V_I \quad (9)$$

Stochastic hops from one electronic surface to another follow the Fewest Switches Surface Hopping (FSSH) prescription¹¹⁰ and are governed by changes in the coefficients of the electronic wave function (eq 6).⁵² This original TSH method is implemented in NEXMD¹¹¹ and NEXMD v2.0, and several empirical schemes for corrections for decoherence¹¹² in the TSH approach can be used. Both EHR and TSH make use of the Min-Cost algorithm¹¹³ to correct for trivial unavoids crossings.

2.2.3. MCE Dynamics. MCE is a natural generalization of Ehrenfest dynamics. In the MCE approach, individual EHR trajectories guide Gaussian basis functions (a.k.a., configurations) φ_n ⁵³ which form the basis for the molecular wave function Ψ . Each configuration includes a single nuclear term χ_n and a sum of electronic wave functions $\phi_I^{(n)}$.

$$\Psi = \sum_n c_n \varphi_n = \sum_n c_n \chi_n \sum_I a_I^{(n)} \phi_I^{(n)} \quad (10)$$

The nuclear terms are coherent states (CS),⁵⁵ i.e. minimum uncertainty wave packets, which in the coordinate representation are frozen Gaussian functions centered over an Ehrenfest trajectory $\mathbf{R}_n(t)$, $\mathbf{P}_n(t)$

$$\chi_n = \left(\frac{2\alpha}{\hbar} \right)^{N_{\text{DOF}}/4} \exp \left(-\alpha (\mathbf{R} - \mathbf{R}_n(t))^2 + \frac{i}{\hbar} \mathbf{P}_n(t) (\mathbf{R} - \mathbf{R}_n(t)) + \frac{i}{\hbar} \gamma_n \right) \quad (11)$$

where α is the Gaussian CS width depending on the type of atom,¹¹⁴ N_{DOF} is the number of degrees of freedom, $\mathbf{P}_n$ is the nuclear momentum, and γ_n is a phase of the nuclear part which is propagated semiclassically according to

$$\dot{\gamma}_n = \frac{\mathbf{P}_n \dot{\mathbf{R}}_n}{2} \quad (12)$$

The electronic part of the molecular wave function $\sum_I a_I^{(n)} \phi_I^{(n)}$ is represented in the Time-Dependent Diabatic Basis (TDDB).⁵³ The electronic wave functions $\phi_I^{(n)}$ are calculated at the center $\mathbf{R}_n$ of the n^{th} Gaussian CS (11) and implicitly depend on time due to the time dependence of $\mathbf{R}_n$. In TDDB, nonadiabatic couplings between electronic states originate from this time dependence, which is different from the Born-Huang approach,¹¹⁵ where coupling between electronic states originates from their parametric dependence on electronic coordinates. Nevertheless, the TDDB equations for coupled amplitudes $a_I^{(n)}$ are the same as those obtained on an adiabatic Born-Huang basis (eqs 5–6).

The time evolution of complex amplitudes c_n is calculated on-the-fly by the time dependent Schrödinger equation

$$\sum_n \langle \varphi_m | \dot{\varphi}_n \rangle \dot{c}_n = -\frac{i}{\hbar} \sum_n \left(H_{mn} - i\hbar \left\langle \varphi_m \left| \frac{d\varphi_n}{dt} \right\rangle \right) c_n \quad (13)$$

where

$$H_{mn} = \sum_{I,J} (a_j^{(m)})^* a_I^{(n)} \langle \chi_m \phi_j^{(m)} | (\hat{T} + \hat{V}) | \chi_n \phi_I^{(n)} \rangle \quad (14)$$

and

$$\begin{aligned} \left\langle \varphi_m \left| \frac{d\varphi_n}{dt} \right\rangle &= \left\langle \chi_m \left| \frac{d\chi_n}{dt} \right\rangle \sum_{I,J} \langle \phi_j^{(m)} | \phi_I^{(n)} \rangle (a_j^{(m)})^* a_I^{(n)} \right. \\ &\quad \left. - \frac{i}{\hbar} \langle \chi_m | \chi_n \rangle \sum_{I,J} \langle \phi_j^{(m)} | \phi_I^{(n)} \rangle (a_j^{(m)})^* a_I^{(n)} V_I^{(n)} \right. \end{aligned} \quad (15)$$

where the first and second terms reflect the time-dependence of the nuclear and electronic parts of the basis functions, respectively. Notice that for the electronic part, both amplitudes $a_I^{(n)}$ and electronic states $\phi_I^{(n)}$ are time-dependent resulting in the cancellation of the terms associated with the nonadiabatic coupling. The kinetic and potential matrix elements in equation 14 are evaluated as

$$\langle \chi_m \phi_j^{(m)} | \hat{T} | \chi_n \phi_I^{(n)} \rangle = \langle \phi_j^{(m)} | \phi_I^{(n)} \rangle \left\langle \chi_m \left| -\frac{\hbar^2}{2} \nabla_{\mathbf{R}} M^{-1} \nabla_{\mathbf{R}} \right| \chi_n \right\rangle \quad (16)$$

and

$$\begin{aligned} \langle \chi_m \phi_j^{(m)} | \hat{V} | \chi_n \phi_I^{(n)} \rangle &= \frac{1}{2} \langle \phi_j^{(m)} | \phi_I^{(n)} \rangle \langle \chi_m | \chi_n \rangle \\ &\quad \cdot \left\{ (V_j^{(m)} + V_I^{(n)}) + \frac{i}{4\alpha\hbar} (\mathbf{P}_n - \mathbf{P}_m) \cdot (\nabla_{\mathbf{R}} V_j^{(m)} + \nabla_{\mathbf{R}} V_I^{(n)}) \right. \\ &\quad \left. - \frac{1}{2} (\mathbf{R}_n - \mathbf{R}_m) \cdot (\nabla_{\mathbf{R}} V_I^{(n)} - \nabla_{\mathbf{R}} V_j^{(m)}) \right\} \end{aligned} \quad (17)$$

where equation 16 is exact, while equation 17 utilizes the first-order averaged Taylor expansion of the potential energy.¹¹⁶ The first-order linear interpolation of (17) does not involve any additional computational cost, as the electronic energies and gradients were calculated to propagate the trajectories $\mathbf{R}_n(t)$, $\mathbf{P}_n(t)$ and $\mathbf{R}_m(t)$, $\mathbf{P}_m(t)$ of Gaussian CSs (11). All nuclear matrix elements $\langle \chi_m | \chi_n \rangle$ and $\left\langle \chi_m \left| \frac{d\chi_n}{dt} \right\rangle$ can be calculated analytically,¹¹⁶ and the electronic overlaps are calculated on-the-fly according to

$$\frac{d}{dt} \langle \phi_j^{(m)} | \phi_I^{(n)} \rangle = \sum_K \langle \phi_K^{(m)} | \phi_I^{(n)} \rangle \dot{\mathbf{R}}_m \cdot \mathbf{d}_{KJ}^{(m)} + \sum_K \langle \phi_j^{(m)} | \phi_K^{(n)} \rangle \dot{\mathbf{R}}_n \cdot \mathbf{d}_{KI}^{(n)} \quad (18)$$

For the MCE method, the calculation of the expectation value of any operator includes contributions from all configurations and crossed terms between configurations. For example, the expectation value of the electronic populations is given by⁵⁴

$$\langle \hat{P}_K \rangle = \sum_{n,m} c_m^* c_n \langle \chi_m | \chi_n \rangle (a_K^{(m)})^* \sum_{I,J} a_I^{(n)} \langle \phi_K^{(m)} | \phi_I^{(n)} \rangle \quad (19)$$

The sum of electronic populations over K (eq 19) is the norm of the molecular wave function Ψ and should always be equal to unity. This property can be used to check the numerical integration scheme. Another example of an

observable expectation value is the fraction of transition density localized over a fragment of the molecule, expressed as

$$\langle \hat{\rho}_X \rangle = \sum_{n,m} c_m^* c_n \langle \chi_m | \chi_n \rangle \sum_{I,J} (a_j^{(m)})^* a_I^{(n)} \langle \phi_K^{(m)} | \phi_I^{(n)} \rangle \rho_{I,X}^{(m)} \quad (20)$$

where $\rho_{I,X}^{(m)}$ is the fraction of transition density localized over the fragment X of the molecule for excited state I in the centroid of configuration m .⁵⁴

2.2.4. AIMC Sampling Technique. EHR dynamics is meaningful only when the nuclei experience similar forces across all populated electronic states included in the calculation. Otherwise, the average EHR force lacks physical significance, and configurations φ_n likely fail to explore dynamically important regions of the configurational space. AIMC is a sampling technique for MCE that overcomes this problem allowing bifurcations of the wave packet in a similar fashion to the Ab-Initio Multiple Spawning method,^{117,118} therefore increasing the number of configurations. After a bifurcation or cloning event, a configuration φ_n

$$\varphi_n = \chi_n \sum_I a_I^{(n)} \phi_I^{(n)} \quad (21)$$

is replaced by two new configurations (i.e., clones) φ_{n_1} and φ_{n_2} having the same nuclear components but different electronic distributions. One of these new configurations (or clones) will be subsequently propagated starting from a pure electronic excited state M

$$\varphi_{n_1} = \chi_n \left(\frac{a_M^{(n)}}{|a_M^{(n)}|} \times \phi_I^{(n)} + \sum_{J \neq M} 0 \times \phi_J^{(n)} \right) \quad (22)$$

while the other configuration will continue propagating on a mixture of the remaining electronic states:

$$\varphi_{n_2} = \chi_n \left(0 \times \phi_M^{(n)} + \frac{1}{\sqrt{1 - |a_M^{(n)}|^2}} \sum_{J \neq M} a_J^{(n)} \times \phi_J^{(n)} \right) \quad (23)$$

The excited state M is chosen to be the state having the largest population just before the cloning point. The corresponding new nuclear amplitudes are set to

$$c_{n_1} = c_n |a_M^{(n)}| \quad (24)$$

and

$$c_{n_2} = c_n \sqrt{1 - |a_M^{(n)}|^2} \quad (25)$$

In this way, the continuity of the contribution of φ_n to the molecular wave function Ψ (eq 12) is guaranteed according to

$$c_n \varphi_n = c_{n_1} \varphi_{n_1} + c_{n_2} \varphi_{n_2} \quad (26)$$

In order to limit the additional computational cost introduced by each cloning event, the number of cloning events should be restricted. This is done by introducing three cloning criteria.⁵⁴ The first criterion quantifies whether the electronic distribution for a given configuration is sufficiently spread over several excited states

$$W_n = \frac{1}{\sum_I |a_I^{(n)}|^4} > \delta_1 \quad (27)$$

where W_n takes values between 1 and the number of excited states N considered. For $W_n = 1$, only one of the excited states is populated, while for $W_n = N$, the electronic population is evenly distributed among all of the excited states considered. Following previous studies on combinations of PPE dendrimer building blocks such as the one selected here as a representative example, a value of $\delta_1 = 1.5$ was used.

The second criterion compares both the direction and magnitude of the weighted sum of gradients and the gradient of the state M with the highest population by means of the generalized angle

$$\theta^{(n)} = \arccos \left(2 \frac{\nabla_{\mathbf{R}} V_M^{(n)} \cdot \sum_I |a_I^{(n)}|^2 \nabla_{\mathbf{R}} V_I^{(n)}}{|\nabla_{\mathbf{R}} V_M^{(n)}|^2 + \left| \sum_I |a_I^{(n)}|^2 \nabla_{\mathbf{R}} V_I^{(n)} \right|^2} \right) > \delta_2 \quad (28)$$

where a value of $\delta_2 = \frac{\pi}{18}$ was used in the simulations presented in this work.

Finally, the third criterion prevents the algorithm from cloning in the strong coupling regime. Otherwise, uncontrolled exponential growth of the basis set could occur in this region, leading to an inefficient sampling with several trajectories exploring the same configurational space

$$\sum_I \left| 2 \frac{\mathcal{R}\{a_I^{(n)}(a_M^{(n)})^*\} \dot{\mathbf{R}} \cdot \mathbf{d}_{IM}}{|a_M^{(n)}|^2} \right| < \delta_3 \quad (29)$$

where $\mathcal{R}$ stands for the *real part*. A value of $\delta_3 = 0.005$ was set for the simulations in this work. The selection of these combination of δ_1 , δ_2 , and δ_3 has guaranteed a substantial amount of cloning events for a diverse set of dendritic molecules as reported previously,⁸⁸ which that allows to analyze the effects that the presence of different branching relaxation pathways has on the simulations without increasing the computational cost to prohibitive values.

2.3. Other Essential Features Related to Computational Efficiency and Vibrational Analysis. Additional NEXMD features implemented in the original release of the software package and retained in the updated NEXMD v2.0 release include useful tools for molecular dynamics simulations such as the Langevin thermostat,¹¹⁹ geometry optimization routine, continuum solvation models,^{120,121} trivial unavoids crossings,^{113,122} and decoherence corrections.¹¹² The package also incorporates practical analyses of electronic excitations in terms of orbital distribution of transition density and its time-dependent flux^{67,123} as well as real-space representation of transition density matrices.^{96,124,125} These features are discussed in detail elsewhere.⁵⁰ NEXMD v2.0 incorporates additional new features besides the implementation of EHR and AIMC methods (Table I).

NEXMD v2.0 has been particularly developed to deal with the photophysics of large conjugated molecules involving hundreds of atoms and large densities of states. Most of the initial excited states are ultrafast depopulated during the very first few femtoseconds after photoexcitation, transferring their energy to intermediate states. In order to improve the computational efficiency, NEXMD v2.0 includes an on-the-fly state limiting method to eliminate states that are no longer essential for the nonradiative relaxation dynamics during TSH dynamics.¹²⁶ A threshold of n states is used, and all states above the current state $\alpha + n$ are removed throughout the simulations.

The photophysics of large conjugated molecular systems involves electronic and vibrational energy relaxation and redistributions that frequently occur concomitantly. These processes can involve one or a few vibronic relaxation pathways in which only a few vibrational degrees of freedom are active. In order to facilitate this vibrational analysis, NEXMD v2.0 incorporates Hessian and normal-mode calculation,¹²⁷ that are computed numerically from finite differences of the analytical ground- or excited-state gradients. Besides, the impact of specific vibrations can be evaluated by performing simulations by selectively freezing certain motions. NEXMD v2.0 incorporates the possibility to apply distance and normal mode constraints in the simulations. Distance constraints are implemented according to the Rattle algorithm,¹²⁸ and normal mode constraints are enabled by the FrozeNM algorithm.⁸⁹

3. EXEMPLARY SIMULATIONS OF PHOTOINDUCED DYNAMICS

The photoinduced dynamics of a PPE dendrimer building block has been simulated to illustrate the different NAMD methods implemented in NEXMD v2.0 using the CIS/AM1 electronic structure description. Technical details and parameters for these simulations can be found in the [Supporting Information](#). The inset in Figure 1 shows the geometry of the

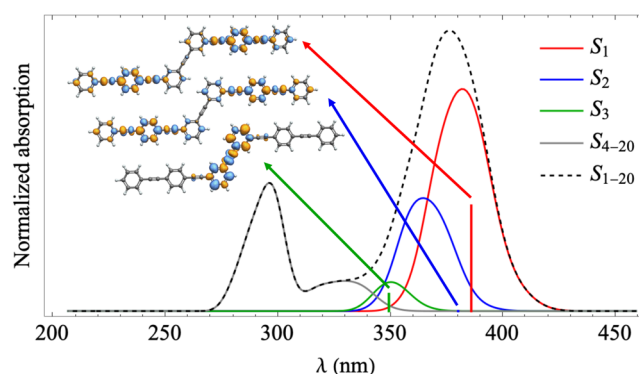


Figure 1. Normalized simulated absorption spectra of the PPE dendrimer building block with contributions from the first 20 excited states (black dashed line). Individual contributions from the first three excited states are shown as colored solid lines. Vertical lines show the corresponding energies and relative oscillator strengths for these three states at the minimum ground-state energy configuration. Arrows point to insets depicting the corresponding CIS electronic transition density localizations in real space.

molecule and the orbital localization of the respective transition densities for the first three singlet excited states calculated at the ground state minimum energy geometry. While S_3 is localized in the center of the dendrimer, S_2 and S_1 are Frenkel-exciton-like states resulting from symmetric and antisymmetric superpositions of contributions from the individual side branches. The delocalization between equivalent branches is expected for symmetric configurations such as the ground state optimal geometry for PPE. Thermal structural fluctuations break the delocalization pronounced for the ground state structure and lead to localized exciton states. This initial analysis predicts the expected mechanism of electronic relaxation after the initial excitation to S_3 : an electronic energy transfer from the center of the molecule to the branches, followed by coherent or incoherent vibrational oscillations between the branches. In order to describe this

mechanism, nonadiabatic excited-state molecular dynamics was performed using TSH, EHR, and AIMC methods. Simulations starting from the pure S_3 state provide information about the relaxation process from the center of the molecule to the branches (these simulations are provided for reference in the Supporting Information), while calculations starting from S_2 reveal the coherent interplay between the branches, as illustrated below.

Figure 2 shows the evolution in time of the excited state populations for the first two excited states after an initial

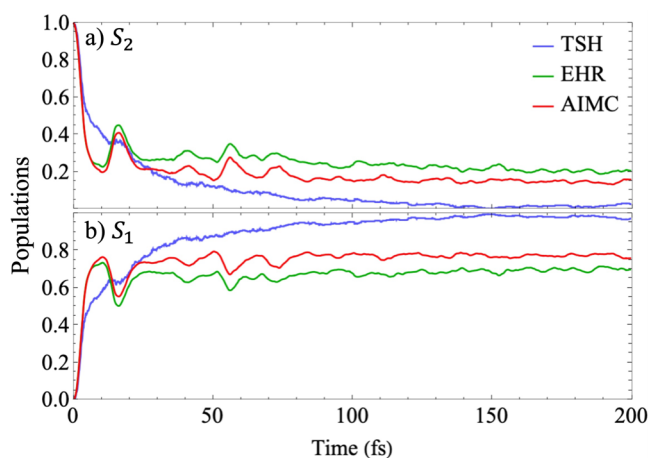


Figure 2. Evolution in time of the populations of a) S_2 and b) S_1 when the system is excited initially at S_2 for different nonadiabatic molecular dynamics methods.

vertical excitation to the S_2 state using TSH, EHR, and AIMC. The three methods show similar relaxation time scales. TSH leads to the fastest relaxation as was observed previously for many molecular systems.⁸⁸ While TSH electronic populations are calculated as the fraction of trajectories evolving on each state at any given time,¹²⁹ EHR and AIMC electronic populations are evaluated using the adiabatic population operator $\langle \hat{P}_K \rangle$ (eq 19) neglecting the nuclear overlap between different initial conditions. In the case of EHR simulations, $\langle \hat{P}_K \rangle$ is simplified to the average values of $|a_K^{(p)}|^2$, and for AIMC, it only includes clones that originated from the same initial conditions. Note that TSH uses the instantaneous decoherence (ID) approach that resets the quantum amplitude of the current state to unity after every attempted hop (regardless of whether hops are allowed or forbidden).¹¹² EHR and AIMC lead to very similar dynamics showing slower relaxations, revealing coherent oscillations in the population, which are not observed in TSH dynamics. This coherence is observed as an oscillatory interchange of electronic populations between S_1 and S_2 states during the first 20 fs of EHR and AIMC dynamics after photoexcitation. These oscillations reveal a coherent vibronic interplay that is missing in the TSH dynamics. The lack of coherence in TSH is partially attributed to an instantaneous decoherence correction,¹⁵ which assumes that the divergent wave packets become immediately decoupled. At the end of modeled excited-state dynamics, the S_1 population obtained by AIMC dynamics is positioned between TSH and EHR final values. The AIMC dynamics may be more physically relevant compared to the average Ehrenfest force, as discussed in the preceding section.

The evolution in time of $\langle \hat{\rho}_X \rangle$ (eq 20), i.e., the fraction of transition density localized in the two 3-ring fragments, is

shown in Figure 3. As shown in the inset, the two 3-ring fragments are assigned as “higher” (H) and “lower” (L) 468 469

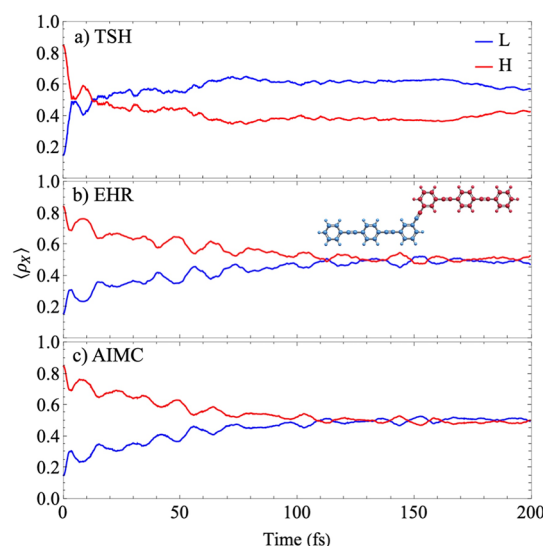


Figure 3. Evolution in time of $\langle \hat{\rho}_X \rangle$, i.e., the fraction of transition density localized over different fragments X of the molecule during a) TSH, b) EHR, and c) AIMC dynamics after photoexcitation to S_2 . The spatial descriptor assigns as “higher” (H) or “lower” (L) the 3-ring linear fragments with higher and lower transition density at $t = 0$, respectively. The inset in b) depicts the molecule delineation into fragments.

according to their correspondingly higher or lower values of $\langle \hat{\rho}_X \rangle$ at $t = 0$ for each initial condition. Thermal fluctuations initially localize the states that otherwise should be delocalized by symmetry, as shown in Figure 1 for the ground-state geometry. The results obtained during TSH, EHR, and AIMC dynamics simulations are similar qualitatively, with a faster energy redistribution between the 3-ring linear fragments observed during TSH dynamics compared to EHR and AIMC. We observe an equivalent distribution of $\langle \hat{\rho}_X \rangle$ between the 3-ring linear fragments toward the end of the simulation due to the thermally induced reorganization of the exciton over the equivalent fragments, irrespective of its initial localization.¹⁶ Further analysis of individual trajectories indicates that this final distribution of $\langle \hat{\rho}_X \rangle$ between the two fragments is attributed to a localization of the exciton on either fragment with H and L having equal probability across the ensemble rather than to a uniform delocalization over the entire dendrimer. Overall, the evolution in time of $\langle \hat{\rho}_X \rangle$ is in line with the results displayed in Figure 2. That is, TSH dynamics shows very fast damping of the oscillations, while for EHR and AIMC dynamics, oscillations persist for more than 100 fs after photoexcitation. These oscillations are damped slightly faster for AIMC due to the natural decoherence introduced by the bifurcations of the wave packet in the algorithm, as reported previously.⁸⁸

The use of the “on the fly” state limiting method can significantly decrease the computational expense in trajectory surface hopping simulations of realistically large molecular systems with a dense manifold of excited states participating in the dynamics.¹²⁶ In order to exemplify this approach, we photoexcite the PPE dendrimer building block at the S_{20} state. The use of the on-the-fly state limiting method increases the computational efficiency up to 5 times. This is achieved by the

fast reduction in the number of states during simulations (see Figure 4(a, b)).

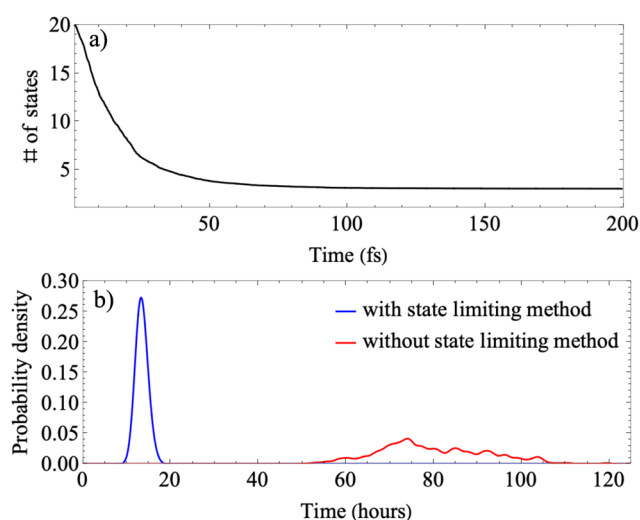


Figure 4. (a) Evolution in time of the number of states applying the on-the-fly state limiting method to eliminate states that are no longer essential for the nonradiative relaxation dynamics during TSH simulations; (b) Comparison of the distribution of computational time required for simulations with and without applying the on-the-fly state limiting method. A threshold of 2 states is used, and all states above the current state $\alpha + 2$ are removed throughout the simulations.

NEXMD v2.0 allows us to analyze the impact of specific nuclear motions by performing TSH nonadiabatic excited state molecular dynamics in the presence of constraints on certain distances or vibrational normal modes. In order to illustrate this feature, simulations constraining the four triple bonds localized in the 3-ring linear units in a PPE dendrimer building block have been performed. Figure 5 shows that these

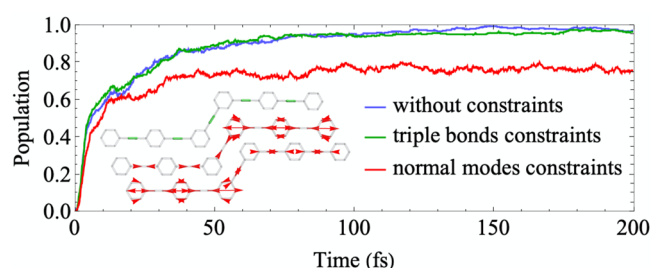


Figure 5. Evolution in time of the average population of the S_1 electronic state without constraints, with constraints applied to the four triple bonds localized on the 3-ring linear units, and with normal mode constraints applied to the two normal modes that overlap the most with the nonadiabatic coupling vector. The inset shows the triple bonds' localizations (green) and the two normal modes (red).

constraints do not have a significant impact in the electronic relaxation. Nevertheless, a more efficient slowdown of the electronic relaxation can be achieved by performing normal-mode constraints. Figure 5 shows the results of introducing constraints into the two normal modes that overlap the most with the direction of the $S_2 \rightarrow S_1$ transition, dictated by the nonadiabatic coupling vector d_{12} . Despite that these normal modes involve concerted motions of stretching in the direction of the triple bonds, they also imply minor motions associated with the highest frequency vibrational normal modes of phenyl

rings. This result reveals the main role of these selective vibrational motions on the energy transfer process and can be a useful guide for the development of reduced dimensionality Hamiltonians.

4. CONCLUSIONS

The second release of the NEXMD (Nonadiabatic EXcited state Molecular Dynamics) software package incorporates Ehrenfest (EHR) hybrid quantum-classical dynamics and the Ab-Initio Multiple Cloning (AIMC) sampling technique for the Multiconfigurational Ehrenfest quantum dynamics method, complementing the previously implemented trajectory surface hopping (TSH) method. Besides, other significant features are summarized in Table 1. NEXMD v2.0 expands the range of applications to a larger variety of photophysical processes in multichromophore organic molecules. In particular, the AIMC nonadiabatic molecular dynamics algorithm is a controlled approximation allowing for an appropriate description of electron-vibrational coherences appearing in many molecular systems. The implementation of TSH, EHR, and AIMC on the same footing within the updated NEXMD v2.0 framework permits users to explore individual algorithms and directly compare different methods applied to a particular molecular system or a process of interest. Further, additional NEXMD v2.0 capabilities such as extensive analysis of vibrational degrees of freedom and ability to artificially exclude structural degrees of freedom of choice from nonadiabatic dynamics provide practical tools for designing flexible numerical experiments. The presented illustrative examples demonstrate some of the weaknesses and strengths of these NAMD methods for the case of a PPE dendrimer. While both TSH and EHR dynamics may not properly treat decoherence in electronic systems, AIMC describes decoherences in a natural way. Therefore, the AIMC method is suitable for practical applications, such as time-dependent nonlinear spectroscopic signals conditioned by the presence of vibronic coherences. Broader application with NEXMD v2.0 can thus validate various nonadiabatic algorithms and stimulate further method development toward a more accurate description of photophysical processes in multichromophore organic molecules.

Altogether, the NEXMD version 2.0 software represents a numerically efficient method to perform excited state dynamics on molecules and molecular clusters. Perhaps the largest weakness of the current method is in the underlying semiempirical Hamiltonians underpinning the numerical efficiency but allowing only a semiquantitative accuracy. Here we mention that most of the NEXMD features and algorithms have been recently implemented into the NWChem software package⁴² allowing interfacing a more accurate but numerically expensive time-dependent Density Functional Theory description of electronically excited states. Further, recent advances into interfacing machine learning techniques with semiempirical quantum mechanics^{130–133} promise to provide a breakthrough in semiempirical accuracy. Additionally, the development of SIMD architectures provides an avenue for significantly decreasing the computational challenges associated with simulations involving many distinct trajectories. Future code additions such as periodic boundary conditions will open possibilities toward modeling solids. Besides, future implementations of nonlinear spectroscopic signal calculations from dynamical information, like transient absorption, 2D electronic spectroscopy, and X-ray nonlinear probes,^{14,16} will provide a more direct comparison with

583 experiments. These additional capabilities promise to provide
584 significant advances in the modeling of photocatalyzed
585 reactions, light absorption, and reactive chemistry critical to
586 a green energy future.

587 ■ ASSOCIATED CONTENT

588 Data Availability Statement

589 Program code, license, and documentation may be accessed at:
590 <https://github.com/lanl/NEXMD>.

591 ■ Supporting Information

592 The Supporting Information is available free of charge at
593 <https://pubs.acs.org/doi/10.1021/acs.jctc.3c00583>.

594 Computational and technical details for the exemplary
595 simulations and a comparison between nonadiabatic
596 excited state methods when exciting to S_3 (PDF)

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678 Notes

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