

# Modeling Non-adiabatic Dynamics in Nanoscale and Condensed Matter Systems

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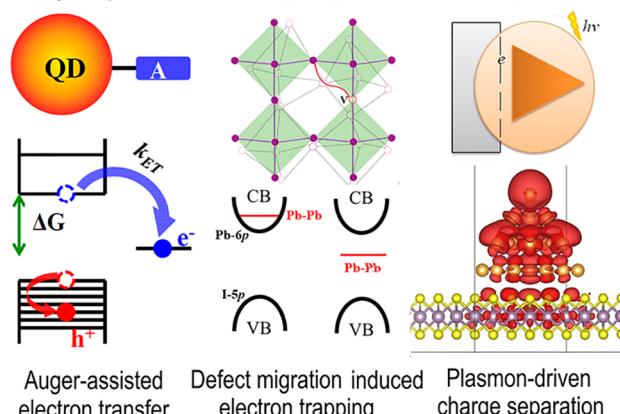
**CONSPECTUS:** Rapid, far-from-equilibrium processes involving excitation of electronic, vibrational, spin, photon, topological, and other degrees of freedom form the basis of modern technologies, including electronics and optoelectronics, solar energy harvesting and conversion to electrical and chemical energy, quantum information processing, spin- and valleytronics, chemical detection, and medical therapies. Such processes are studied experimentally with various time-resolved spectroscopies that allow scientists to track system's evolution on ultrafast time scales and at close to atomistic level of detail. The availability of various forms of lasing has made such measurements easily accessible to many experimental groups worldwide, to study atoms and small molecules, nanoscale and condensed matter systems, proteins, cells, and mesoscopic materials. The experimental work necessitates parallel theoretical efforts needed to interpret the experiments and to provide insights that cannot be gained through measurements due to experimental limitations.

Non-adiabatic (NA) molecular dynamics (MD) allows one to study processes at the atomistic level and in the time domain most directly mimicking the time-resolved experiments. Atomistic modeling takes full advantage of chemical intuition and principles that guide design and fabrication of molecules and materials. It provides atomistic origins of quasi-particles, such as holes, excitons, triions, plasmons, phonons, polarons, polaritons, spin-waves, momentum-resolved and topological states, electrically and magnetically polarized structures, and other abstract concepts. An atomistic description enables one to study realistic aspects of materials, which necessarily contain defects, dopants, surfaces, interfaces, passivating ligands, and solvent layers. Often, such realistic features govern material properties and are hard to account for phenomenologically. NA-MD requires few approximations and assumptions. It does not need to assume that atomic motions are harmonic, that electrons are Drude oscillators, that coupling between different degrees of freedom is weak, that dynamics is Markovian or has short memory, or that evolution occurs by exponential kinetics of transitions between few states. The classical or semiclassical treatment of atomic motions constitutes the main approximation of NA-MD and is used because atoms are 3–5 orders of magnitude heavier than electrons. NA-MD is limited by system size, typically hundreds or thousands of atoms, and time scale, picoseconds to nanoseconds. The quality of NA-MD simulations depends on the electronic structure method used to obtain excited state energies and NA couplings.

NA-MD has been largely popularized and advanced in the chemistry community that focuses on molecules. Modeling far-from-equilibrium dynamics in nanoscale and condensed matter systems often has to account for other types of physics. At the same time, condensed phase NA-MD allows for approximations that may not work in molecules. Focusing on the recent NA-MD developments aimed at studying excited state processes in nanoscale and condensed phases, this Account considers how the phenomena important

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## Complex phenomena and synergies require new approaches



Auger-assisted electron transfer

Defect migration induced electron trapping

Plasmon-driven charge separation

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on the nanoscale can be incorporated into NA-MD and what approximations can be made to increase its efficiency with complex systems and processes.

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- Zhou, G. Q.; Lu, G.; Prezhdo, O. V. Modeling Auger Processes with Nonadiabatic Molecular Dynamics. *Nano Lett.* **2021**, *21*, 756–761.<sup>3</sup> Method for modeling Auger-type particle–particle scattering due to Coulomb interactions in nanoscale systems, also including electron–vibrational coupling.
- Wang, B. P.; Chu, W. B.; Tkatchenko, A.; Prezhdo, O. V. Interpolating Nonadiabatic Molecular Dynamics Hamiltonian with Artificial Neural Networks. *J. Phys. Chem. Lett.* **2021**, *12*, 6070–6077.<sup>4</sup> Acceleration of nonadiabatic molecular dynamics with machine learning by time extrapolation of trajectories and time interpolation of more complex properties, such as the non-adiabatic coupling, along the trajectories.

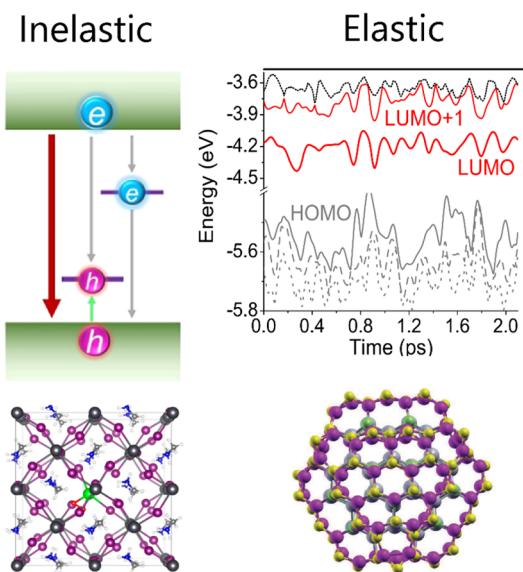
## INTRODUCTION

Non-adiabatic (NA) molecular dynamics<sup>1–6</sup> (MD) plays a particularly important role among theoretical techniques used to study far-from-equilibrium quantum processes and ranging from full quantum dynamics of small systems to kinetic models and phenomenological theories that can describe essentially any system and experiment. The basic NA-MD ideas date to the very early days of quantum mechanics. In 1927, Ehrenfest<sup>7</sup> considered equations of motions for quantum-mechanical expectation values and showed that they have the same form as the classical equations of motion, thereby allowing one to couple classical variables to quantum-mechanical averages. This gave rise to the quantum–classical mean-field approximation, known as the Ehrenfest approach. In 1932, Landau<sup>8</sup> and Zener<sup>9</sup> investigated transitions between quantum (electronic) states induced by a classical (atomic) motion and derived semiclassical transition probabilities. The Landau–Zener expressions were generalized by Nikitin,<sup>10</sup> Miller,<sup>11</sup> Zhu and Nakamura,<sup>12</sup> and others and are used in modern NA-MD simulations.<sup>13,14</sup> Scattering experiments performed on molecules in the gas phase and on surfaces, combined with the rise of computers, stimulated rapid development of NA-MD in the 1960s and 1970s,<sup>10,11,15–17</sup> most notably, a family of trajectory surface hopping (SH) approaches originated by Tully.<sup>17</sup> The experimental shift toward condensed matter and nanoscale created new theoretical challenges and spurred further NA-MD developments in the 1990s,<sup>18,19</sup> as exemplified by Tully's modification<sup>18</sup> of the original<sup>17</sup> SH technique.

The properties of condensed phases and nanoscale materials are quite different from molecular properties. NA transitions in molecules occur through conical intersections and avoided crossings. Usually, electronic energy levels are widely spaced at the initial time and approach closely during transitions. Decay of electronic excitations to the ground state in semiconductors occurs across large energy gaps, while intraband relaxation happens through dense state manifolds. Photoinduced geometric changes are observed much less frequently in materials<sup>20</sup> than in molecules.<sup>5</sup> Molecules are small and often not in thermal equilibrium. In contrast, quantum dynamics in condensed phases rapidly approach equilibrium, and different particles, for example, electrons vs phonons, can reach local equilibria on different time scales.<sup>21</sup> Besides energy exchange resulting from inelastic scattering, elastic scattering leads to rapid loss of quantum coherence in condensed phases. For example, electronic decoherence in quantum dots, carbon nanotubes, and other nanosystems takes femtoseconds,<sup>22</sup> while coherence in molecules can be maintained for a long time<sup>23</sup> and exhibit a nontrivial evolution.<sup>24</sup> Electronic excitations in molecules involve few electrons, while nanoscale objects can support many excited electrons. Perturbation of even a single electron in a molecule can drastically change the electron density distribution, for example, transition from a bonding to an antibonding orbital causing bond breaking. In contrast, excitation of a few electrons in a nanoscale object containing thousands of electrons has little influence on the overall electron density and geometric structure. Often, thermal atomic fluctuations are more important than geometric changes induced by photoexcitation. Multiple electrons and holes present in nanoscale systems interact through Coulomb forces, scatter off each other via Auger-type processes, and form complex quasi-particles, such as excitons, triions, multiexcitons, and collective plasmon states. Coulomb interactions can be screened by a material's intrinsic dielectric response or excitation of multiple charge carriers that behave in a plasma-like manner and dissociate excitons into free particles.<sup>25</sup> van der Waals interactions can be particularly important in large systems composed of multiple components. Such interactions occur through plasmon-like collective states<sup>26</sup> and can lead to new electron dynamics regimes.<sup>27</sup> NA-MD approaches need to capture these phenomena, in order to successfully describe nanoscale and condensed matter systems.

## DETAILED BALANCE AND THERMODYNAMIC EQUILIBRIUM

Condensed phase and nanoscale systems contain many degrees of freedom that dissipate the excess energy deposited into the system by an external perturbation, such as an absorbed photon, an injected electron, or a chemical species, to initiate a nonequilibrium dynamic. Productive processes, for example, charge separation, photoelectrochemical reactions, and spin or electron-momentum transfer, constantly compete with energy and phase dissipation, Figure 1. The simplest Ehrenfest approach errs in describing dissipation.<sup>28,29</sup> Fortunately SH, developed to capture correlation between electronic states and atomic trajectories, also gives detailed balance between transitions upward and downward in energy. It is achieved by



**Figure 1.** (left) Inelastic electron–phonon interactions induce nonradiative relaxation, as in metal halide perovskites exposed to oxygen and light. Adapted with permission from ref 41. Copyright 2019 American Chemical Society. (right) Out-of-phase fluctuations of electronic levels cause decoherence, which rationalizes phonon bottleneck in quantum dots through the quantum Zeno effect. Adapted with permission from ref 34. Copyright 2013 American Physical Society.

velocity rescaling performed after an electronic transition, introduced<sup>18</sup> to conserve the total quantum–classical energy. Energy conservation and detailed balance are less important for strongly perturbed systems and short-time dynamics. Performed along the direction of the NA coupling vector,  $\langle \varphi_j | \nabla_R | \varphi_k \rangle$ ,

$$\langle \varphi_j | \frac{\partial}{\partial t} | \varphi_k \rangle = \langle \varphi_j | \nabla_R | \varphi_k \rangle \dot{\mathbf{R}} = \frac{\langle \varphi_j | \nabla_R H | \varphi_k \rangle}{\varepsilon_k - \varepsilon_j} \dot{\mathbf{R}} \quad (1)$$

the rescaling was justified by Coker<sup>30</sup> considering Pechukas force,<sup>15</sup> which is analogous to the Ehrenfest force but takes the system from one state to another. Due to ergodicity in large systems, the probability that the velocity component to be rescaled has the needed kinetic energy is given by the Boltzmann factor. Hops upward in energy are accepted by the Boltzmann probability, leading to thermodynamic equilibrium.

Although trajectory SH is most popular in NA-MD, the Ehrenfest approach has important advantages. It can be rigorously derived,<sup>31</sup> while SH methods are models. SH requires random sampling to determine a hop sequence, while the Ehrenfest method is fully deterministic. For a given initial condition, only one Ehrenfest trajectory is needed, while multiple SH trajectories should be generated, raising the computational expense. The Ehrenfest method was modified to achieve detailed balance by Bastida et al., who considered quantum correction factors to classical correlation functions.<sup>28</sup> The correction factors introduce detailed balance not satisfied by classical correlation functions and recover correct rates when energy is exchanged far-from-resonance, between systems with different intrinsic frequencies. Subsequently, Akimov and Prezhdo<sup>32</sup> combined the Bastida approach with another nonlinear modification of the Schrödinger equation incorporating decoherence, to develop the Ehrenfest approach satisfying both detailed balance and decoherence.<sup>29</sup>

## ■ LOSS OF QUANTUM COHERENCE

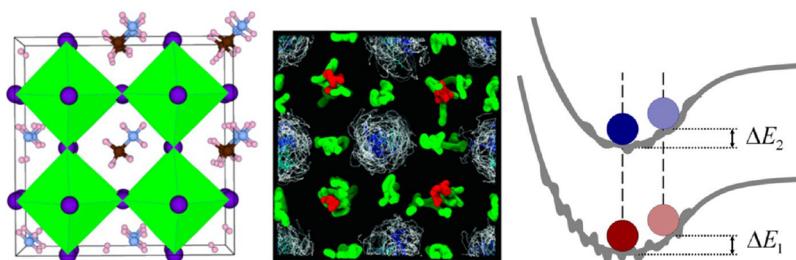
Similar to inelastic processes that cause energy relaxation, elastic scattering is essential in large systems, Figure 1. It randomizes quantum phase information and is known as pure dephasing in the optical response theory<sup>22</sup> and decoherence in quantum mechanics.<sup>23,33</sup> Decoherence can alter dramatically transition times, as exemplified by the quantum Zeno<sup>34</sup> and anti-Zeno<sup>35</sup> effects. Decoherence occurs by coupling of a quantum-mechanical subsystem to a quantum-mechanical bath, and its description requires generalization of the unitary evolution that conserves wave function norm. Decoherence can be obtained by averaging over bath variables under a simplified model. For example, vibrating atoms can be described as Gaussian wave packets centered at classical trajectories.<sup>36</sup> The quantum Brownian motion concept provides an alternative description. For individual systems, it generalizes the Schrödinger equation to include friction and noise, making it analogous to the classical Langevin equation. Using a minimal number of postulates Lindblad derived the simplest form of such stochastic Schrödinger equation.<sup>37</sup> Evolution of ensembles is described by density matrices. Then, decoherence generalizes the Liouville–von Neumann equation to the quantum Fokker–Planck equation.<sup>33</sup> Decoherence collapses superposition wave functions into pure states and gives decay of off-diagonal density matrix elements.

Bittner and Rossky<sup>38</sup> considered the density matrix formulation and modified Tully's SH approach.<sup>18</sup> Prezhdo<sup>39</sup> introduced decoherence into NA-MD at the wave function level and coupled the stochastic Schrödinger equation to a classical trajectory in a mean-field/Ehrenfest manner, providing the physical mechanism for trajectory branching through decoherence.<sup>6,39,40</sup> Decoherence induced SH<sup>1</sup> is fundamentally rooted in the theory of quantum open systems, employs traditional quantum-mechanical probabilities avoiding ad hoc SH expressions, and uses the quantum jump interpretation of measurement to achieve an efficient and robust NA-MD methodology that includes simultaneously decoherence and detailed balance.

Pure dephasing of the optical response theory provides a robust estimate of decoherence time for condensed phase systems.<sup>22</sup> It can be benchmarked to homogeneous optical line widths and photon-echo experiments. Decoherence in smaller molecular systems is more complex, can involve both dephasing and rephasing, and may require more complex models.<sup>24</sup>

To incorporate decoherence into the Ehrenfest approach, Akimov and Prezhdo<sup>32</sup> considered the Meyer–Miller–Stock–Thoss representation of the time-dependent Schrödinger equation, making it equivalent to classical dynamics for a simple Hamiltonian but with the number of variables equal to the Hilbert space dimensionality. Such mapping provides an intuitive classical representation of the decoherence process. The mapped decoherence measure was included in the classical Hamiltonian, adding energy to regions with large coherence. The coherence penalty prevented development of coherences. Mapped back into the Hilbert space, the coherence penalty made the Schrödinger equation nonlinear. In combination with the nonlinear modification of Bastida et al.,<sup>28</sup> the development gave the Ehrenfest method with decoherence and detailed balance,<sup>29</sup> the two key features needed for application of Ehrenfest dynamics to nanoscale and condensed matter.

Decoherence is very important if transition takes longer than coherence loss between states, that is, if inelastic scattering is



**Figure 2.** (left and middle) Thermal fluctuations in condensed phase, for example, metal halide perovskites, are often more significant than geometry changes induced by excitation, justifying the classical path approximation (CPA). Adapted with permission from ref 42. Copyright 2017 American Chemical Society. (right) Fluctuations also lead to quantum coherence loss. Adapted with permission from ref 23. Copyright 2013 American Chemical Society. Modeling NA dynamics of polarons and lowest energy excitons can be performed under the CPA as well.

slower than elastic scattering. Decoherence can be ignored in the opposite limit, if transitions are faster than coherence loss. The former situation is encountered during transitions across large energy gaps.<sup>25,41–43</sup> The latter is seen during relaxation across dense manifolds of states, for example, bands,<sup>2,44</sup> or if avoided crossings make electronic states energetically close.<sup>5</sup>

## CLASSICAL PATH APPROXIMATION

Excited state energies, forces, and NA couplings determine the computational cost of NA-MD simulations in most cases. Typically, excited states are orders of magnitude harder to study than ground states. Effective single-particle theories, such as density functional theory (DFT), provide good descriptions of ground states. Excited states can be described by linear response time-dependent (TD) DFT. More advanced theories are required in some cases, for example, for doubly excited states. A simple description of excited states is provided by constrained DFT, in which constraints are imposed on occupations of Kohn–Sham (KS) orbitals, as in delta self-consistent-field<sup>45</sup> (SCF) calculations, or on electron spatial localization.<sup>46</sup> The cost of constrained DFT is similar to that of ground state DFT, provided SCF convergence is easily achieved. KS excitations give an even simpler description of excited states, for example, based on the Koopmans theorem, since the SCF procedure is performed only for the ground state. Such simplified models work particularly well for condensed phases, since excitation of one or a few electrons from hundreds or thousands creates little change to the total electron density. Then, the DFT functional used for excited state properties can be calculated using the ground state electron density. When employed in real-time time-dependent DFT calculations, such approximation provides significant savings, since the electron density is updated every atomic time step, for example, femtosecond, rather than every electronic time step, for example, attoseconds, and the SCF procedure is repeated 100–1000 times less frequently.

The classical path approximation (CPA) provides large savings even compared to the KS and other simple descriptions of excited states. One assumes that atomic trajectories drive electronic evolutions, while electronic excitations have little influence on atom dynamics. Initially employed for studying collisions of small molecules in gas phase,<sup>10,11,16,17</sup> the CPA is valid for many nanoscale and condensed matter systems, which either oscillate near equilibrium geometries or undergo large scale anharmonic motions driven by finite temperature rather than electronic excitation, Figure 2. Then, a single ground state trajectory can be used to drive electronic evolution. CPA validity can be evaluated by comparing changes in equilibrium geometries between excited and ground states with amplitudes

of thermally induced geometry fluctuations. Even if a system undergoes a photocatalytic process or an electronically driven structural change, such as photoinduced melting or phase transition,<sup>20,47</sup> electronic relaxation through dense manifolds of states to the lowest energy excited state typically proceeds faster than the structural change. Then, the CPA can be applied with the excited state trajectory obtained by constrained DFT, for example, delta-SCF.<sup>45,46</sup> An ensemble of excited state trajectories is replaced with a single ground state trajectory, which can be the trajectory used to sample initial conditions for the standard NA-MD calculation. Not only the need for generating hundreds of excited state trajectories is eliminated, but also the trajectory ensemble is replaced with one trajectory. Even if the costs of excited and ground state calculations are comparable, the CPA provides large computational savings.

The CPA was applied to SH<sup>2,48</sup> and the Ehrenfest method corrected for decoherence and detailed balance.<sup>29</sup> The CPA replaces velocity rescaling responsible for detailed balance in SH with multiplication of probabilities of transitions up in energy by the Boltzmann factor. The CPA was used successfully with Tully's fewest switches SH<sup>2,18</sup> and decoherence induced surface hopping<sup>1,48</sup> to study excited state dynamics in many nanoscale and periodic materials.

The CPA eliminates the need to evaluate the vector form of the NA coupling,  $\langle \varphi_j | \nabla_R | \varphi_k \rangle$ , eq 1, used for the velocity rescaling. Instead, one can calculate the scalar NA coupling,  $\langle \varphi_j | \frac{\partial}{\partial t} | \varphi_k \rangle$ , which enters the time-dependent Schrödinger equation. Analytic expressions can be derived and implemented for the vector form using  $\frac{\langle \varphi_j | \nabla_R H | \varphi_k \rangle}{\varepsilon_k - \varepsilon_j}$ , which is a corollary of the

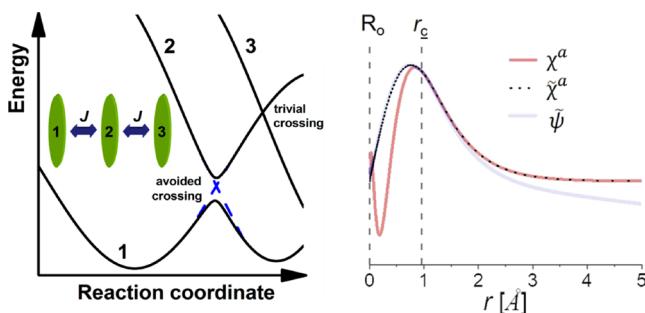
Hellmann–Feynman force derivation. If analytic NA coupling is not available, numeric calculation of the NA coupling vector is computationally expensive in high dimensions. In contrast, the NA scalar can be easily computed by overlap of adiabatic wave functions at adjacent time steps.<sup>49</sup> The calculations of both forms in large systems carry additional caveats.

## ACCURATE CALCULATION OF NON-ADIABATIC COUPLING

A key quantity in NA-MD, the NA coupling depends on adiabatic wave functions that are solutions of the time-independent Schrödinger equation and adiabatic wave functions are defined up to a sign, or more generally phase, for example, in periodic calculations with  $k$ -points. Consequently, NA couplings evaluated at different time steps along a trajectory can differ by random sign or phase, typically making transitions artificially fast. The NA coupling sign or phase should be adjusted if it

changes abruptly, for example, by computing adiabatic wave function overlap between sequential MD time steps.<sup>50</sup>

Trivial<sup>51</sup> or “unavoided” crossings, Figure 3, are another critical issue that also can be addressed through overlap of



**Figure 3.** (left) NA coupling diverges when energy levels of weakly coupled subsystems, 1 and 3, cross. Adapted with permission from ref 51. Copyright 2014 American Chemical Society. (right) Core pseudopotentials require complex expressions for the NA coupling, while allowing for approximations, since the core wave function,  $r < r_0$ , moves with the atom. Adapted with permission from ref 49. Copyright 2021 American Chemical Society.

adiabatic wave functions at sequential time steps. If different parts of a large system are coupled weakly and their states become degenerate, the NA coupling diverges, since it is inverse with the energy gap, eq 1. This can happen in molecular crystals, polymers, dendrimers, quantum dot assemblies, van der Waals structures, etc. The situation is trivial, because the population should simply remain on the same fragment after the abrupt switch of the adiabatic state energies, implying that the NA transition should happen with 100% probability. The trivial crossing can be handled once it is identified by an abrupt change in the adiabatic wave function overlap.

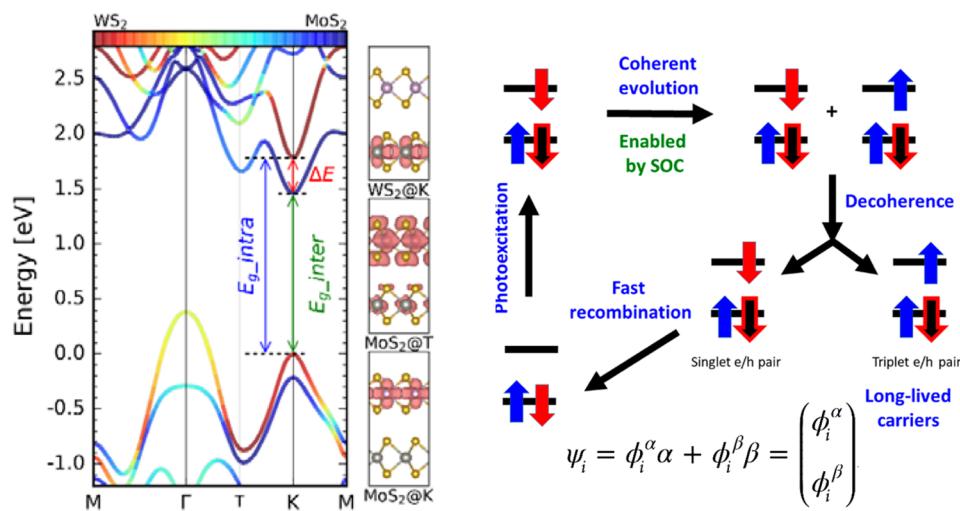
The time-dependent Schrödinger equation can be solved in a diabatic basis, such as atomic orbitals, or a position or momentum (plane-waves) grid. Still, the NA coupling may be needed to compute SH probabilities, as in Tully's fewest

switches SH.<sup>18</sup> In such case, probability conservation laws may be found and used to compute the problematic transition probability.<sup>51</sup> The trivial crossing problem becomes more complex when small electronic coupling between quasi-degenerate fragments cannot be ignored. Then, trivial crossings can be defined using a carefully chosen threshold. Reducing the atomic time step around the trivial crossing can help as well. The trivial crossing issue is particularly important in transport calculations.<sup>52</sup> Since the modified Ehrenfest<sup>29</sup> and decoherence induced SH<sup>1</sup> methods use the standard quantum-mechanical probability, solving the time-dependent Schrödinger equation in a diabatic basis resolves the trivial crossing issue. Still, decoherence and transport processes require definition of a “pointer” or hopping basis, which can cause similar problems.<sup>52</sup>

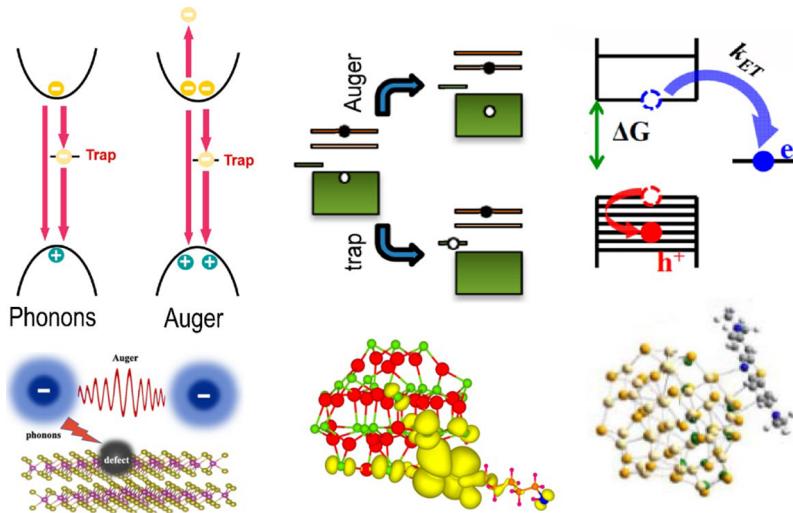
Core pseudopotentials are commonly used in electronic structure calculations, Figure 3, and the NA coupling should be properly evaluated in the core region. Since the core region changes little as atoms move, its contribution can be calculated only once, giving an efficient approximation for elements without d-electrons, while d-elements have to be treated with care.<sup>49</sup>

## ■ SPIN AND ELECTRON-MOMENTUM RESOLVED DYNAMICS

Nanoscale and periodic systems can exhibit more complex physics than molecules. For example, spin-orbit coupling created by heavy elements, such as Pb present in metal halide perovskites,<sup>42,43,53</sup> mixes spin states and causes band inversion producing topological states.<sup>54</sup> Electron wave functions become two- or four-component spinors, and the NA coupling has to be calculated in the spinor space. This was done by Akimov and co-workers,<sup>53</sup> who demonstrated that spin-orbit coupling notably accelerates electron-vibrational relaxation in metal halide perovskites. If spin-orbit interaction is not very strong, a spin-pure representation of NA-MD can be used and spin-orbit elements can be calculated to investigate intersystem crossing. The choice of spin-diabatic vs spin-adiabatic representation for NA-MD depends on both spin-orbit coupling strength and the process under investigation. A similar choice often has to be



**Figure 4.** (left) Charge and energy transfer across van der Waals heterojunctions formed by transition metal dichalcogenides require electron momentum ( $k$ -point) analysis. Adapted with permission from ref 56. Copyright 2017 American Chemical Society. (right) Spin-orbit coupling (SOC) opens new channels and involves spinor wave functions. Adapted with permission from ref 53. Copyright 2018 American Chemical Society. Both  $k$ -points and SOC require advanced NA coupling expressions and analyses.



**Figure 5.** Auger-type transitions driven by Coulomb interactions are particularly important on nanoscale due to quantum confinement and high densities of states. (left) Energy released by trapped particle can go to either vibrations or another particle. Adapted with permission from ref 25. Copyright 2019 American Chemical Society. (middle) Bottleneck to electron–phonon relaxation in semiconductor quantum dots is broken by electron–hole energy exchange and can be recovered by hole trapping. Adapted with permission from ref 58. Copyright 2015 American Chemical Society. (right) Auger-assisted electron transfer eliminates the Marcus inverted regime, allowing fast charge separation even for large driving forces ( $\Delta G$ ). Adapted with permission from ref 57. Copyright 2014 American Chemical Society.

made with respect to the Coulomb coupling between non-interacting particles in nanoscale systems.<sup>55</sup> Coulomb interactions are strong in molecules, and NA-MD calculations are performed in the traditional Coulomb-adiabatic representation. Coulomb interactions are weaker in nanoscale systems, and the Coulomb-diabatic representation can be beneficial.<sup>3</sup> Whether or not one uses diabatic or adiabatic representation for the spin–orbit and Coulomb interactions, the electron–vibrational interaction still can be represented by the NA derivative coupling between the corresponding electronic states, eq 1.

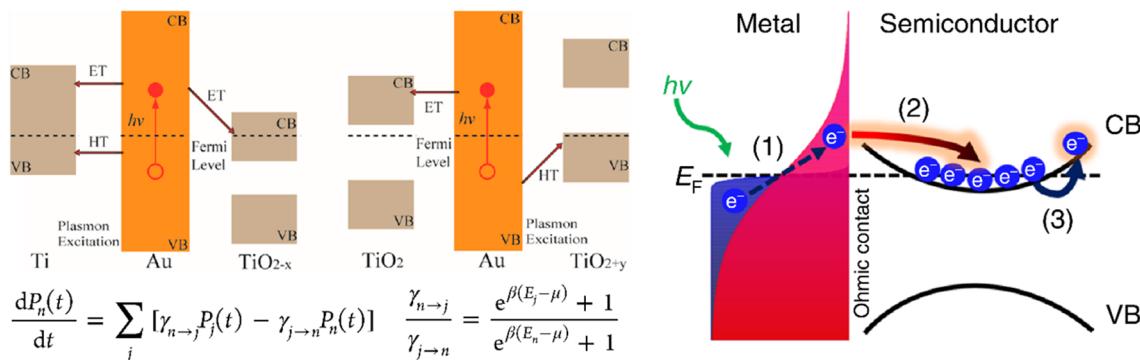
Electronic states of periodic systems are classified into bands using  $k$ -points reflecting electron momentum, Figure 4. Many time-resolved measurements present  $k$ -point resolution, and NA-MD simulations have to be performed and analyzed accordingly.<sup>56</sup> The  $k$ -points nomenclature is used even for finite systems, for example, nanocrystals, which are composed of multiple unit cells of the parent bulk. Often, nanoscale systems are studied by condensed matter physicists who use infinite bulk concepts, for example, excitons, phonons, and  $k$ -points, with finite nanoscale objects. One can apply traditional NA-MD to supercells and use zone-folding analysis to assign  $k$ -points associated with unit cells. Alternatively, one can include  $q$ -points for atomic motions and consider NA coupling between different electronic  $k$ -points. The  $q$ -points are needed to conserve the overall electron–vibrational momentum. Since atomic motions are anharmonic in NA-MD,  $q$ -points of harmonic phonons should be generalized. One may assume that anharmonic “phonons” generating NA coupling between different electronic  $k$ -points exhibit flat dispersion, for example, their instantaneous frequency is independent of the  $q$ -point.

Controlling transitions between electronic states that differ in spin or electron-momentum gives rise to emerging spintronics and valleytronics technologies, and therefore, NA-MD methods capable of modeling such processes can find exciting applications in the near future.

## ■ MANY-PARTICLE PROCESSES

Nanoscale systems are special in exhibiting multiple interacting excitations, as exemplified by multiple exciton generation and recombination.<sup>22</sup> Interactions are strong in molecules; however, they become unstable with more than 1–2 excited electrons. Bulk can support many particles; however, they are far from each other and interact very weakly. Nanoscale objects combine both features. They can contain many particles with relatively strong interactions between them due to quantum confinement. Electrons, the fundamental particles, can interact and form complex quasi-particles, for example, excitons, trions, biexcitons, or plasmons. Electrons, holes, and more complex particles can scatter through Coulomb coupling. Such Auger-type processes can drastically change expectations stemming from molecular intuition, for example, eliminating the Marcus-inverted regime with Auger-assisted charge transfer,<sup>57</sup> Figure 5. Auger processes compete with phonon driven dynamics, providing efficient nonradiative charge trapping and recombination channels.<sup>25</sup> NA-MD methods for nanoscale systems should include many-particle processes.

Just as DFT provides an effective independent-particle description that in principle can capture all many-body interactions, it is possible to model many-particle transitions through NA coupling between independent-particle states.<sup>22,58</sup> The electronic structure component of such calculations is simple, since Coulomb matrix elements obtained with expensive GW and Bethe–Salpeter theories are not required. Challenges arise because the NA coupling is a single-particle operator and cannot couple independent-particle states that differ in occupations of more than one particle. Many-particle transitions occur as higher order processes through intermediate states, analogously to the Raman process. Large basis sets are required to achieve convergence with intermediate states, but sparse matrix techniques can be used.<sup>22</sup> Combining many-particle transitions with electron–vibrational relaxation requires detailed balance that is missing from the time-dependent Schrödinger equation for electrons interacting with classical



**Figure 6.** Metals and intrinsically doped semiconductors contain many active electrons. Master equations with SH transition probabilities can model such systems. (left) Plasmon-driven charge transfer from Au films depends strongly on nonstoichiometric  $\text{TiO}_x$  composition. Adapted with permission from ref 63. Copyright 2020 American Chemical Society. (right) Energy transfer from metals to semiconductors occurs through ballistic interactions between charges. Adapted with permission from ref 21. Copyright 2021 Springer.

atoms. SH gives detailed balance but can have problems with many-particle transitions. For example, the most popular method, Tully's fewest switches SH,<sup>18</sup> can be regarded as a first order theory with respect to the NA coupling, since the SH probability is linear in the coupling. Hence, transitions between independent-particle states differing in more than one particle are not possible in the absence of Coulomb coupling, while transitions through high-energy virtual states are forbidden due to detailed balance: hops to high energy states are rejected. To resolve this problem, Wang and Prezhdo generalized Tully's method by re-summing state-to-state population fluxes<sup>59</sup> and formulated Tully's SH for Liouville space.<sup>60</sup> NA-MD methods based on standard quantum-mechanical probabilities, such as decoherence induced SH<sup>1</sup> and Ehrenfest with decoherence and detailed balance,<sup>29</sup> do not exhibit this problem.

Modeling many-particle processes through Coulomb coupling provides a more rigorous approach.<sup>3,55,61</sup> Coulomb matrix elements can be calculated via linear-response time-dependent DFT<sup>3</sup> or GW and Bethe–Salpeter theories.<sup>55</sup> Dielectric screening is important and can be included using the bulk dielectric constant, through tuning the separation parameter of range-separated DFT functionals,<sup>3</sup> or by computing the dielectric function encountered in the GW theory.<sup>55</sup> Since GW calculations are expensive, they can be repeated only when the system undergoes significant changes in geometric or electronic structure.

NA-MD simulations can be carried out in an electronically adiabatic or diabatic representation, depending on the process of interest and the initial conditions. Energy exchange between electrons and holes in semiconductor quantum dots, breaking the phonon bottleneck to nonradiative relaxation of “hot” electrons, can be modeled in the electronically diabatic picture,<sup>3</sup> since Coulomb interactions are weak and experiments are interpreted using independent particles. Coulomb interactions are strong in transition metal dichalcogenides and other two-dimensional semiconductors, due to weak dielectric screening perpendicular to material's plane. Then, the adiabatic (exciton) basis is typically more appropriate; however, the diabatic basis can be used to describe spin-valley dynamics of spin-polarized electron–hole pairs.<sup>55</sup> In the latter case, the exchange part of the Coulomb operator matrix element plays the key role. Further, the basis used can be adiabatic with respect to the Coulomb interaction and diabatic with respect to spin–orbit coupling or vice versa. The adiabatic basis requires time-consuming diagonalization of the Coulomb matrix. Performing NA-MD

in the electronically diabatic representation, with Coulomb interactions providing off-diagonal matrix elements that, together with the NA coupling, couple many-body independent-particle states can be more computationally efficient.<sup>3</sup>

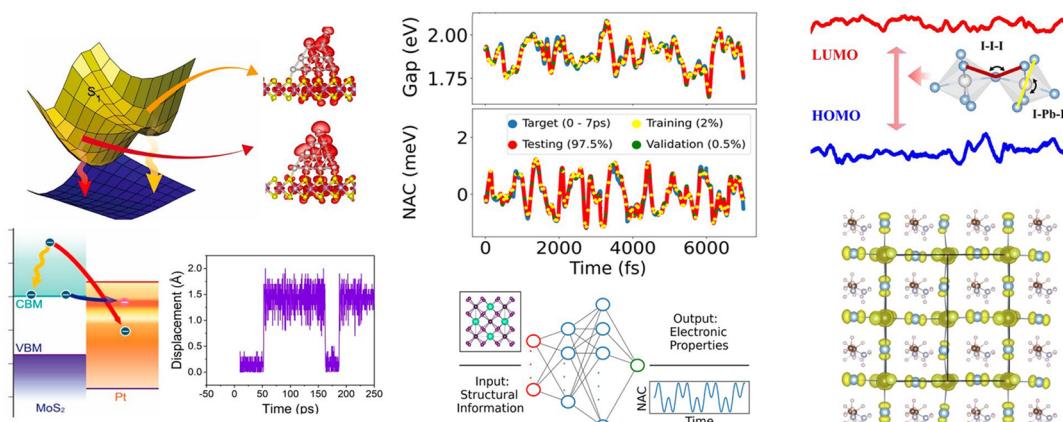
## ■ EVOLUTION OF ENSEMBLES OF PARTICLES

SH approaches can be viewed as master equations, with transition rates exhibiting complex time dependence. The time-dependent Schrödinger equation is auxiliary in SH.<sup>19</sup> It is only used to determine transition probabilities. Observables are obtained by averaging over the trajectory ensemble, not from the Schrödinger equation. Transition rates in traditional master equations, such as the Boltzmann transport equation,<sup>62</sup> are constants and usually obtained with perturbation theories assuming weak coupling. In this sense, SH rates are non-perturbative and non-Markovian, exhibiting complex time-dependence.

The analogy of SH with master equations is particularly useful for modeling nanoscale and condensed matter systems containing a large number of evolving particles, Figure 6. Photoexcitation of a metal<sup>21,63</sup> or intense excitation of a semiconductor<sup>25</sup> generate large ensembles of out-of-equilibrium electrons. Their evolution cannot be obtained with the time-dependent Schrödinger equation because of the enormous dimensionality of the Hilbert space. In comparison, master equations can easily evolve particle distributions. Wang and Prezhdo used SH transition probabilities in a Pauli master equation to study relaxation of electrons in a metal,<sup>64</sup> obtaining results similar to ensemble SH calculations in a more efficient manner. This direction is worth exploring further, in order to study systems and processes that are too highly dimensional for traditional NA-MD and too complex for common master equations that assume weak coupling, harmonic vibrations, and geometry and time independent rates.

## ■ ANALYZING AND ACCELERATING NON-ADIABATIC DYNAMICS WITH MACHINE LEARNING

Machine learning (ML) has gained significant success in all areas of science, and its application to NA-MD can lead to interesting discoveries and faster calculations. Unsupervised learning can be employed to analyze NA-MD Hamiltonians and simulation results,<sup>65</sup> while supervised learning can help construct NA Hamiltonians and accelerate simulation.<sup>4,66,67</sup> Zhou et al. analyzed geometric features influencing nonradiative elec-



**Figure 7.** Machine learning (ML) helps accelerate and analyze NA-MD. (left) Long trajectories obtained with ML force field identified a rare structural deformation and long-lived hot electrons in a Pt particle on MoS<sub>2</sub>. Adapted with permission from ref 44. Copyright 2020 American Chemical Society. Hot electrons contribute to plasmonic and other types of electro- and photocatalysis with metal clusters. (middle) ML interpolates NA coupling and excitation energies along trajectories to accelerate NA-MD. Adapted with permission from ref 4. Copyright 2021 American Chemical Society. (right) Unsupervised ML uncovered surprising factors influencing the NA Hamiltonian in metal halide perovskites. Adapted with permission from ref 65. Copyright 2020 American Chemical Society.

tron–hole recombination, which limits efficiencies of perovskite solar cells,<sup>65</sup> Figure 7. Surprisingly, geometries rather than motions govern the NA coupling, although it explicitly depends on atomic velocity, eq 1. This discovery rationalized the anomalous temperature dependence of the charge carrier lifetime,<sup>43</sup> which increases at higher temperatures because thermal disorder localizes wave functions and decreases the NA coupling. Components that do not support charge carriers still influence carrier lifetimes via long-range electrostatic coupling with the charges and short-range steric interactions with the charge-carrying lattice. Such analyses are straightforward and can uncover a priori unanticipated phenomena.

Supervised learning can produce NA Hamiltonians and accelerate NA-MD. Development of DFT quality ML force fields is already well-established.<sup>68</sup> Predicting geometry-dependent excited state properties and NA couplings is more challenging,<sup>66,67</sup> since they exhibit complex dependence on atomic structure and because calculations needed for training are computationally demanding. Initially, one can employ ML force fields to generate long trajectories that may exhibit rare events. Chu et al.<sup>44</sup> uncovered fluctuation of a corner atom in a Pt nanoparticle adsorbed on MoS<sub>2</sub>, Figure 7. The fluctuation produced a long-lived “hot” electron state that can rationalize nonthermal effects in plasmonic photochemistry and contribute to photo- and electrocatalysis with small metallic clusters. Further steps in ML training of NA Hamiltonians were taken by Wang et al.<sup>4</sup> Noting that prediction of excitation energies and NA coupling is more challenging compared to ground state forces, they precomputed ground state trajectories and, under the CPA, interpolated the NA Hamiltonian sampling only 2% of points. The method provided high-quality NA-MD results for nonradiative electron trapping and recombination in metal halide perovskites. Further ML efforts can stimulate application of NA-MD to complex nanoscale systems and longer time scales.

## CONCLUDING REMARKS

This Account discussed the methodological and physics aspects of nanoscale NA-MD, in which the author was involved directly. There are many other important aspects of modern NA-MD. Development of linear-scaling electronic structure methods,<sup>69</sup> semiempirical Hamiltonians,<sup>70</sup> and ML quantum chemistry<sup>71</sup>

accelerates NA-MD. Proper treatment of many-body dispersion<sup>26</sup> and collective plasmonic excitations<sup>27</sup> is important with nanometer scales and multicomponent systems. Dimensionality of electronic spaces can be enormous, involving millions of states.<sup>22,61</sup> Studying quantum dynamics in such spaces may require different methods, such as stochastic electronic structure<sup>61</sup> and master equations.<sup>62,64</sup>

Polaritonic chemistry is developing rapidly and can be described by NA-MD.<sup>72</sup> Electron–photon coupling is analogous to electron–phonon coupling, since bosonic electromagnetic field quanta are represented by harmonic oscillators. Mean-field and SH methods can be applied to describe dynamics of electron polaritons. Interaction of matter with strong laser fields, causing Mott and Peierls metal–insulator transitions, transformation from exciton to plasma regime, and melting and decomposition of materials and molecules,<sup>20,25,47</sup> require advanced electronic structure methods describing band gap renormalization, variable dielectric screening, and dissociative resonances. Simultaneously, strong excitations may relax the detailed balance and energy conservation requirements. Quantum nuclear effects are important in photocatalytic water splitting and can be incorporated by centroid<sup>73</sup> and ring-polymer<sup>74</sup> MD and quantized Hamilton dynamics.<sup>75</sup> NA-MD describes local phenomena, such as trapping by defects.<sup>25,42</sup> Diffusion can be modeled with model Hamiltonians. Longer spatial and time regimes can be achieved by multiscale modeling, in which NA-MD is combined with reaction diffusion.

Many modern technologies based on chemical, physical, and materials sciences involve nonequilibrium processes. These are probed by time and spatially resolved spectroscopies, which continue rapid development and become more accessible and popular. The technological and experimental advances provide strong motivation for NA-MD simulations, which have to be constantly adapted to the currently studied systems and phenomena.

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## Notes

The author declares no competing financial interest.

## Biography

Oleg Prezhdo obtained Diploma in Theoretical Chemistry from Kharkiv University, Ukraine, under Anatoly Luzanov. He completed Ph.D. studies within 4 years with Peter Rossky at UT-Austin. After a 1-year postdoctoral fellowship with John Tully at Yale, he joined University of Washington in 1998, achieving Associate and Full Professor in 2002 and 2005. In 2010, he was offered a Senior Professorship at University of Rochester, and in 2014 he moved to University of Southern California, where he is Professor of Chemistry, Physics & Astronomy, and Chemical Engineering. He served as Editor for *Journal of Physical Chemistry and Surface Science Reports*. Currently, he is Executive Editor for *Journal of Physical Chemistry Letters*. Recipient of multiple national and international awards, he held visiting professorships in France, Germany, Spain, Ukraine, Russia, Japan, China, and Luxembourg. His research interests range broadly from semiclassical physics and time-dependent density functional theory to quantum dynamics and far-from-equilibrium processes in nanoscale, condensed matter, molecular, and biological systems.

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