OVERVIEW



Algorithm advances and applications of time-dependent first-principles simulations for ultrafast dynamics

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Abstract

Far from equilibrium phenomenon is a central theme of contemporary material research. Such phenomenon can exhibit itself in atomic structure and dynamics, but very often it also happens as non-equilibrium phenomenon in the electronic structure. In ab initio material simulation, density functional theory (DFT) has played an essential role in studying electronic ground state problems. For excited states, besides many-body perturbation theory, another powerful tool is the time dependent DFT (TDDFT) method. In particular, the real-time TDDFT (rt-TDDFT) method can be used to simulate many non-equilibrium phenomena directly. Here we introduce our works on some algorithm advances based on our recently rt-TDDFT method. This method uses the plane-wave basis set, and significantly accelerates its efficiency by increasing the time step from 0.1-1 as in traditional methods to 0.2-0.5 fs. The noncollinear magnetic moments and spin-orbit coupling have also been included in our rt-TDDFT method. Furthermore, a Boltzmann-TDDFT algorithm has been developed to solve the hot carrier overheating problem in Ehrenfest dynamics, and a natural orbital branching algorithm has been developed to overcome the mean-field approximation in Ehrenfest dynamics nuclear trajectory, thus allows stochastic multiple paths in chemical reactions. Utilizing these methods, we have studied the photoinduced ultrafast demagnetization, ultrafast phase transition, energy transfer between plasmon and hot carriers, as well as the high-energy ion implantation and low-energy atomic diffusion in semiconductors. We believe the tools as the ones introduced here can enable us to study a wide range of phenomena which are of great interest in modern day material research.

This article is categorized under:

Structure and Mechanism > Computational Materials Science Electronic Structure Theory > Ab Initio Electronic Structure Methods Electronic Structure Theory > Density Functional Theory

KEYWORDS

electronic stopping power, interaction of ion with matter, photoinduced ultrafast dynamics, real-time time-dependent density functional theory, ultrafast molecular dissociation

1 | INTRODUCTION

Ab initio molecular dynamics (AIMD) simulation based on density functional theory (DFT) has played an important role in studying a wide range of physical problems, from liquid water behavior,¹⁻³ to polymers,^{4,5} to chemical reactions.⁶⁻⁸ The AIMD is often carried out under the framework of Born–Oppenheimer approximation, hence is also called Born-Oppenheimer molecular dynamics (BOMD). Within BOMD (or AIMD), the electronic structure of the system always stays at its ground state at any time step during the MD. This is also called adiabatic approximation. However, there are many physical problems where the electronic states become excited during the MD process, 9-20 and the electronic state transition is not adiabatic from one time step to the next. This is obviously the case when there is a strong electromagnetic field excitation (e.g., laser excitation).⁹⁻¹² This is also true when the system is under collision with a high-speed particle.¹³⁻¹⁶ The recent focus on the non-equilibrium and ultrafast phenomena also highlights the need of nonadiabatic molecular dynamics (NAMD),¹⁷⁻²⁰ since most of such phenomena are beyond the region of BOMD. Interestingly, under the DFT, the AIMD was initially popularized by the invention of Car-Parrinello algorithm,²¹ in which the electronic structure is not forced to be on its ground state, instead some artificial dynamics is introduced to evolve the electronic degree of freedom. Nevertheless, such electronic dynamics is artificial, and its purpose is to make it approximately close to the ground state while avoiding the self-consistent calculations. It thus cannot be used to describe the true electronic excitation during MD. To describe NAMD, in principle, one just needs to integrate the time-dependent Schrodinger's equation.²² But the small mass of the electron poses unique numerical challenges in solving the time-dependent Schrodinger's equation. Due to the fact the electron mass is more than 10,000 times lighter than that of the nuclear, its movement is thus also much faster. This results in a requirement of a much smaller numerical time step (dt) in the MD. In practice, whereas the BOMD can used a dt of about 1 fs,²³ in time dependent DFT (TDDFT), the dt is typically in the order of 1 as.^{24–27} This makes the simulation much more expensive than the BOMD.

Another issue is the formalism in doing nonadiabatic MD. The solution for time-dependent Schrodinger's equation is a problem as old as the ground-state calculation, especially in quantum chemistry. There are many time-dependent algorithms developed in quantum chemistry.^{28,29} In condensed matter physics, the development of TDDFT has opened the door for time-dependent simulations of relatively large systems.^{30,31} While in the earlier days, the TDDFT has often been used to calculate the optical absorption spectra under linear-response theory,^{32,33} it has been used more and more in recent days with direct real-time evolution of the single-particle orbitals (the real time TDDFT [rt-TDDFT]) to simulate the ultrafast dynamics directly.^{30,31}

Compared with quantum chemistry many-body wave function approach, the rt-TDDFT has its own unique challenges. This is especially true when one likes to include other effects beyond simple TDDFT, for example, the decoherence effect between different eigen states, and detailed balance.³⁴ Direct rt-TDDFT has some serious shortcomings when it is used to describe the carrier dynamics. One major problem is the lack of detailed balance when used to describe the electron-phonon coupling.³⁵⁻³⁷ Within rt-TDDFT, an Ehrenfest dynamic is used to describe the nuclear movement.^{34,38} Due to this classical Newtonian dynamics for the nuclear movement, the electron transition from lower eigen state to higher eigen state will have the same transition rate as the opposite transition from higher eigen state to lower eigen state. This violates the detailed balance in thermal dynamics, which states the transition rate from high energy to low energy will be larger than the opposite transition by a Boltzmann factor.³⁹ This violation of detailed balance in Ehrenfest dynamics can lead to overheating of the electron degree of freedom, and also lead to numerical divergence during its time integration.^{34–37} If a quantum mechanical treatment for the nuclear degree of freedom could be used, due to the energy conservation rule and zero phonon modes, the detailed balance can be restored.³⁴ In quantum chemistry calculation, various types of empirical methods have been employed to introduce such detailed balance.^{28,29} But their applications for the rt-TDDFT is still relatively rare. Another effect is the decoherence and decoherence time.⁴⁰ In a full quantum mechanical treatment for both the electron and nuclear degree of freedom, under the Franck-Condon expansion, the electron plus nuclear combined wave functions on different electron adiabatic states will lose their overlaps with time.^{34,41} If only the electronic wave function is represented in the formalism (like in Ehrenfest dynamics of rt-TDDFT), the decoherence exhibits itself as a loss of coherence (the ability to have quantum mechanical interference with each other) between different states.^{34,41} This also goes beyond the original Ehrenfest dynamics. Its effects can be treated in different ways, for example, the wave function collapsing algorithms.⁴⁰ But the implementation of such algorithms in rt-TDDFT is still a research topic.

The TDDFT simulation belongs to a general class of NAMD simulation. Within this general class, there are two subclasses. One is like the TDDFT where electronic dynamics influences strongly the nuclear dynamics. This "back reaction" is important to explain the laser induce phase transition,³¹ radiolysis process,⁴² and polaron reactions⁴³ just listing a few examples. Such coupled simulation between the electronic degree of freedom and nuclear degree of freedom is important when the electron wave function is highly localized as in a molecule, or when the electronic excitation is strong as in strong laser illumination. In the second class, the back reaction might not be so important, and we are more interested in the electron degree of freedom. One typical example is the weakly optically excited hot carrier cooling.^{44,45} In such cases, one can ignore the back reaction from electronic dynamics to nuclear dynamics. Note that, we have also developed several algorithms for NAMD under classical path approximation (CPA), where the effects (back reaction) of electronic structure excitation to the nuclear movement have been ignored.⁴⁶ Such CPA is justified for systems where the electronic excitation is weak and spatially extended, and we only concern about the dynamics of the electronic degree of freedom, not the nuclear movements.^{44,45} For the NAMD, ordinary BOMD can be carried out, and the wave function overlaps between consecutive time steps are calculated during BOMD.⁴⁶ The carrier dynamics is done as a postprocessing. In this review, we will only focus on the first class through the use of TDDFT although there are many common issues for these two subclasses. What common to both of these two subclasses are the issues of decoherence.⁴⁰ This issue comes up when we use quantum mechanics to describe only the electronic degree of freedom, while use classical trajectory to describe the nuclear movement. In reality, both electron and nuclear degrees of freedom should be described using quantum mechanics wave functions, and a good approximation is to expand the whole wave function under a Frank-Condon expansion.^{34,41} In each term of the Frank-Condon expansion, the nuclear wave function depends on the corresponding electronic adiabatic state (the electronic configuration). The overlaps of the nuclear wave functions of different terms in the Frank-Condon expansion can decrease with time, with a given decoherence time.^{34,41} This effectively means the electronic wave function part can no longer interface with each other (interference means a finite overlap of the whole wave function term), thus lose their coherence. Various wavs have come up to deal with this phenomenon empirically when formalism consists of only the electronic wave function. Wave function collapsing is one way, which changes the pre-collapse system into an after-collapse classical ensemble (hence without interference between a different member of the ensemble).⁴⁰ This changes the original deterministic time-evolving Schrodinger's equation approach (but with both the electron and nuclear degree of freedom) into a stochastic process with only the electronic degree of freedom. This is an essential issue we will deal with in our Boltzmann-TDDFT method and natural orbital branching (NOB) method.

In this short review, we will summarize the recent developments from our group in these areas, especially for algorithms which accelerates the rt-TDDFT calculations, as well as algorithms which introduce detailed balance and decoherence effect beyond straight-forward Ehrenfest dynamics.³⁹ For the applications, we will use our rt-TDDFT methods to study: pure electronic structure excitation (e.g., the plasmon excitation)⁴⁷; laser-induced ultrafast phase transitions³¹; laser-induced demagnetization processes^{48,49}; high-energy particle collisions⁵⁰; and radiolysis molecule damage process.⁴² In terms of methods, we will discuss the following specific topics:

The traditional rt-TDDFT methods have a huge computational cost due to the need to use a very small timestep $(\Delta t = t_2 - t_1)$.^{24–27} To increase this time step in wave function time integration, we utilize an approximate linear Hamiltonian approach within a period $[t_1, t_2]$.^{35,51} This has allowed us to increase the time step by two orders of magnitude, for example, from 0.001 to 0.2 fs.⁵¹ This algorithm has now been implemented in PWmat,^{31,52} as well as in TDAP^{30,53} and ELK.^{54,55}

Based on the above rt-TDDFT method, we have implemented the electron-light interaction, spin–orbit coupling (SOC), and noncollinear magnetic moment in the plane-wave Hamiltonian, to study the ultrafast demagnetization mechanism in ferromagnetic metals and semiconductors.^{48,49} Spin-orbit interaction is important in many physical problems, and our rt-TDDFT algorithm is effective in dealing with systems with SOC.^{56–58} The generation of ultrafast spin current^{59,60} and optically driven fast demagnetization is an intensely studied contemporary topic.^{61,62} The application of rt-TDDFT has opened up a way to theoretically investigate such problems.

As discussed above, the straight-forward implementation of the Ehrenfest dynamics in rt-TDDFT will not have the detail balance, and can lead to overheating of the electron degree of freedom. Because of this, it cannot be used to describe hot-carrier cooling.^{35–37} This is problematic in dealing with many laser-induced phenomena like phase transition.^{63–65} The early stage of such phase transitions can be described without hot-carrier cooling, but in order to yield the recovery of the system from the initial excitation, typically in the 200–1000 fs range, the hot-carrier cooling becomes important.^{63–65} We have implemented a special scheme with Boltzmann factor in the rt-TDDFT wave function integration, which guarantees the detailed balance.³⁹ As will be shown later, the simulations with the Boltzmann-TDDFT can accurately describe the phase recovery process.⁶⁶

Although Boltzmann-TDDFT can solve the hot-carrier cooling problem, it is a mean-field approximation for the nuclear motion, so the nuclear path is deterministic.³⁴ In reality, in many problems, like chemical reactions, there could

be several possible reaction outcomes.^{17,67} These outcomes have certain probabilities, and the whole process is stochastic. Such "branching" behavior is usually described by potential energy surface (PES) hopping in quantum chemistry calculation. One of the most widely used algorithm is the fewest switches surface hopping (FSSH) algorithm by Tully.^{41,68,69} But the original FSSH algorithm has several shortcomings.⁶⁹ For example, it does not use decoherence time, thus cannot describe the decoherence effect. Besides, the FSSH is designed for many-body wave functions, thus cannot be directly applied to rt-TDDFT, where the electronic structure is consisted with many single-electron wave functions.⁶⁹ We have developed a NOB scheme, where the density matrix is used to evolve the electronic structures, while the system can collapse into the natural orbitals of the density matrix.³⁹ This method falls to the general category of wave function collapsing scheme. The NOB can be used to study radiolysis where an ionized molecule can break down into several fragments.³⁹ A repeated simulation using NOB can tell us the probability of different fragments for the radiolysis process.

2 | METHODOLOGY

2.1 | rt-TDDFT of linear Hamiltonian

The time-dependent Kohn-Sham's single-particle equation is:

$$i\frac{\partial\psi_{j}(t)}{\partial t} = H[\rho(t)]\psi_{j}(t), \qquad (1)$$

where $\psi_j(t)$ is the time-dependent single-particle wavefunction of index *j*, and $\rho(t)$ is the time-dependent charge density. $\rho(t)$ can be obtained from $\{\psi_j(t)\}$ as $\rho(t) = \sum_j O_j(t) |\psi_j(t)|^2$ where $O_j(t)$ is the electron occupation on state $\psi_j(t)$. The ion positions $\{\mathbf{R}_k(t)\}$ (*k* is the atom index) also enter the Hamiltonian via the Coulomb interactions among nuclei and electrons, and the trajectories of $\{\mathbf{R}_k(t)\}$ are described by Newton's second law using ab initio forces $\{\mathbf{F}_k(t)\}$ and ion masses $\{M_k(t)\} d^2 \mathbf{R}_k(t)/dt^2 = \mathbf{F}_k(t)/M_k(t)$. Under the instantaneous approximation often used in TDDFT method, the $H[\rho(t)]$ is calculated using conventional exchange-correlation functionals. The solution of Equation (1) is usually integrated with the formula $\psi_j(t + \Delta t) = \exp(-iH\Delta t)\psi_j(t)$ which requires a time step Δt satisfying $|H\Delta t| \ll 1$, leading to an effective $\Delta t \le 1$ as (since the energy spectrum of Hamiltonian under the plane-wave basis set is usually larger than 10^2 eV). Such an extremely tiny time step Δt results in one of the most critical efficiency bottlenecks, and makes the rt-TDDFT algorithms a few orders of magnitudes slower than the conventional BOMD.

To improve the efficiency of rt-TDDFT to a level comparable to BOMD⁵¹ we firstly expand the time-dependent electron wavefunctions $\{\psi_j(t)\}$ on the adiabatic eigenstate basis set:

$$\psi_j(t) = \sum_i C_{j,i}(t)\phi_i(t).$$
(2)

Here $\{\phi_i(t)\}\$ are the eigenstates of Hamiltonian at time t, $H(t)\phi_i(t) = \epsilon_i(t)\phi_i(t)$. From Equations (1) and (2) we have:

$$\dot{C}_{j,i}(t) = -i\epsilon_i(t)C_{j,i}(t) - \sum_l C_{j,l}(t)V_{i,l}(t),$$
(3)

where the transition matrix $V_{i,l}(t) = \langle \phi_i(t) | \partial \phi_l(t) / \partial t \rangle$.

To solve $\{\psi_j(t)\}\$, one now needs to solve $\{C_{j,i}(t)\}\$ and $\{\phi_i(t), \epsilon_i(t)\}\$. Notice that the off-diagonal term $V_{i,l}(t)$ describes the coupling between $\phi_i(t)$ and $\phi_l(t+dt)$. It can show a sharp peak when these two states anti cross each other in energy. Since we only use a finite number of adiabatic states $\{\phi_i(t)\}\$ in the expansion of Equation (2), the above procedure has converted the original problem into a small size matrix problem of Equation (3).

The second step is to apply a linear approximation on the Hamiltonian to carry out its integration. To be more precise, for a time interval $[t_1, t_1 + \Delta t]$, we use the eigenstates at $t_1 \{\varphi_l(t_1)\}$ as the basis set to expand the Hamiltonian. Hamiltonian at t_1 has only diagonal terms $\{\epsilon_l(t_1)\}$, while it is diagonal at $t_1 + \Delta t$ under the basis set of $\{\varphi_l(t_1 + \Delta t)\}$. We then assume that the Hamiltonian evolves linearly in $[t_1, t_1 + \Delta t]$: For any $t \in [t_1, t_1 + \Delta t]$

$$H(t) = H(t_1) + \frac{t - t_1}{\Delta t} [H(t_1 + \Delta t) - H(t_1)].$$
(4)

Using Equation (4), we only need H(t) at t_1 and $t_1 + \Delta t$, for example, the $\{\phi_i(t_1), e_i(t_1)\}$ and $\{\phi_i(t_1 + \Delta t), e_i(t_1 + \Delta t)\}$ from the original plane wave pseudopotential code. The reduced size matrix of H(t) under the $\{\phi_i(t_1)\}$ basis set can be obtained from Equation (4). This can then be used to carry out Equation (3). The main efficiency improvement comes from several factors as discussed below.

The linear approximation of Hamiltonian under the adiabatic eigenstate basis set allows a good description of the real H(t) with a $\Delta t \leq 0.2$ fs, which is orders of magnitudes larger than the 1 as time step in conventional rt-TDDFT. We have tested the results from such linear approach, with the ones obtained from conventional integral solution of Equation (1) using a tiny Δt , and have found negligible differences.³⁵ To solve Equation (3) within $[t_1, t_1 + \Delta t]$ it still requires a multiple step integration with a much smaller dt in $[t_1, t_1 + \Delta t]$ (here, $dt = 10^{-1}-10^0$ as). But instead of solving $\{\varphi_l(t), \varepsilon_l(t)\}$ directly from $H(t)\phi_i(t) = \varepsilon_i(t)\phi_i(t)$, we solve it by generating H(t) from Equation (4) then diagonalizing it under the small basis set of $\{\phi_l(t_1)\}$. The generation and diagonalization of the $M \times M$ matrix H(t) (M is the number of adiabatic states used in Equation (2)) cost only relatively short time (Equation (4)). To further increase the computation (4) with the fixed basis set of $\{\phi_i(t_1)\}$ without repeated diagonalization. Thus the $C_{j,i}(t)$ will be the expansion coefficients of $\psi_j(t)$ with basis set $\{\phi_i(t_1)\}$, instead of $\{\phi_i(t)\}$. These coefficients are converted from the $\{\phi_i(t_1)\}$ basis set to $\{\phi_i(t_1+\Delta t)\}$ basis set at $t_1 + \Delta t$.

Finally, the integration of Equation (3) (or the equivalent one without diagonalization) can predict the wavefunction $\{\psi_j(t_1 + \Delta t)\}$ from $\{\psi_j(t_1)\}$. However, before $\{\psi_j(t_1 + \Delta t)\}$ is known, $\rho(t_1 + \Delta t)$, hence $H(t_1 + \Delta t)$ of Equation (4) cannot be obtained. Thus, a leapfrog self-consistent field (SCF) loop needs to be carried out, until convergence. The usual charge mixing scheme can be used for this SCF loop. Usually, only a few SCF steps are needed for each rt-TDDFT step.

The advantage of Equation (1) is that it is the original formalism without any approximation, in contrast, for Equation (3), the wave function $\psi_j(t)$ is expanded on an eigenstate basis set. The expansion might introduce errors if there are excitations to the very high energy adiabatic eigenstates which are not in the expansion basis set in some extreme cases. However, for most cases (e.g., the ones shown in the review), one can be based on physical intuition to judge how many adiabatic states to be included in the expansion. The advantages of Equation (3) are twofolds. First, for the computation, especially for the plane-wave pseudopotential method, Equation (3) is much faster to evolve than Equation (1). In the plane-wave pseudopotential method, the most time-consuming step is $H(t) \psi_j(t)$. In Equation (3), we only solve the adiabatic state for every Δt step, while Δt can be in the order of 0.2 fs. In Equation (1), the Δt needs to be in the order of attosecond or smaller. Note, we still evolve Equation (3) with an attosecond dt, from t to $t + \Delta t$, but that is in a reduced space of a matrix of dimension M (M is the number of adiabatic states in Equation (3)). This reduced space is hundreds of times smaller than the plane-wave basis dimension, which makes the cost to evolve Equation (3) from t to $t + \Delta t$ negligible. Second, for all the algorithms discussed in the review, for example, the Boltzmann factor and wave function collapsing, they are based on adiabatic states. Thus, having the adiabatic states in the formalism, making the development and implementation of such algorithms more natural.

2.2 | Noncollinear magnetic moments and SOC in rt-TDDFT

Compared to the common ultrafast dynamics phenomena (e.g., chemical reaction in molecular), magnetic dynamics in bulk systems and thin films is much more complicated.^{12,60,61} Many additional effects (e.g., noncollinear spin and SOC) have to be included in the simulations.⁴⁸ In order to describe the magnetic dynamics, we used the following time-dependent Kohn–Sham equation:

$$\left[\frac{1}{2}(-i\nabla + A(t))^{2} + V_{\text{ion}} + V_{\text{H}} + V_{\text{XC}} + V_{\text{SOC}} + V_{\text{ext}} + \frac{1}{2}\sigma \cdot B\right] \begin{bmatrix} \psi_{jk}^{\uparrow}(r,t) \\ \psi_{jk}^{\downarrow}(r,t) \end{bmatrix} = i\frac{\partial}{\partial t} \begin{bmatrix} \psi_{jk}^{\uparrow}(r,t) \\ \psi_{jk}^{\downarrow}(r,t) \end{bmatrix},$$
(5)

where the noncollinear wave function ψ_{jk} contains spin up and spin down components; *j* is the band index and *k* is *k*-point index for periodic systems. The Hamiltonian is a 2 × 2 matrix, in which V_{ion} , V_{H} , V_{XC} , V_{SOC} , and V_{ext}

are the ionic local potential, Hartree potential, exchange-correlation potential, nonlocal SOC term, and external potential (e.g., electric potential), respectively; σ is the Pauli matrix; A and B represent the magnetic vector potential and magnetic field of laser. Because the laser wavelength is usually much longer than the simulated supercell size, we ignore the spatial dependence of A and B field and use their dipole approximation. In this approximation, the high-order terms of laser field (e.g., electric quadrupole transition matrix) are set to zero, thus are not included in the rt-TDDFT Hamiltonian. We also ignore the valence orbital induced magnetic moment effect.

To efficiently solve the above time dependent Kohn–Sham equation, we used adiabatic spinor states to expand the noncollinear time-dependent wave functions and used iterative leap-frog method to do the time evolution as described in previous section. To be specific, ψ_{ik} is expanded as:

$$\left[\psi_{jk}^{\uparrow}(r,t)\psi_{jk}^{\downarrow}(r,t)\right]^{\mathrm{T}} = \sum_{i} C_{ji}^{k}(t) \cdot \left[\phi_{ik}^{\uparrow}(r,t_{1})\phi_{ik}^{\downarrow}(r,t_{1})\right]^{\mathrm{T}},\tag{6}$$

where $\left[\phi_{ik}^{up}(r,t_1),\phi_{ik}^{dn}(r,t_1)\right]$ is the adiabatic spinor states at the time t_1 , and satisfies:

$$H[\rho(\mathbf{r},t_1)] \left[\phi_{ik}^{\uparrow}(\mathbf{r},t_1) \phi_{ik}^{\downarrow}(\mathbf{r},t_1) \right]^T = \epsilon_{ik}(\mathbf{r},t_1) \cdot \left[\phi_{ik}^{\uparrow}(\mathbf{r},t_1) \phi_{ik}^{\downarrow}(\mathbf{r},t_1) \right]^T, \tag{7}$$

where $\rho(r, t_1)$ is the charge matrix, $H[\rho(r, t_1)]$ is the corresponding 2 × 2 Hamiltonian matrix, and $\epsilon_{ik}(r, t_1)$ is the eigen energy. After this, the same equations as Equations (3) and (4) are used to integrate the wave-function from t_1 to $t_1 + \Delta t$.

In the dynamic simulation, we have included all the effects of noncollinear magnetic moment, light–spin, light– orbital, spin–orbit, electron–electron, electron–phonon (by nuclear movements) interactions and external potential as well as the effect of initial finite temperature disorder in the magnetic moment.⁴⁸ This enables us to study the fundamental physics for many complicated phenomena.^{48,49} Due to the treatment of laser field, the inclusion of multiple *k*-points, and the accuracy of plane-wave basis, this rt-TDDFT is capable of simulating the ultrafast phenomena for different types of systems, including periodic crystals, two-dimensional materials, molecules, and so on. It is capable of simulating their spin, electron, and structure dynamics at the same time under the excitation of different external field (e.g., light, electric field, and magnetic field).^{59–62}

2.3 | Boltzmann-TDDFT

As discussed above, the original rt-TDDFT evolution does not satisfy the detailed balance, hence cannot be used to describe hot carrier cooling.^{35–37} The detailed balance is based on adiabatic states. Since we expand our wave function with the adiabatic states as shown in Equation (2), this provides a unique opportunity for us in dealing with the detailed balance. In order to introduce detailed balance, we first need to define a charge flow between adiabatic states *i* and *i'*. This can be defined as:

$$T(i,i',t) = -\sum_{j=1}^{N} 2Re \Big\{ i C_{j,i}^{*}(t) V_{i,i'}(t) C_{j,i'}(t) \Big\}.$$
(8)

Here *V* is the quantity in Equation (3), and $C_{j,i}$ is the wave function expansion coefficient. This T(i, i', t) describes the charge flow from adiabatic state *i'* to adiabatic state *i*. This charge flow comes from all wave functions $\psi_j(t)$, not just from any one of them. The T(i, i', t) is invariant under unitary rotations in the occupied subspace of $\psi_j(t)$. Note: T(i, i', t) = -T(i, i', t). To introduce the decoherence effect, we first define time averaged T(i, i', t) as:

$$I(i,i',t) = \frac{1}{\tau_{i,i'}} \int_0^\infty T(i,i',t-t') e^{-\frac{t'}{\tau_{i,i'}}} dt'.$$
(9)

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$$t) = \begin{cases} I(i,i',t) \left(e^{-|\epsilon_{i} - \epsilon_{i'}|/kT} - 1 \right), \ I(i,i',t) (\epsilon_{i} - \epsilon_{i'}) > 0\\ 0, \qquad I(i,i',t) (\epsilon_{i} - \epsilon_{i'}) \le 0 \end{cases}.$$
(10)

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Here ε_i , $\varepsilon_{i'}$ are the adiabatic eigen states, *T* is the temperature. Thus, $\Delta I(i, i', t)$ can be considered as the correction to the charge flow T(i, i', t). This correction can be realized by modifying the wave function $C_{j,i}(t)$ by adding a $\Delta C_{j,i}(t)$ after every wave function evolution step from t_1 to $t_1 + \Delta t$.

$$\sum_{i=1}^{M} C_{j_{1},i}(t) \Delta C_{j_{2},i}^{*}(t) + \Delta C_{j_{1},i}(t) C_{j_{2},i}^{*}(t) = 0,$$
(11)

$$2\sum_{j=1}^{N} Re\left[C_{j,i}(t)\Delta C_{j,i}^{*}(t)\right] = \Delta t \sum_{i'} \Delta I(i,i',t).$$
(12)

The first equation is used to satisfy the orthonormal condition for $\psi_j(t)$, while the second equation is used to modify the occupation of the adiabatic states by introducing $\Delta I(i, i', t)$. The above linear equation is solved by conjugate gradient method. Note that, usually there are more unknown parameters than the number of equations. Thus, minimum amplitude $\Delta C_{j,i}(t)$ solution is sought which satisfies the above equations. After the introduction of $\Delta C_{j,i}(t)$, the energy is not conserved. The energy conservation is restored by subtracting a velocity in the transition degree of freedom, which can be calculated from $\Delta I(i, i', t)$.³⁹

In addition, there are different ways to estimate the decoherence times. The simplest is to use the eigen energy fluctuations with time.⁴⁶ However, for a TDDFT calculation, it is difficult to use that to get the decoherence time between each pair of eigenstates. Nevertheless, we found that the results are not so sensitive to the decoherence time.⁶⁶ As a result, we typically use the same decoherence time for all the pairs of eigenstates. Note that, there are debates about the exact definition of decoherence time anyway, since all the current estimation is based on Gaussian wave package overlaps of a nuclear degree of freedom between different trajectories, which decays in a Gaussian form, not an exponential form as a function of time. Second, this parameter τ between adiabatic states i and i' can be estimated from the fluctuation of their adiabatic eigen energies according to the following formula⁴⁶:

$$\tau_{i,i'} = \sqrt{\frac{24(k_{\rm B}T)^2}{\left\langle \left|\frac{\partial}{\partial t} \left[\varepsilon_i(t,t') - \varepsilon_{i'}(t,t')\right]\right|^2 \right\rangle t}}.$$
(13)

Here, $k_{\rm B}$ is the Boltzmann constant. *T* is the lattice temperature. $\varepsilon_i(t,t') = \langle \phi_i(t) | H(t') | \phi_i(t) \rangle$, $\phi_i(t)$ represents the wave function of the adiabatic state *i* at time *t'*. H(t') is the Hamiltonian at time *t'*. $\langle x \rangle t$ represents the average of variable *x*.

2.4 | NOB-TDDFT

While the Boltzmann factor restores the detailed balance, the atomic movement is under a mean field theory and is deterministic.³⁹ There is no branching for chemical reactions where different products might be realized in the same reaction. In order to do that, some stochastic process must be used. One such approach is the wave function collapsing method, where the $\psi_j(t)$ stochastically collapses into the adiabatic states $\phi_i(t)$ after the decoherence time. However, the implementation of such scheme on the rt-TDDFT is not so straightforward. One reason is that, in DFT, the wave functions are described by a set of single particle functions $\psi_j(t)$, and they have to be orthogonal to each other. On the other hand, most of the wave function collapsing schemes developed before are based on many-body wavefunctions.

use the Slater determinant $S[\psi_j(t)]$ as the many body wave functions, then collapse into all the possible *N* particle *S* $[\phi_i(t)]$, where the *N* adiabatic states $\phi_i(t)$ are chosen from the *M* possible states (*N* is the number of electrons when spin-dependent orbitals are used, and *M* is the number of total calculated orbitals). The implementation of such a scheme is not trivial, since there are C_M^N possible adiabatic Slater determinants $S[\phi_i(t)]$ to collapse into, and even to calculate the coefficients of these $C_M^N S[\phi_i(t)]$ from the $C_{j,i}(t)$ of Equation (2) can be time consuming.

We have developed a stochastic method which is more natural to rt-TDDFT.³⁹ First, instead of evolving the single particle electron wave function according to Equation (1), we integrate the density matrix D(i, i', t) according to Liouville–von Neumann equation:

$$i\frac{\partial}{\partial t}D(i,i',t) = (\epsilon_i(t) - \epsilon_{i'}(t))D(i,i',t) + \left[V,D\right](i,i',t) - \frac{iD(i,i',t)}{\tau_{i,i'}}.$$
(14)

Here [V, D] = VD - DV. One advantage of using the density matrix Liouville-von Neumann equation is that, the decoherence effect can be represented clearly as an off-diagonal decay term (the last term in the above equation). One can show that, introducing the last term will not violate the total energy conservation rule. However, because of the decoherence term, the density matrix D(i, i', t) can no longer be represented by a single Slater determinant, or say by a single N wave function set $\{\psi_j(t)\}$. Instead, if we diagonalize D(i, i', t), we get the natural orbitals $\theta_k(t)$, with the eigen value λ_k as their occupations. In our scheme, we will collapse our N wave functions density matrix stochastically into N natural orbitals $\{\theta_k(t)\}$, instead of N adiabatic states $\{\phi_i(t)\}$. The λ_k is used as a guide, so statistically, after the collapsing, the average occupation of $\theta_k(t)$ is λ_k . Numerically, after each time integration step Δt , we determine whether a collapsing event will happen, based on the entropy of $\{\lambda_k\}$: $S(t) = -\sum_k [\lambda_k(t) \ln \lambda_k(t) + (1 - \lambda_k(t)) \ln(1 - \lambda_k(t))]$. If S(t) is bigger than a preset critical value S_c (e.g., 0.5), then a collapsing event will happen, and after the collapse, S(t) will be reset to zero.

To conserve the energy, after the collapsing, a velocity vector (on all the atoms) will be added to the transition degree of freedom. This represents a transfer of moment, for example, a pulse force, in that transition degree of freedom. For the NOB-TDDFT, the transitional degree of freedom is:

$$F_{\text{TDF}}(R_a, t) = \sum_{j' \in N; j'' \notin N} \left(1 - \lambda_{j'} \right) \lambda_{j''} Re \left\{ \left\langle e^{i\beta_{j'}} \theta_{j'} \left| \frac{\partial H(t)}{\partial R_a} \right| e^{i\beta_{j''}} \theta_{j''} \right\rangle \right\}.$$
(15)

Here, j' are the selected *N* natural orbitals after collapse, j'' are the unselected natural orbitals, and $\theta_{j'}$, $\theta_{j''}$ are their natural orbital wave functions, and $\beta_{j'}$, $\beta_{j''}$ some random phase factors. Note, in above, $F_{\text{TDF}}(R,t)$ defines an orientation. More physically, it defines the direction of a force impulse on each atom. Thus, after the transition, the velocities of each atom are updated as: $V(R,t) + \alpha F_{\text{TDF}}(R,t)$, the α is solved to satisfy the energy conservation. Note, the above procedure is physical since the force impulse is directly calculated based on the orbitals and their force operators involved in the transition. If after the collapsing, the total potential energy increased, then it is possible that this added velocity will not be able to satisfy the energy conservation (the transition degree of freedom does not have sufficient energy). In that case, such collapsing event will be rejected, and a different collapsing choice will be tried, until a successful one is chosen. Such requirement for total energy conservation restores the detailed balance.

3 | APPLICATIONS

3.1 | Photoinduced ultrafast dynamics

Due to the development of femtosecond laser pulse, photoinduced ultrafast dynamics have become an intensely study phenomena in material science in recent years. The related phenomena might be so complex, without numerical simulation, the process is difficult to be understood. In the photoinduced ultrafast dynamics, the charge, spin, orbital, and lattice degrees of freedom are interweaved with each other. Revealing their roles is extremely important to understand the process and to design future experiments for potential applications.^{70–72} We have used out methods and codes to study ultrafast demagnetization process, resonant energy transfer between plasmon and single particle hot carriers, as well as ultrafast non-thermal phase transition process.

3.1.1 | Light-induced ultrafast demagnetization in ferromagnetic metals

The manipulation of ferromagnetic metal magnetic moment by the femtosecond laser has attracted a large number of studies ever since its discovery about 20 years ago.⁷³ It is regarded as one of the most promising technology for the magnetic storage device beyond the Moore's law.⁷⁴ Despite the major experimental progresses and more than 20 years of theoretical studies, the fundamental physics of the laser-induced demagnetization process is still not well understood.^{75,76} There are many debates about the pictures of angular momentum transfer and the roles of different interactions.⁷⁷ Previous theoretical studies mainly relied on phenomenological simulations, for example, by atomic Landau–Lifshitz–Gilbert model and three-temperature model.^{78,79} These models can fit well the experiments by adjusting the parameters, but they lack the predictive power and the understanding of the fundamental physics from electronic structure point of view. There are some recent advances using ab initio time-dependent simulations to study the demagnetization process.^{80–82} However, these ab initio calculations suffer the drawbacks in terms of simulation accuracy and efficiency. For example, the simulated demagnetization rate for the ferromagnetic metal is at least 10 times smaller than the experimental value, which casts some doubt on whether the real physics is included in the simulation.⁸³

Our group started to study these problems from 2014. We have developed a new rt-TDDFT algorithm (as described in Section 2.1) and a further fix-basis rt-TDDFT (FB-rt-TDDFT) algorithm where the initial spinor basis at t = 0 is used throughout the simulation. These algorithms dramatically reduce the computational cost, enabling us to calculate bigger systems and study many complicated physics effects. Our rt-TDDFT simulations have considered the effect of noncollinear magnetic moment, light-spin, light-orbital, spin-orbit, electron-electron, and electron-phonon (by nuclear movements) interactions as well as the effect of finite-temperature spin disorder in large systems. We yielded a demagnetization rate similar to experiments and uncovered the underlying physics for the metal demagnetization process.⁴⁸ Through our study on the ferromagnetic Ni systems, we found that (i) the angular momentum flow from photon to the system by the Zeeman effect (the $\sigma \cdot B$ term in the Hamiltonian) is negligible. If any, such flow goes to the electron orbital, not directly to the spin. These are confirmed by turning on/off the $\sigma \cdot B$ term in the Hamiltonian and using different light polarizations (Figure 1a). (ii) The phonon can play a role and can change the demagnetization rate greatly (Figure 1a). However, including the phonon effect alone cannot yield the experimental rate of demagnetization. (iii) There are major roles for the initial spin disorder at room temperature and the self-consistent update of the electron-electron interaction (Figure 1b) also plays an important role. Initial disorder significantly increases the demagnetization rate and helps the system to reach the experiment observations. The spin disorder also connects the electronic structure theory with the phenomenological three-temperature model. The importance of the self-consistency of the electron-electron interaction casts some doubts about many current analytical explanations which are based on non-self-consistent treatment. (iv) All the angular momentum needed for the spin demagnetization comes from the electron orbital via SOC (Figure 1a), as turning off SOC will lead to zero demagnetization. Overall, through our simulation, we arrived at the following picture of the ferromagnetic metal demagnetization process: The absorption of light induces excitation of the electron orbital, which further excites the spin degree of freedom via SOC. Such excitation is much like the thermal noise in the Landau-Lifshitz-Gilbert model, hence assigning an effective high temperature to the spin degree of freedom. In such a picture, the demagnetization is a random and collective process. As a result, the initial spin randomness (in a lesser degree, the phonon can also provide some randomness) is essential to describe this process.

3.1.2 | Angular momentum transfer channels and timescales in ferromagnetic semiconductor GaMnAs

Compared to the above ferromagnetic metals, ferromagnetic semiconductors have the advantage of the easy adaption to the current semiconductor technology. Therefore, ultrafast manipulation of ferromagnetic semiconductor by light has also attracted intense studies.^{77,84} In particular, the ferromagnetic (III,Mn)V semiconductors are among the most promising candidates for future multifunctional spintronic devices.⁸⁵ A large number of experimental progresses on their spin control have been achieved in the last few years. Nevertheless, there remain many open theoretical questions regarding the demagnetization mechanisms following the femtosecond laser excitation.^{85,86} As magnetism is related to angular momentum, the focus of demagnetization mechanism is connected to the fundamental questions of angular momentum transfer channels and timescales. Under the excitation of the femtosecond laser, there are many types of interactions with different angular momentum transfer channels involved in the demagnetization process (Figure 2a),



FIGURE 1 (a) Evolution of magnetic moment per atom for Ni bulk under six different cases: original linear polarization laser simulation, linear polarization laser without the $\sigma \cdot B$ Zeeman term in Equation (5), linear polarization laser with fixing atoms (i.e., turning off the phonon effect), left circular polarization laser, and linear and left circular polarization laser without the SOC term in Equation (5). The polarization direction of all the light is perpendicular to the magnetization. (b) Maximal demagnetization rate (Δm) as a function of the initial spin disorder ($\Delta \theta$) in the 8 × 1 × 1 Ni system. Each circle represents one independent simulation with different initial disorder. The blue circle is the original FB-rt-TDDFT simulation, while the red circle is the corresponding simulation with fixing electron–electron interaction (i.e., the Coulomb and exchange interaction potential is taken from time *t* = 0 and is not self-consistently updated) (reprinted with permission from Reference 48. Copyright 2019 Science Advances)

including light-induced electron/hole excitation, electron–electron interaction with spin exchange, SOC, and electron– phonon interaction. Understanding the roles of these interactions as well as the angular momentum transfer channels and timescales are critical for future semiconductor spintronic device design.

We have used our rt-TDDFT method to study the laser-induced ultrafast demagnetization process in GaMnAs.⁴⁹ Our simulations well reproduced the experimental femtosecond demagnetization. We found that the localized Mn-d electrons transfer the major part of their spins to the itinerant carriers within 20 fs, confirming the dominant role of sp-d coupling in angular momentum transfer (Figure 2b). However, the total spin of Mn-d and itinerant carriers is not conserved even within the first 10–20 fs due to the SOC (Figure 2b). Within 1 ps, there is a growing percentage of angular momentum transferred from spin to orbital via SOC, which is followed by the relaxation of orbital angular momentum via electron-phonon coupling in a few picoseconds (Figure 2c). This explains the experimentally observed two-stage process. The spin-relaxation time via SOC is about 300 fs for itinerant carriers and about 700 fs for Mn-d electrons. The direct relaxation of Mn-d spin via SOC (not via the medium of itinerant carriers), which plays a dominant role in the ferromagnetic metal demagnetization (but is often neglected in many current models for the GaMnAs demagnetization), is demonstrated to be important here. These results provided ab initio pictures for the demagnetization process of ferromagnetic semiconductor GaMnAs, and unraveled the angular momentum transfer channels and their related timescales.

3.1.3 | Resonant energy transfer between plasmons and hot carriers in metal nanoclusters

Plasmons are a collective excitation of electron degree of freedoms. Plasmon excitation depends critically on the electron–electron Coulomb interaction, which is qualitatively different from single particle excitations. Metal nanoclusters can serve as antennae to absorb sunlight efficiently through plasmon excitations,⁸⁷ they are the sources for the colors in stained glasses. A long sought idea is to use metal nanoparticle plasmon light absorption in applications like photovoltaic and photochemical reactions.^{88,89} But in these applications, the energy absorbed by plasmon must be converted to single particle hot carrier excitation in order to be collected by the electrode, or to induce subsequent chemical reactions.^{89–91} Thus, the plasmon excitation to single particle excitation conversion becomes an important topic. Earlier theoretical works in this area include (1) treating nanoclusters as bulk-like or homogeneous, jellium-like systems,⁹² and/or (2) calculating plasmons as classical oscillating fields, with a perturbative model to obtain the hot-carrier generation.⁹³ However, a unified quantum mechanical framework of the interplay between the plasmons and hot carrier excitations in metal nanoclusters will be useful.

We have applied the rt-TDDFT methodology to simulate the plasmons and hot carrier generations in Ag₅₅ clusters⁹⁴ (Figure 3a). It provides a fully ab initio description and an atomistic resolution for the electronic dynamics. (i) We first



FIGURE 2 (a) Schematic diagram of various interactions involved in the laser-induced ultrafast demagnetization process: electron/hole excitation, electron–electron Coulomb interaction with spin exchange, spin-orbit coupling with angular momentum transfer between spin (*S*) and orbital (*L*), and electron–phonon interaction. (b) Spin magnetic moment (*m*) evolution in the demagnetization process of the Ga₇MnAs₈ system. (c) Angular momentum flow in GaMnAs. τ is the angular momentum relaxation time, as an estimation of the transfer speed of these channels. The τ for sp–d coupling depends on the laser setting (reprinted with permission from Reference 49. Copyright 2019 PNAS)

show how to distinguish the plasmon excitation from single particle excitation: the plasmon excitation is indicated by transitions with band-to-band transition coefficients ($C_{j,i}(t)$) oscillating at the plasmon frequency, whereas the hot-carrier (single-particle) excitation shows a slowly varying $C_{j,i}(t)$ (Figure 3b). (ii) The absence of a peak at $\omega = 0$ of $C_{j,i}(\omega)$ (Figure 3c) is a hallmark of the plasmon, which is different from the transitions described by the single-particle perturbation theory. (iii) In Ag₅₅, there exists the single-particle d-to-s excitations, which is resonant to the plasmon frequency. As a result, the energy in plasmon excitation decays while the energy in single particle excitation increases with time (Figure 3d-f). In comparison, in a negatively charged Ag₅₅, most hot-carrier generation channels are blocked, and the plasmon decays much slower (Figure 3g-i). (iv) We also find that the electron-phonon interactions do not play important roles in the plasmon decay in nanoclusters. (v) Most importantly, we found that, in the Ag₅₅ nanoparticle, eventually, over 80% of the energy has converted from plasmon excitation to single particle excitation.

3.1.4 | Nonthermal ultrafast phase transition in IrTe₂

Laser-induced phase transition has been widely researched by experiments in the transition-metal dichalcogenides (TMDCs), such as materials with charge density wave (CDW) in low-temperature (LT) phases.^{64,95,96} Many of the current understanding of photoinduced phase transitions in these quantum materials are based on models with modified PES induced by light absorption. The change of PES causes the anharmonic coupling between coherent lattice modes and triggers the phase transitions.^{97,98} However, owing to their complexity, a detailed microscopic description of the PES modifications and especially their time dependent dynamics is still lacking. Dynamics simulation can also provide another angle to view the situation. Taking $IrTe_2$ as an example, based on our rt-TDDFT simulations, we find that the fundamental microscopic driving force for structural phase transition originates from the energy lowering through the dissociation of the dimers caused by the photoelectron occupations of the antibonding states.

Unlike other types of TMDCs, there is no CDW bandgap in the LT structure of $IrTe_2$, and the LT structure is accompanied by a periodic modulation with a wave vector of $q_{1/5} = (1/5, 1/5, 1/5)$ as a result of the dimerization of Ir–Ir pair with a shorter bond length of 3.07 Å.^{99,100} Thus, the LT-to-HT phase transition can be judged by the dimer dissociation from 3.07 to 3.93 Å. We define that the portion of the photoexcited electrons is the ratio of the electronic number



FIGURE 3 (a) The calculated atomic structure and DFT eigen energies of the icosahedral Ag₅₅. The Fermi energy is set to zero. (b) The band-to-band transition coefficients $|C_{304,i}(t)|^2$ in Ag₅₅ after laser excitation, calculated by our rt-TDDFT method. $|C_{304,i}(t)|^2$ indicates the transition from the *i*th state to the LUMO (304th) state. Two distinct types, that is, rapidly oscillating and slowly varying, of transitions can be observed, which reveal the plasmonic and single-particle excitations, respectively. (c) The Fourier transform (FT) of $C_{304,i}(t)$ in laser-excited Ag₅₅; note that there is no peak at $\omega = 0$ for the rapidly oscillating transition (i = 292), showing the hallmark of the plasmon. (d–f) The time-dependent excitations in Ag₅₅, calculated by our rt-TDDFT method. (d) The dipole moment oscillations as a function of time. (e) The energies stored in the plasmon and single-particle excitations. The blue line is the single-particle energy generated by the plasmon, which is defined as the energy difference in the single-particle mode between the real system (rt-TDDFT simulation) and the non-interacting system (in which plasmons cannot exist) under the same laser illumination. The pink-dashed line is an exponential decay. (f) The charge density difference $\Delta \rho(t)$ when the dipole moment achieves a local maximum or local minimum as labeled in (d), which shows a significant decay of the plasmonic oscillation. (g–i) the same properties as shown in (d–f), but for time-dependent excitations in negatively charged Ag₅₅ calculated by our rt-TDDFT method. Compared with (f), the significant charge sloshing on the surface shown in (i) still exists around 40 fs, which shows the plasmon is not fully decayed. (reprinted with permission from Reference 47. Copyright 2015 American Physical Society)

excited into the conduction bands at the end of laser excitation to the total number of valence electrons. In the case of 6% photoexcited valence electrons, the majority of excited electrons occupy the Ir–Ir dimerized antibonding states, as shown in Figure 4b,d. The real-space plots of the photoexcited electrons and holes are shown in Figure 4a. The photoholes are located at the center of the Ir–Ir dimer bond, and the photoelectrons are located at the outside ends of the Ir–Ir dimer bond. Such reoccupation of different bands generates atomic driving forces to stretch the Ir–Ir dimer bonds (Figure 4c) in order to lower the energy of the excited system. Note that, the photoinduced phase transition belongs to a non-thermal process because the lattice temperature is always below the transition temperature $T_s \sim 280$ K.



FIGURE 4 The microscopic force driving the structural transition arising from photoinduced electron modulation. (a–d) for the case of photoexcited 6% valence electrons; (e–h) for the case of photoexcited 10% valence electrons. (a,e) Real-space distribution of photoexcited electrons and holes on the (111) plane for (a) photoexcitation of 6% electrons and (e) photoexcitation of 10% electrons to empty bands above the Fermi level at the end of the laser pulses (~120 fs). (b,f) Partial density of states (PDOS) of the LT phase. Shaded areas represent electronic occupation right following the photoexcitation. (c,g) Evolution of the atomic structure under photoexcitation, showing the time dynamics of bond lengths of selected bonds which chart the progress of the photoinduced structural transitions. (d,h) Schematic diagram of the bonding and antibonding bands of intralayer Ir–Ir dimers and interlayer Te–Te bonds. The white hollow arrows in (a) and (e) mark the direction of force driving the atoms away from equilibrium positions. The white cross symbols in (e) indicate the breaking of Ir–Te bonds during structural transition (reprinted with permission from Reference 31. Copyright 2020 American Physical Society)

For a stronger laser intensity to which excite 10% of valence electrons, the photoelectrons begin to fill in the interlayer orbitals of Te–Te dimers in Figure 4e–h. The orbital occupations of the interlayer Te–Te dimers tend to reduce the bond length of the interlayer Te–Te dimers, which in turn also reduces the Ir–Ir dimer distance through the Poisson ratio of the Ir–Te–Ir–Te parallelogram, as shown in Figure 4g. In such strong excitation cases, we failed to observe the LT-to-HT phase transition, but observed a LT-to-MS (a new metastable phase) phase transition. Our understanding for such phase transition can help us to design new excitations in the future, to selectively induce different phase transitions.

3.1.5 | The role of hot carrier cooling in $IrTe_2$

The majority of experiments have reported the ultrafast melting and recovery of structures following photoexcitation.^{63–65,101} However, the rt-TDDFT methods used by most researchers do not satisfy the detailed balance of electron



FIGURE 5 Photoinduced ultrafast dynamics with hot carrier cooling strongly coupled to the lattice. (a) Laser-induced the electron-hole pairs within 120 fs. (b) Hot carrier cooling from high-energy levels to low-energy levels. (c) The recombination of electron-hole pairs. (d–f) The structural dynamics following photoexcitation are driven by electron-phonon couplings. (g) Simulated PLD diffraction intensity *I*(*t*) is obtained through the Debye–Waller formula,¹⁰² *I*(*t*) = exp[$-Q^2 < u^2(t) > /3$], where *Q* is the magnitude of the reciprocal lattice vector for the reflection probed, and $u^2(t)$ is average mean-square atomic displacements. Red diamonds show relative diffracted intensity changes ($\Delta I/I$) measured by FED experiments.⁶³ Note that the zero-point time in the experiment is labeled after photoexcitation so that the diffracted intensity is far less than 0 at *t* = 0 fs. We reinstall the experimental data at *t* = -380 fs in Reference 49 as zero-point time in our work, giving a maximum value of the diffracted intensity at *t* = 0 fs (reprinted with permission from Reference 66. Copyright 2021 American Physical Society)

state transitions, and it cannot describe the hot carrier cooling process.^{30,31,98} Such simulations cannot be used to describe the recovering of the original phase after photoexcitation, and cannot get the related time scale. In this work, using our newly developed algorithm (Boltzmann-TDDFT), we can incorporate the detailed balance in our simulation and can describe the hot carrier cooling accurately. We can theoretically describe the recovery process and get an excellent agreement with the experiment, as shown in Figure 5g.

In our simulation, following the experiment, the 3% of valence electrons in the IrTe2 system are optically excited by a femtosecond laser pulse (central wavelength 400 nm, pulse duration 120 fs).⁶³ The subsequent evolution of the system is simulated by the Boltzmann-TDDFT methods. We find that the Ir–Ir dimers following the initial photoexcitation are dissociated coherently in 300 fs in which the hot carrier cooling already plays an important role, as shown in Figure 5a–e. The hot carrier cooling allows the higher-level electrons to relax to the lower-level Ir–Ir dimer antibonding states, giving rise to the driving forces for Ir–Ir dimer dissociation. Meanwhile, it converts the hot carrier cooling energy into atomic vibrational energy. These two factors help the Ir–Ir dimer dissociation. Interestingly, the subsequent recombination of photoexcited electrons and holes causes the recovery of Ir–Ir dimers due to the disappearance of the hot carrier and the driving forces. The recovery time scale is in excellent agreement with experimental results, as shown in Figure 5c,f. Our simulation provides a complete picture for the creation and recovery of the phase transitions.

3.2 | Interaction of ions and matter

The interaction between implanting ion and target materials causes irreversible damage and affects the service life of materials. Ion radiation can be roughly divided into two categories: one is a high-energy ion implanting, and another is a low-energy ion implanting. The kinetic energy of the high-speed ions is mainly transferred to the electrons, causing the electronic excitation within the as–fs timescale which is usually expressed as electronic stopping power (S_e), but the lattice atoms will not be responded instantaneously.¹⁰³ For the low-energy heavy-ion implanting, it not only can induce part of the electronic excitations but also directly interact with the lattice atoms, showing a more complex dynamic

process.^{104,105} The interaction between the low-energy ion and solid also plays an important role in atomic dopant and diffusive processes in semiconductors.

3.2.1 | High-energy proton collision with silicon

The electronic excitations in the target materials induced by the high-energy ions are usually expressed as the electronic stopping power ($S_e = -dE/dx$). There have been many methods to calculate S_e for high energy ions, such as the Bethe formula,¹⁰³ Lindhard–Winther theory,¹⁰³ and the open-source software package SRIM (Stopping and Range of Ions in Matter) which is based on the Monte Carlo method and binary collision approximation.¹⁰⁶ However, these semi-empirical methods cannot describe the real-time interactions of the high-energy ions with the target materials, in particular in energy regions which transits from one mechanism to another mechanism. To precisely understand the collision process, the rt-TDDFT is generally known as an effective method.^{13,14,107}

We take high-energy proton implantation into silicon as an example. First, the proton is set with an initial velocity v along <001> direction to cross the Si system. According to the different velocity projectile v, we chose the suitable timestep Δt (i.e., $\Delta t \times v \sim 0.1$ Å). To obtain accurate results, we discuss the convergence of the number of adiabatic states (N₁) to electronic excitation. We see that the energy of excited electrons increases steadily as N₁ increasing, but nearly saturates after N₁ reaches 1500, as shown in Figure 6c. Figure 6b shows the distribution of excited electrons which further illustrates that the valence electrons are indeed excited to the high-energy levels during proton irradiation, thus we need a lot of adiabatic states (~1500). The energy loss of a projectile ion to the host electrons is formally defined as electronic stopping power (S_e). Figure 6d shows the energy of excited electrons as a function of proton projectile displacement in which the slope represents the electronic stopping power (S_e) versus proton velocity from our rt-TDDFT simulations. Here, to obtain the experimental bandgap in Si crystal, we slightly modify the LDA potential (r) of the 3s orbital for Si atom so we have the correct bulk Si band gap.³¹ Compared to the calculated S_e before the uncorrected gap, the S_e after the gap correction is almost same, so the S_e excited by high-energy proton irradiation is not directly related to the bandgap. Our rt-TDDFT simulation is nearly analogous to the SRIM data in which the S_e has the maximum value at v = 1.2 a.u.

3.2.2 | High-energy proton collision with liquid lithium

Liquid lithium is generally considered to be a good coating material in fusion reaction chambers.^{109–111} Its coating can improve the power output by two times. Liquid lithium will eventually be bombarded by high-energy neutrons and protons.¹¹² The collision process between liquid lithium and high-energy particles causes electronic excitation and atomic sputtering. It is useful to study these dynamic processes.

Using rt-TDDFT methods, we have simulated the collision between high-energy proton and liquid lithium (~1000 K), as shown in Figure 7a. Figure 7b shows the energy loss of different proton projectile energies from 30 eV to 1 MeV in which the computational detail is similar to the case in Figure 6. The results from our rt-TDDFT simulations are excellent consistent with the experimental data¹¹³ and SRIM data,¹⁰⁶ as shown in Figure 7b. Herein, we decompose the energy loss into the electronic stopping power (S_e) and the nuclear stopping power (S_n). The S_e is far larger than S_n at high projectile energy which illustrates the electronic excitations play a dominant role. At low-energy region (E < 200 eV), the Li nuclear recoiling effect is prominent which can be also described by the ground-state BOMD in Figure 7b,c. Besides, there is an interesting issue: whether the core level can contribute significantly to the electronic stopping power. To understand this problem, we re-simulate the S_e (the asterisk in Figure 7b) with electronic pseudopotentials including Li 1s core electrons. Compared to the previous results, the difference is small. We thus can conclude that the core-level contribution is not important for the electronic excitations at high-energy collision. Finally, we also discover the electronic stopping power cannot be predicted solely by the eigen-energy excitation profile, as shown in Figure 7d.

3.2.3 | "Dynamic donors" during impurity diffusion in silicon

Impurity diffusion is one of the most basic processes in semiconductors. In previous studies on impurity diffusion, the researchers mostly use ground state methods, like the BOMD simulation or nudged elastic band (NEB) method to study



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FIGURE 6 The electronic stopping power of proton projectile in silicon. (a) Electronic stopping power (S_e) as a function of the projectile velocity v along the <001> channeling trajectory (see the inset). The red and orange curves represent the results from our rt-TDDFT simulations in the uncorrected gap (0.6 eV) and corrected gap (1.12 eV), respectively. The solid and dashed blue lines show the electronic stopping power (S_e) and nuclear stopping power (S_n) from "The Stopping and Range of Ions in Matter" (SRIM).¹⁰⁶ (b) Density of state (DOS). The blue line shows the total DOS and the red shaded area represents electronic occupations. The yellow pentagon shows the ionization level $(E_i = 5.1 \text{ eV})$.¹⁰⁸ The inset displays the DOS near the bandgap. (c) Under the projectile velocity v = 1.2 a.u., the energy of excited electrons as a function of the number of adiabatic states. (d) The energy of excited electrons as a function of proton displacement in the different number of adiabatic states. The slope is the electronic stopping power (S_e)

the diffusion barrier^{114,115} We have used nonadiabatic rt-TDDFT algorithm to study the diffusion of low-energy impurities in semiconductors. Surprisingly, we found that in some cases, the thermally activated impurity diffusion not an adiabatic process. In particular, we found that the charge states of the impurity can change during the atomic diffusion. Thus, the simple diffusion process might be more complicated than we thought.⁵²

Figure 8a shows an example of Au diffusion along the <111> pathway in Si. Au impurity prefers to stay at the most stable tetrahedral site (T site) in Si which is treated as the initial position (t = 0 fs). Compared BOMD and rt-TDDFT simulations, we discover that there is an obvious difference of the Au atomic pathway, as shown in Figure 8b-e. The Au atom crosses the H site and is trapped at the next T site at the end in the BOMD simulation in Figure 8b. On the other hand, it vibrates around the hexagonal site (H site) in the rt-TDDFT simulation in Figure 8c. During the Au diffusion, the electron originally located at the defect level 1 is excited into the conduction band through the anti-crossing of two defect levels, as shown in Figure 8g. This leads to the change of the original neutral Au impurity into a positively charged impurity. The change of Au charge state leads to a change of the PES, as shown in Figure 8h, makes the H site a local minimum, hence the Au ion can be trapped at the H site near the end of the simulation. We call this electronic excitation phenomenon "dynamic donor." However, the "dynamic donor" phenomenon cannot be discovered in adiabatic BOMD simulation (Figure 8f). Besides the Au impurity, we also showed several other examples of nonadiabatic diffusion, for example, the diffusion of impurities Zn and Cd in Si, the self-diffusion of Ti in TiO₂, and so on. Thus, we believe the nonadiabatic effect of impurity diffusion in semiconductors may be a relatively common phenomenon, worthy of more studies in the future.

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FIGURE 7 (a) The calculated atomic structure with a proton and 72 liquid lithium atoms and the electronic density at t = 0. (b) Stopping power as a function of projectile initial kinetic energy in the range of 30 eV to 1 MeV in rt-TDDFT simulations. The red line and triangle are the total stopping power (TSP), blue line and circle indicate electronic stopping power (ESP), the navy line and diamond are the nuclear stopping power (NSP), and the green open circle represents the stopping power of the experimental data (ExDa).¹¹³ The SRIM model extrapolated to low velocity is also shown as the dashed line,¹⁰⁶ and the asterisk represents the result from all electronic potential (AEP) calculation. (c) BOMD simulations (red line). (d) Electronic excitation profiles at different initial proton energies (reprinted with permission from Reference 50. Copyright 2017 American Physical Society)

3.3 | Ultrafast chemical reaction

The chemical reactions in molecules are often accompanied by charge transfer or electron excitation which leads to a non-equilibrium nonadiabatic process.^{17,19,116,117} However, there is insufficient theory to study the molecule dissociation at the non-equilibrium conditions due to the lack of appropriate nonadiabatic methods. Here, we provide three nonadiabatic methods, such as rt-TDDFT, Boltzmann-TDDFT, and NOB-TDDFT, to discuss several important problems about molecule dissociation.

3.3.1 | Nonadiabaticity of CO reduction reaction

Most theoretical catalytic studies, for their transition barriers, are often done under adiabatic assumption, either through BOMD or NEB for transition barrier.^{6,118,119} There is nevertheless always an issue whether nonadiabatic process could play any role. This is particularly true for electrochemistry reactions where the chemical reaction is accompanied with charge transfer.¹²⁰ To investigate this possibility, we have carried out a comparison between the ground-state BOMD and nonadiabatic rt-TDDFT simulations of CO₂ reduction, for the particular reaction step: $CO + H_3O^+ + e^- \rightarrow COH + H_2O$ on copper (111) surface, as shown in Figure 9a. Based on NEB static calculation, the energy barrier is around 0.5 eV for this reaction. To prepare the reaction, we first place the system at the transition point, and let is relax to the reaction initial state using BOMD. We then start the system from this initial state, but inverse the velocity (increase slightly for their amplitude), thus it can reach the transition point under BOMD. The same initial kinetic velocities are given in BOMD and rt-TDDFT calculations. We find the reaction can only happen in BOMD simulation, but fails to happen in rt-TDDFT simulation, as shown in Figure 9b. The failure of the reduction reaction in rt-TDDFT is attributed to the charge transfer from Cu which reduces 0.13 electrons than BOMD, leading to a higher energy barrier, as shown in Figure 9d. Afterward, we give a small increase (12 meV which account for 6.1% of the barrier energy) for the H initial kinetic energy in rt-TDDFT simulation, and the reaction is successful at the end (Figure 9c). In summary, we find the rt-TDDFT result with the nonadiabatic effect increases the 6% reaction barrier than the ground-state BOMD result in aqueous conditions. Overall, this effect is small in this case. But it does not exclude the possibility of larger effect in other reactions. The main point is whether there is an occupied state which becomes unoccupied during the reaction due to some state crossing. If the answer is yes, and if the transition is fast, then nonadiabatic effect might be significant.



FIGURE 8 (a) The diffusion path of interstitial Au atom along the <111> direction. The big blue balls represent Si atoms, and the small orange balls track the trajectory of the interstitial Au atom. The high symmetry sites such as tetrahedral site (T-site) and hexagonal site (H-site) are marked. (b,c) The diffusion trajectory of Au impurity in the BOMD and TDDFT simulations when the initial kinetic E_k $(t_0) = 0.45$ eV. (d,e) The corresponding Au impurity movement distance and kinetic energy as a function of time. (f,g) Evolution of adiabatic state energy levels as functions of time in BOMD and rt-TDDFT simulations. Green (blue) lines represent the impurity level-1 (level-2) inside the Si band gap. Red solid circles indicate the occupations of the impurity electron with its size represent the amplitude of the occupation. (h) The PES along the diffusion path of Au and Au^+ based on NEB method. Here, we set the minimum energy of the PES to zero (reprinted with permission from Reference 52. Copyright 2019 American Physical Society)

3.3.2 Radiolysis of organic molecules

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Radiolysis is an important process in many phenomena such as degradation of polymers, radiation damage of material, and molecule damage under electron beam microscope.¹²²⁻¹²⁵ The radiation damage induced by electron beams can be roughly divided into two categories: elastic scattering and inelastic scattering.^{126,127} The inelastic scattering exhibits a more complicated process which is mainly related to electron excitations. In radiolysis, typically, a molecule can be ionized by the electron beam, or a Gamma-ray radiation, or other initial excitations.^{122,127} Very often, the initial ionization cross section can be calculated with analytical formula together with the ab initio calculated electronic states of the molecule.^{128,129} However, what happen next is usually not so clear. Roughly speaking, the deep hot hole will relax to the highest occupied molecular orbital (HOMO), in the meanwhile release its energy to the nuclear. It is this released energy which breaks down the molecule. However, this is not necessarily a thermal process. The bond breaking often happens during the hot hole relaxation process. Unfortunately, so far there are not many viable methods to simulate such process. The traditional quantum chemistry method might be too expensive to study relatively large molecules. Our Boltzmann-TDDFT and NOB methods provide an approach to study this process under rt-TDDFT.

We have first performed Boltzmann-TDDFT to study the relaxation process in $C_2H_6O_2$ after it has been ionized into $C_2H_6O_2^+$ by electron beam radiation in Figure 10. We found that $C_2H_6O_2^+$ is broken down into $C_2H_5O^+$ and OH fragments when one of the electrons at the deep valence states 1 or 2 is ionized. The $C_2H_6O_2^+$ molecular is always dissociated into two CH₃O⁺ fragments due to hot hole cooling effect when one of the electrons at 3 to 11 valence states is ionized. The breakdown from $C_2H_6O_2^+$ to two CH_3O^+ fragments all happen within 300 fs as shown in Figure 10.



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FIGURE 9 (a) Atomic structures of the initial and final structures. Top: top view; bottom: side view of the two structures. During the reaction, one proton of hydronium moves from O of H_3O^+ to O of CO. Golden: Cu; red: O; brown: C; light violet: H. (b) Reaction paths computed by adiabatic BOMD and nonadiabatic rt-TDDFT. It records the distance of the proton to oxygen of hydronium and the proton to oxygen of CO. If the reaction proceeds, the black line and red line switch, indicating the proton transferring from hydronium to CO. Otherwise, these two lines will return back. (c) Both simulations have proton bonding to CO to make the reaction successful (thus rt-TDDFT has a higher initial velocity than BO-MD). (d) Measured change of total charge counted above the plane. This horizontal plane has its *z*-value in the middle, between C and the top Cu layer. Here, simulation—"TDDFT reaction fail" has the same initial velocity to "BO-MD reaction successful," while "TDDFT reaction successful" has higher initial velocity than "BO-MD reaction successful" (reprinted with permission from Reference 121. Copyright 2020 American Physical Society)

Besides, when the initial ionization orbital is deep enough, the system has sufficient energy to cause a secondary ionization which is the Auger process induced by strong electron–electron interaction. The Auger process causes the double ionization and subsequently Coulomb explosion which results in the new dissociated products (CH_5O^+ and CHO^+), as shown in Figure 10. No molecule breakdown is observed in the rt-TDDFT simulations when the initial ionization is on the high-energy levels 12 and 13. Thus, there is no kinetic breakdown in such ionizations. Nevertheless, thermodynamically, they can have sufficient thermal energy to cause a breakdown if enough time is provided. From total ground state energy and transition barrier analysis, we conclude that in the levels 12 and 13 excitations, the system can be dissociated into CH_5O^+ and CH_3^+ (Figure 10). The simulation results agree qualitatively with the experiments in the fragments found in the final products. This study shows us the radiolysis can be a rather complicated process, where different mechanisms play different roles in different energy regions.

The above radiolysis process for $C_2H_6O_2^+$ is done with Boltzmann-TDDFT, thus it does not include the branching effect. We have also applied our NOB approach to study the radiolysis of C_3H_7OH molecule as shown in the inset of Figure 11b. First, we calculated the orbital eigen energies of the molecule at its neutral charge, as shown in Figure 11a. The difference between the first valence state and the HOMO is about 18 eV. We then mimic the dynamics of molecular dissociation when one of the electrons at valence states is ionized (e.g., by the high-energy electron beam, or ultraviolet light). In NOB simulation, repeated runs (with different random number seeds) need to be performed, so to yield a statistic average for different products. When the valence state 1 is ionized, the two possible trajectories of molecular dissociation are found, as shown in Figure 11b,c. Due to the wave function of valence state 1 around the O–C bond, this bond is immediately dissociated after the electron ionization. In trajectory-1, the O–H bond is dissociated at about



FIGURE 10 Picture of the hot carrier decay processes on different electronic levels and the structural dissociation processes of $C_2H_6O_2$ after radiolysis ionization (reprinted with permission from Reference 42. Copyright 2019 American Physical Society)



FIGURE 11 Bond breaking in different NOB trajectories at different initial valence state ionizations. (a) DFT eigen energy spectrum for the neutral charge C_3H_7OH molecule. (b) Trajectory-1 when valence state 1 is ionized. The number in the bond (e.g., 3, O-C) corresponds to the numbers in the inset, (c) Trajectory-2 when valence state 1 is ionized. (d) Trajectory-1 when valence state 7 is ionized. (e) Trajectory-2 when valence state 1 is ionized. 39. Copyright 2020 American Physical Society)

100 fs, perhaps due to its electronic wave function collapsing. In trajectory-2, the OH group is not broken, but a C—H bond is dissociated at about 100 fs because of the thermal vibrations from hot hole cooling. Besides, we calculate another example where one of the electrons at valence state 7 is ionized. Figure 11d shows an undamaged picture after

the electron ionization for trajectory 1. However, a C–C bond is broken in trajectory 2, and the initial molecular is dissociated into final CH_2OH and CH_2CH_3 , as shown in Figure 11e. Overall, we can see that the NOB simulations from the same initial condition allow the description of the multi-path images in the molecular radiolysis process. This could be important for radiolysis studies.

4 | CONCLUSION AND OUTLOOK

In this short review, we have summarized our rt-TDDFT algorithms to study the non-equilibrium carrier dynamics. Compared with the traditional TDDFT methods, our new method allows us to use a much larger time step, so it can simulate a 100-atom system for its ultrafast process on a picosecond time scale in a routine basis. This new scheme reduces the original time dependent Schrodinger's equation into a reduced dimension (the size of the expansion adiabatic states) problem. The method can also be implemented in an existing ground-state DFT code, using many of its existing functionalities (e.g., the SCF charge mixing). It can be used for different exchange correlation functionals, including the hybrid functionals. In our rt-TDDFT Hamiltonian, it has included the electron–electron, electron–phonon, electron–light interactions, noncollinear magnetic moment, SOC effects. This provides a powerful tool to explore different kinds of physical problems in condensed matter physics. To deal with hot carrier cooling, we have developed the Boltzmann-TDDFT method. To include the multiple path problem in chemical reactions, we have developed the NOB-TDDFT.

Our applications of the above methods reveal that, many of the ultrafast experimental phenomena can be described quantitatively by the rt-TDDFT approach. This includes the laser induced phase transition and recovery times, the dependence on the laser intensity, and the laser frequency dependence. The direct rt-TDDFT simulation on these phenomena allows us to analyze the problem in systematic ways, for example, by changing the laser intensity, frequency, or turn on/off some of the effects (e.g., SOC effect, or electron-phonon effect in demagnetization process). In recent years, there are great advance in experimental measurement of ultrafast dynamics. For example, the photoexcited phase transition in VO₂ is probed by X-ray pulses⁹; ultrafast manipulation of the topological properties in WTe₂ is measured by ultrafast electron diffraction⁹⁵; and macroscopic magnetic states can be manipulated by light-driven phonons.¹² In the past, many of these experimental results were explained by static calculations (e.g., the PES change under a constraint orbital occupation), or analytical perturbation method (e.g., the electron-phonon, and spin induced scattering for demagnetization process). However, such static PES explanation might have ignored many important factors, like the speed of the dynamics, the actual relaxation process, the kinetic versus thermodynamics movements and phase transition process. The perturbation theory can also miss many physical factors, like the electron-electron interaction and its time evolution. These factors are very difficult to be dealt with using analytical treatments. The rt-TDDFT simulation thus becomes the method of choice in studying these problems. Besides the laser induced phase transition and magnetic moment changes, we have also applied our methods to simulate the plasmon excitation and its decay, ion collision with materials, and radiolysis process. Recently, we have also used it to study semiconductor device degradation caused by channel electron current interaction with defect states. Our ion-material interaction simulation found a novel phenomenon where during an impurity diffusion process, the impurity might lose an electron and becomes a charged impurity. Such dynamic donor phenomena might play an important role in fundamental semiconductor physics. The ability for radiolysis study can open a new way to study such complicated phenomena, and achieve a new level of understanding for problems like electron beam damaging in transmission electron microscope.

There are however, many remaining challenges. The simulation for demagnetization is still extremely expensive due to the use of SOC. In practice, only systems with about 30 atoms can be simulated. However, for many problems, one needs to use much larger systems. It will be useful if one can simulate the spin dynamics for systems with about 500 atoms, hence to make a connection with the empirical Landau–Lifshitz–Gilbert model. For wave function collapsing scheme, it is also not clear whether the dephasing has to happen between adiabatic states. It is quite possible the dephasing can also happen between diabatic states based on their localization. For bulk system, one major challenge under rt-TDDFT is its limitation for hot carrier transfer between different k-points. In order to allow such inter k-points transitions, one has to use a very large supercell, which increase the computational costs. This might not be a major issue under strong laser excitation where the carrier cooling is fast due to strong perturbation of the system. However, for weak excitation, this can be problematic. In such cases, the analytical perturbation treatment has its advantages due to the use of explicit electron–phonon coupling constants. All these however, can perhaps be overcome by future

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methodology and algorithm developments. Overall, we feel there is a bright future for direct rt-TDDFT simulations of ultrafast dynamics and their related phenomena.

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CONFLICT OF INTEREST

The authors have declared no conflicts of interest for this article.

DATA AVAILABILITY STATEMENT

Date sharing is not applicable to this article as no new data were created or analyzed in this study.

AUTHOR CONTRIBUTIONS

Wenhao Liu: Writing – original draft (equal); writing – review and editing (equal). **Zhi Wang:** Writing – original draft (equal); writing – review and editing (equal). **Zhanghui Chen:** Writing – original draft (equal); writing – review and editing (equal). **Jun-Wei Luo:** Conceptualization (equal); writing – original draft (equal); writing – review and editing (equal). **Shu-Shen Li:** Supervision (equal). **Lin-Wang Wang:** Conceptualization (lead); methodology (lead); writing – original draft (equal).

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