Real-time time-dependent electronic structure theory

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Real-time time-dependent electronic structure theory is one of the most promising methods for investigating time-dependent molecular responses and electronic dynamics. Since its first modern use in the 1990s, it has been used to study a wide variety of spectroscopic properties and electronic responses to intense external electromagnetic fields, complex environments, and open quantum systems. It has also been used to study molecular conductance, excited state dynamics, ionization, and nonlinear optical effects. Real-time techniques describe non-perturbative responses of molecules, allowing for studies that go above and beyond the more traditional energy- or frequency-domain-based response theories. Recent progress in signal analysis, accurate treatment of environmental responses, relativistic Hamiltonians, and even quantized electromagnetic fields have opened up new avenues of research in time-dependent molecular response. After discussing the history of real-time methods, we explore some of the necessary mathematical theory behind the methods, and then survey a wide (yet incomplete) variety of applications for real-time methods. We then present some brief remarks on the future of real-time time-dependent electronic structure theory. © 2017 Wiley Periodicals, Inc.

INTRODUCTION

Ab initio real-time time-dependent electronic structure theory seeks to solve the time-dependent Schrödinger equation (TDSE) for quantum systems in order to predict and simulate the response to any combination of perturbations, be they electromagnetic fields,[1–11] complex environments,[12–29] thermal baths,[30–37] and so on. Real-time methods have been applied to many types of spectroscopy[38–52] as well as studies of coherence and charge-transfer dynamics.[25,53–63] They have also proven effective for studies of molecular conductance.[12–20] Recently, they have been extended to *ab initio* spin dynamics[64,65] as well as relativistic molecular Hamiltonians.[66–69] Continuing improvements in computing power have also renewed interest in explicit time-propagation of correlated methods such as multi-

configurational self-consistent-field (MCSCF),[70–73] configuration interaction,[74–80] algebraic diagrammatic construction,[81–84] and equation-of-motion coupled cluster theory.[75,76,85–88] Recently, there has been a growing interest in treating the molecular interaction with a quantized electromagnetic field[89–94]—a real-time quantum electrodynamics (QED)—leading to first-principles studies of photon absorption and emission and simulations of cavity QED experiments.

Real-time methods, like other *ab initio* methods, must numerically approximate the underlying Schrödinger equation through mean-field approximations, such as density functional theory (DFT), or wave function-based techniques. Furthermore, real-time methods distinguish themselves from other time-dependent approaches, such as time-dependent (frequency-domain) linear-response theory or equation-of-motion coupled cluster, in that real-time methods *explicitly* consider the time-dependence of the quantum system and its interactions with itself and its environment. That is, in addition to numerical approximation to the Hamiltonian, real-time methods must also develop robust numerical techniques to explicitly

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propagate the quantum system in time. Given the complexity of the quantum system, as well as the underlying strongly connected unitary nature of the quantum propagator (Stone's theorem[95]), standard algorithms to solve time-dependent partial differential equations (PDEs)—such as the Runge–Kutta class of methods[96]—are not always well suited to describe the time evolution of the TDSE. However, techniques based off the Magnus expansion,[97–102] which we will discuss in a later section, as well as other symplectic integrators,[103–114] have proven useful to the development of arbitrarily accurate quantum propagators.

HISTORICAL DEVELOPMENT OF REAL-TIME METHODS

Historically, the first *ab initio* studies of explicitly time-dependent solutions of the TDSE began in the field of nuclear physics.[115–117] (Here we do not include solutions of the TDSE-based on Gaussian wave-packets, see e.g., Ref 118, which do not explicitly consider the electronic structure of the system.) In a series of papers in the 1970s, these numerical techniques were applied to the study of nuclear collisions and their scattering profiles. Around the same time, new methods for obtaining ground-state wave functions were developed, based on the idea of propagating the systems in *imaginary* time,[119] which turns a dynamics problem into a wave function search problem. These imaginary-time methods were a fruitful way of obtaining a self-consistent ground-state wave function. Interestingly, a few years prior similar random-walk imaginary-time techniques were being developed independently by Anderson while working on diffusion Monte-Carlo methods.[120–122] Regardless, by the 1980s, explicitly time-dependent methods existed primarily in the nuclear physics community, and came in two flavors: imaginary-time for wave function optimization and real-time for dynamics and computing scattering cross sections.

Why real-time methods were not widely adopted in the quantum chemistry community? One reason may be that around the same time, (frequency-domain) response theory was being developed and applied to chemical systems with remarkable success. An excellent overview of the history and status of response theory has been given in Ref 123. Why propagate a wave function in time to determine its response when one can directly obtain molecular response properties (excited states, transition probabilities) *directly* from the eigenvalues and eigenvectors of the Green's function? Furthermore, efficient and accurate response theories had been developed

for correlated wave functions, such as MCSCF and coupled cluster methods. Although the early ground work for propagating correlated wave functions was laid out by Meyer and coworkers during the development of the multi-configurational time-dependent Hartree (MCTDH),[124–126] explicit time-propagation of correlated wave functions remained expensive, and only recently has matured into a more routine option in the quantum chemistry community.

However, the field changed in the 1990s with the advent of usable and accurate-enough DFT codes. George Bertsch, together with Kazuhiro Yabana, introduced the first use of so-called real-time time-dependent DFT (RT-TDDFT) for studies of dynamic molecular response properties[127] in 1996. Yabana and Bertsch, both nuclear physicists, were well aware of the explicitly time-dependent techniques in nuclear physics, and saw that DFT could provide an accurate and affordable route to compute spectroscopic properties of molecules and small atomic clusters. Their initial foray into explicitly time-dependent electronic structure theory proved successful.[128–130] They called these 'real-time' methods, and the name has stuck since.

Since the late 1990s, there has been an explosion of activity in real-time methods. Applications for real-time methods span the breadth of spectroscopy and have found utility in studies of molecular electronics, electronic coherence, and charge-transfer dynamics. However, before we turn to the stunning variety of applications, we must first take a closer look at the theory behind real-time electron dynamics.

FORMAL THEORY: THE MAGNUS EXPANSION

The goal of real-time electronic structure theory is to explicitly solve the TDSE, given by

$$i\hbar \frac{\partial}{\partial t} \psi(t) = H(t)\psi(t) \tag{1}$$

where $H(t)$ is the time-dependent Hamiltonian and $\psi(t)$ is the time-dependent wave function. Because of the time-dependence in the Hamiltonian $H(t)$, the TDSE does not have a general closed-form solution. This problem led Wilhelm Magnus, in 1954, to propose the Magnus expansion.[97] The goal of the Magnus expansion is to find a general solution for the time-dependent wave function in the case where H is time-dependent, and, more crucially, when H does not commute with itself at different times, e.g., when $[H(t_1), H(t_2)] \neq 0$. In the following we will follow

closely the notation of Blanes et al.[100] First, for simplicity we redefine $\widetilde{H}(t) \equiv \frac{-i}{\hbar} H(t)$ and introduce a scalar $\lambda = 1$ as a bookkeeping device, so that the TDSE can be written as

$$\frac{\partial}{\partial t}\psi(t) = \lambda\widetilde{H}(t)\psi(t) \qquad (2)$$

At the heart of the Magnus expansion is the idea of solving Eq. (2) by using the quantum propagator $U(t, t_0)$ that connects wave functions at different times, e.g.,

$$\psi(t) = U(t,t_0)\psi(t_0) \qquad (3)$$

Furthermore, the Magnus expansion assumes that $U(t, t_0)$ can be represented as an exponential

$$U(t,t_0) = \exp(\Omega(t,t_0)) \qquad (4)$$

This yields the modified TDSE (where $\psi(t_0)$ factors out)

$$\frac{\partial}{\partial t}U(t,t_0) = \lambda\widetilde{H}(t)U(t,t_0); \quad U(t_0,t_0) = I \qquad (5)$$

Now, for scalar $\widetilde{H}$ and U, Eq. (5) has a simple solution, namely

$$U(t,t_0) = \exp\left(\lambda\int_{t_0}^{t}\widetilde{H}(t')\,dt'\right) \qquad (6)$$

However, if $\widetilde{H}$ and U are matrices this is not necessarily true. In other words, for a given matrix A the following expression does not necessarily hold:

$$\frac{\partial}{\partial t}\left(\exp(A(t))\right) = \left(\frac{\partial}{\partial t}A(t)\right)\exp(A(t))$$
$$= \exp(A(t))\left(\frac{\partial}{\partial t}A(t)\right) \qquad (7)$$

because the matrix A and its derivatives do not necessarily commute. Instead, Magnus proved that in general $\Omega(t, t_0)$ satisfies

$$\frac{\partial}{\partial t}(\Omega(t,t_0)) = \lambda\widetilde{H}(t)$$
$$+ \lambda\sum_{k=1}^{\infty}(-1)^k\frac{B_k}{k!}\overbrace{[\Omega(t,t_0),[\cdots[\Omega(t,t_0)}^{k-\text{times}},\widetilde{H}(t)]]\cdots];$$
$$\Omega(t_0,t_0) = 0 \qquad (8)$$

where B_k are the Bernoulli numbers. This equation may be solved by integration and iterative substitution of $\Omega(t, t_0)$. While it may appear that we are worse off than when we started, collecting like powers of λ (and setting $\lambda = 1$) allows us to obtain a power-series expansion for $\Omega(t, t_0)$

$$\Omega(t,t_0) = \int_{t_0}^{t}\widetilde{H}_1\,dt_1 + \frac{1}{2}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\left[\widetilde{H}_1,\widetilde{H}_2\right]$$
$$+ \frac{1}{6}\int_{t_0}^{t}dt_1\int_{t_0}^{t_1}dt_2\int_{t_0}^{t_2}dt_3\left(\left[\widetilde{H}_1,\left[\widetilde{H}_2,\widetilde{H}_3\right]\right] + \left[\widetilde{H}_3,\left[\widetilde{H}_2,\widetilde{H}_1\right]\right]\right) + \cdots \qquad (9)$$

This is the Magnus expansion, and here we have given up to the third-order term. We have also made the notational simplification that $\widetilde{H}_k = \widetilde{H}(t_k)$. This is the basis for nearly all numerical methods to integrate the many-body TDSE in molecular physics. Each subsequent order in the Magnus expansion is a correction that accounts for the proper time-ordering of the Hamiltonian.

The Magnus expansion in Eq. (9) immediately suggests a route to many numerical integrators. The simplest would be to approximate the first term by

$$\int_{t}^{t+\Delta t}\widetilde{H}_1\,dt_1 \approx \Delta t\widetilde{H}(t) \qquad (10)$$

leading to a forward-Euler-like time integrator of

$$\psi(t+\Delta t) = \exp\left(\Delta t\widetilde{H}(t)\right)\psi(t) \qquad (11)$$

which we can re-write as

$$\psi(t_{k+1}) = \exp\left(\Delta t\widetilde{H}(t_k)\right)\psi(t_k) \qquad (12)$$

where subscript k gives the node of the time-step stencil. This gives a first-order method with error $\mathcal{O}(\Delta t)$. A more accurate second-order method can be constructed by approximating the first term in Eq. (9) by the midpoint rule, leading to an $\mathcal{O}(\Delta t^2)$ time integrator

$$\psi(t_{k+1}) = \exp\left(\Delta t\widetilde{H}(t_{k+1/2})\right)\psi(t_k) \qquad (13)$$

Modifying the stencil to eliminate the need to evaluate the Hamiltonian at fractional time steps (e.g., change

time step to $2\Delta t$) leads to the modified midpoint unitary transformation (MMUT) method[99,101]

$$\psi(t_{k+1}) = \exp\left(2\Delta t \widetilde{H}(t_k)\right)\psi(t_{k-1}) \qquad (14)$$

which is a leapfrog-type unitary integrator. Note that the midpoint method assumes $\widetilde{H}$ is linear over its time interval, and the higher order terms (containing the commutators) in this approximation to Eq. (9) go to zero. There are many other types of integrators based off the Magnus expansion that can be found in the literature.[98,102] The key point for all of these integrators is that they are *symplectic*, meaning they preserve phase–space relationships. This has the practical effect of conserving energy (within some error bound) in long-time dynamics, whereas non-symplectic methods such as Runge–Kutta will experience energetic 'drift' over long times.

A final note: in each of these schemes it is necessary to evaluate the exponential of the Hamiltonian. In real-time methods, this requires computing a matrix exponential. This is not a trivial task and aside from the construction of the Hamiltonian itself, is often the most expensive step in the numerical solution of the TDSE. However, many elegant solutions to the construction of the matrix exponential can be found in the literature.[98,131,132]

TIME-DEPENDENT EQUATIONS FOR APPROXIMATE WAVE FUNCTIONS

While the Magnus expansion is formally exact for exact wave functions, in practice, the working equations that govern the evolution of a quantum system must be determined for different approximations to the TDSE. Time-dependent equations for approximate wave functions can be derived by invoking the Dirac–Frenkel,[133,134] McLachlan,[135] or time-dependent variational principles (TDVP).[136] These principles are based off of different ideas, but have been shown to be equivalent under most conditions,[137,138] leading some authors to collectively refer to them as the Dirac–Frenkel–McLauchlan TDVP.[71,72]

The Dirac–Frenkel variational principle is arguably the simplest of the three[139] and states that, starting from the TDSE,

$$\langle\delta\psi|\left(H - i\frac{\partial}{\partial t}\right)|\psi\rangle = 0 \qquad (15)$$

must hold, where $\delta\psi$ denotes possible variations of the wave function with respect to the parameters

defining it. (We have left off the explicit time dependence of $|\psi\rangle$ for brevity.) Notably, this principle also appears in the quasi-energy formalism used to derive working equations in response theory.[123] McLauchlan criticized the Dirac–Frenkel principle for not being a 'true' variational principle and so suggested solving the minimization problem

$$\min||H\psi - i\frac{\partial\psi}{\partial t}||^2 \qquad (16)$$

This expression can also be rewritten as

$$\text{Im}\langle\delta\psi|\left(H - i\frac{\partial}{\partial t}\right)|\psi\rangle = 0 \qquad (17)$$

making it easier to compare with the other variational principles. The TDVP evaluates the stationary conditions ($\delta S = 0$) of the action integral

$$S = \int dt\langle\psi|\left(H - i\frac{\partial}{\partial t}\right)|\psi\rangle \qquad (18)$$

In practice, this action integral should be a Lagrangian including constraints on the approximate wave function. These should be the same constraints used to determine the working equations for optimizing the time-independent wave function. For normalized wave functions, evaluating the variation in the action integral is equivalent to saying that

$$\text{Re}\langle\delta\psi|\left(H - i\frac{\partial}{\partial t}\right)|\psi\rangle = 0 \qquad (19)$$

at all times. Broeckhove et al.[137] showed that the McLauchlan and TDVP are equivalent and thus are equivalent to the Dirac–Frenkel expression.

These principles can be used to derive the working equations for approximate wave functions. They will lead to equations of motion for the parameters that describe the wave function, such as the molecular orbital coefficients or configuration interaction coefficients. A time-dependent bivariational principle has also been used to derive the working equations for an orbital adaptive time-dependent coupled cluster theory.[86]

ABSORPTION IN REAL-TIME TIME-DEPENDENT ELECTRONIC STRUCTURE METHODS

One of the common uses of real-time methods is to compute spectroscopic observables. To show how

real-time time-dependent electronic structure theory leads to observable spectroscopic properties, we will derive an expression for the absorption cross section in terms of time-dependent observables. Here we follow closely the presentation by Tannor.[140] The absorption cross section $\sigma(\omega)$ can be defined as the ratio of the average number of photons absorbed ($\Delta N(\omega)$) to the average number of incident photons per unit area ($N(\omega)/A$) at a given frequency ω,

$$\sigma(\omega) = \frac{\Delta N(\omega)}{N(\omega)} A \tag{20}$$

Given an electronic Hamiltonian H with a time-dependent electric field $E(t)$,

$$H = H_0 - E(t) \cdot \boldsymbol{\mu} \tag{21}$$

where H_0 collects the time-independent terms of the Hamiltonian and $\boldsymbol{\mu}$ is the dipole moment operator (and we are therefore working in the electric dipole approximation), and $E(t)$ and $\boldsymbol{\mu}$ are vector quantities. Expressing H in the energy eigenbasis of H_0, we have

$$H = \sum_n E_n |\psi_n\rangle\langle\psi_n| - E(t) \cdot \sum_{nm} \boldsymbol{\mu}_{nm} |\psi_n\rangle\langle\psi_m| \tag{22}$$

Given this Hamiltonian, and assuming our system is completely in its ground state, we can compute the average rate of photons absorbed, dN/dt. In the presence of a time-dependent electric field, the average rate of photons absorbed is opposite to the rate of electronic population leaving the ground state dN_0/dt, where $N_0 = \langle\psi_0|\psi_0\rangle$:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\frac{\mathrm{d}N_0}{\mathrm{d}t} = -\left(\langle\dot{\psi}_0|\psi_0\rangle + \langle\psi_0|\dot{\psi}_0\rangle\right) \tag{23}$$

Since $|\dot{\psi}_0\rangle$ is given by the definition of the Hamiltonian, exploiting complex conjugation symmetry lets us write

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -2\mathrm{Re}\left[\langle\psi_0|iE_0/\hbar|\psi_0\rangle - E(t)\cdot\sum_n \langle\psi_n|i\boldsymbol{\mu}_{n0}/\hbar|\psi_0\rangle\right] \tag{24}$$

Given that the first term on the right-hand side is totally imaginary, we can simplify the above expression (explicitly showing the time-dependence of the states) to give

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{2}{\hbar}\mathrm{Im}\left[E(t)\cdot\sum_n \langle\psi_n(t)|\boldsymbol{\mu}_{n0}|\psi_0(t)\rangle\right] \tag{25}$$

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{2}{\hbar}\mathrm{Im}[E(t)\cdot D(t)] \tag{26}$$

where $D(t) = \sum_n\langle\psi_n(t)|\boldsymbol{\mu}_{n0}|\psi_0(t)\rangle$ is the time-dependent transition dipole moment. To find the average total number of photons absorbed we can integrate the above to get

$$\Delta N = \frac{2}{\hbar}\mathrm{Im}\int_{-\infty}^{\infty} E(t)\cdot D(t)\,\mathrm{d}t = \frac{4\pi}{\hbar}\mathrm{Im}\int_{-\infty}^{\infty} \widetilde{E}(\omega)\cdot\widetilde{D}(\omega)\,\mathrm{d}\omega \tag{27}$$

where we have utilized the Plancherel theorem, and the tilde notation indicates the Fourier transform pairs. We are using the asymmetric definition of the Fourier transform such that

$$f(t) = \int_{-\infty}^{\infty} \widetilde{f}(\omega)\,\mathrm{e}^{-i\omega t}\,\mathrm{d}\omega \tag{28}$$

and

$$\widetilde{f}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(t)\,\mathrm{e}^{+i\omega t}\,\mathrm{d}t \tag{29}$$

For the absorption cross section, we can look at single frequencies ω, so that the average number of photons absorbed for a given frequency of incident light is given by

$$\Delta N(\omega) = \frac{4\pi}{\hbar}\mathrm{Im}\left[\widetilde{E}(\omega)\cdot\widetilde{D}(\omega)\right] \tag{30}$$

Now, from classical electrodynamics we know that for a given frequency, the average number of photons incident per unit area, $N(\omega)/A$, is given by

$$\frac{N(\omega)}{A} = |\frac{\widetilde{E}(\omega)|^2 c}{\hbar\omega} \tag{31}$$

thus by taking the ratio of Eq. (30) to Eq. (31) in Eq. (20), we have our absorption cross section

$$\sigma(\omega) = \frac{4\pi\omega}{c}\frac{\mathrm{Im}\left[\widetilde{E}(\omega)\cdot\widetilde{D}(\omega)\right]}{|\widetilde{E}(\omega)|^2} \tag{32}$$

Note that this expression is fundamentally nonperturbative within the dipole approximation. Practically, one suitable electric field shape to access $\sigma(\omega)$ is

to consider a delta-impulse function $E(t) = \delta(t - t_0)\boldsymbol{\kappa}$, where $\boldsymbol{\kappa}$ collects the intensity of the applied field. In this case, the Fourier transform of $E(t)$ is given simply by $\widetilde{E}(\omega) = \frac{1}{2\pi}\boldsymbol{\kappa}$. If we consider an impulsive field along a single axis i, then Eq. (32) takes the form

$$\sigma_{ii}(\omega) = \frac{4\pi\omega}{c}\frac{\mathrm{Im}\left[\widetilde{D}_i(\omega)\right]}{\kappa_i} \qquad (33)$$

so that when considering three pulses along each Cartesian axis, we can obtain the rotational (isotropic) average

$$\sigma(\omega) = \frac{4\pi\omega}{3c}\sum_{i=1}^{3}\frac{\mathrm{Im}\left[\widetilde{D}_i(\omega)\right]}{\kappa_i} \qquad (34)$$

In other words, the absorption cross section is the imaginary component of the Fourier transform of the time-dependent transition dipole moment, scaled by the field intensity. In real-time time-dependent electronic structure theory, if the system is initially in its ground state, and the perturbing field is sufficiently weak, $\widetilde{\boldsymbol{D}}(\omega)$ is given by

$$\widetilde{\boldsymbol{D}}(\omega) \approx \frac{1}{2\pi}\int_{-\infty}^{\infty}(\boldsymbol{\mu}(t) - \boldsymbol{\mu}(0))\mathrm{e}^{i\omega t}\,\mathrm{d}t \qquad (35)$$

since $\boldsymbol{\mu}(t) = \mathrm{Tr}(\boldsymbol{P}(t)\cdot\boldsymbol{\mu})$ and the time-dependent density matrix $\boldsymbol{P}(t)$ is given to first-order perturbation theory as

$$P(t) = |\psi(t)\rangle\langle\psi(t)| \approx |\psi_0\rangle\langle\psi_0|$$
$$+ \sum_n\left(c_n(t)\mathrm{e}^{-i(\omega_n - \omega_0)t}|\psi_n\rangle\langle\psi_0| + c.c.\right) \qquad (36)$$

The first term, when traced with $\boldsymbol{\mu}$ gives the static dipole moment, and the second term when traced with $\boldsymbol{\mu}$ gives the time-dependent transition dipole moment. The above expression has remarkable utility for accessing many types of spectroscopic observables within real-time time-dependent electronic structure theory.

SIGNAL PROCESSING

One of the challenges with real-time methods is that a time-dependent observable must be propagated for long times. Because spectroscopic properties are the Fourier transform of time-dependent signals, the signal resolution is limited by the length of the signal: this is the Heisenberg uncertainty principle. So while real-time methods often have favorable scaling with respect to basis size, the cost of the method will be severely limited if the signal must be propagated for many time steps. The number of time steps may drastically increase the prefactor of the real-time method, such that real-time methods are no longer computationally attractive. However, several techniques have been adopted from the signal analysis literature and extended to the analysis of time-dependent signals in real-time time-dependent electronic structure theory. This has had the result of reducing the amount of time a dynamics simulation needs to be performed in order to obtain useful spectra. One technique introduced by Andrade et al.[141] is to use compressed sensing methods to reduce the number of time-points required to reconstruct a frequency-domain signal. The method exploits sparsity in the frequency-domain, as many of the frequency coefficients will be zero. Knowing this feature about the spectrum allows one to reduce the number of time points required to generate spectra by recasting the Fourier transform as a system of under-determined linear equations. Optimizing the solution to this system in order to maximize sparsity allows one to reconstruct the Fourier transform with far fewer time points. In the systems studied by Andrade et al. a fivefold reduction in time points was observed, although the real savings depends on the sparsity of the signal. For systems with a high density-of-states the computational advantage will be reduced, whereas for sparse density-of-states systems compressed sensing techniques offer a significant reduction in cost.

More recently, a signal analysis technique based on Padé transforms of the Fourier transform has been introduced by Bruner et al.[142] This technique, rather than exploiting sparsity in the frequency-domain, instead exploits redundancy in the time signal, leading to significant reduction in the number of necessary time points. It is also suitable for high density-of-states systems. The heart of the technique relies on expressing the Fourier transform of a time-dependent signal with Padé approximants, then recasting this expression as a linear system. Done this way, it is possible to eliminate any frequency-dependent coefficients from the linear system, and the Fourier transform can be computed to arbitrary spectral density. In other words, given a series with M discrete time signal values $\mu(t_k)$, we can write the Fourier transform $\mu(\omega)$ as

$$\mu(\omega) = \sum_{k=0}^{M}\mu(t_k)\mathrm{e}^{-i\omega t_k} \qquad (37)$$

now, for a constant time step $t_k = k\Delta t$, this can be rewritten as a power series

$$\mu(\omega) = \sum_{k=0}^{M} \mu(t_k)\left(e^{-i\omega\Delta t}\right)^k = \sum_{k=0}^{M} c_k(z)^k \quad (38)$$

with $c_k = \mu(t_k)$ and $(z)^k = (e^{-i\omega\Delta t})^k$. This can be fit to a ratio of two power series (the method of Padé approximants), such that

$$\mu(\omega) = \sum_{k=0}^{M} c_k(z)^k = \frac{\sum_{k=0}^{N} a_k(z)^k}{\sum_{k=0}^{N} b_k(z)^k} \quad (39)$$

which can be rearranged to give

$$\sum_{k=0}^{M} c_k(z)^k \cdot \sum_{k=0}^{N} b_k(z)^k = \sum_{k=0}^{N} a_k(z)^k \quad (40)$$

Now, by setting $N = M/2$ (diagonal Padé scheme), equating powers, and rearranging, this can be reduced to a system of linear equations

$$\mathbf{G}b = \mathbf{d} \quad (41)$$

with $G_{km} = c_{N-m+k}$ and $d_k = -c_{N+k}$. The unknown b values are found by solving the linear system. Finally, each a_k coefficient is computed as

$$a_k = \sum_{m=0}^{k} b_m c_{k-m} \quad (42)$$

With the a and b coefficients in hand, the Fourier transform can be reconstructed from Eq. (39). Because a and b do not explicitly depend on frequency ω, the above expression can be computed for an arbitrary frequency density. That is, any selection of $z^k = e^{-i\omega\Delta t}$ is valid, resulting in a user-selected spectral resolution.

Put another way, the method of Padé approximants allows one to fit a rational function to the time-dependent signal, and then extrapolate the signal out to infinite time. Extrapolating a signal is akin to exploiting the redundancy in the oscillatory behavior of the time signal, and, because the signal is effectively of infinite length in time, arbitrary resolution of the spectrum is possible. An example of the Padé accelerated methods compared to traditional Fourier transform methods can be found in Figure 1. The methods are compared for the absorption spectrum
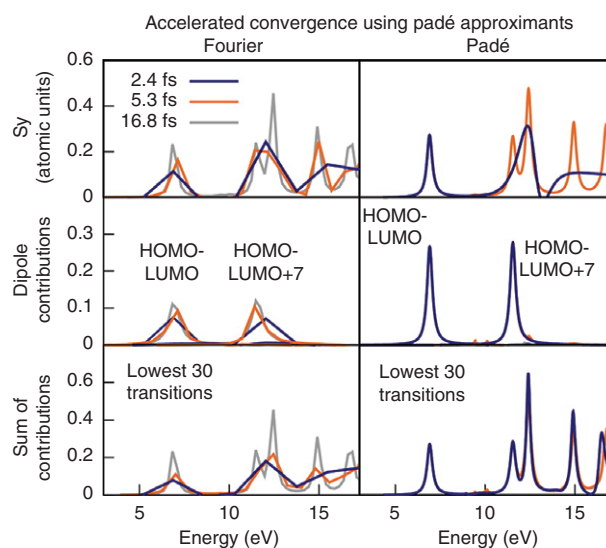

FIGURE 1 | Comparison of time convergence for Fourier (left column) and Padé acceleration (right column), for the total z-dipole contribution to the absorption spectrum (top row), two representative MO contributions to the spectrum (middle), and the resulting total absorption spectrum (bottom row). Note the high spectral density in the Padé accelerated technique, along with the rapid convergence with respect to simulation time. In all, Padé converges seven times faster than conventional Fourier transform—a considerable computational savings. (Reprinted with permission from Ref 142. Copyright 2016 American Chemical Society.)

of a water molecule, where the fast convergence of the Padé accelerated techniques over the Fourier transform can be observed. Note also the high-spectral density at all simulation time-lengths.

There are several modifications of the Padé method to make it even more efficient. For example, decomposing the total dipole signal into molecular-orbital dipole components allows the Padé approximant technique to become more efficient by looking at fewer oscillatory components per time signal, and then reconstructing the full spectrum by summing each MO transition dipole signal. Bruner et al. found that they could achieve a sevenfold reduction in cost with the combination of Padé transforms and transition dipole decomposition. Furthermore, actual solution of the Padé approximant-based method requires the solution of $Ax = b$, where A is $n \times n$, and x and b are n-length vectors, which scales as $\mathcal{O}(n^3)$ using Gauss–Jordan decomposition. However, because the matrix structure of $\mathbf{G}$ is Toeplitz, it is possible to use Levinson recursion[143,144] to solve the most expensive portion of the Padé approximant technique in $\mathcal{O}(n^2)$ time. Regardless, the Padé approximant technique is far less expensive than the real-time dynamics, of which it saves considerable cost.

APPLICATIONS

Magnetization dynamics and relativistic Hamiltonians

In order to study systems where the spin-state may change over time, real-time methods have been developed that are based off spin noncollinear references. Spin noncollinear methods, also known as two-component or generalized Hartree–Fock/Kohn–Sham methods, allow smooth transitions between various spin configurations by allowing each electron to be described by both spin-up and spin-down basis functions. This is necessary to describe the real-time response of molecules under the influence of magnetic fields. These methods can be further modified to include relativistic effects, such as spin–orbit coupling, which mixes spin states internally on account of the spin–orbit operators. In 2014, the first fully *ab initio* noncollinear real-time electronic dynamics[64] was reported. This work reported systems driven in time by an external magnetic field, allowing for the precession of the magnetization vector, giving proof of concept that spin dynamics could be accessed with real-time noncollinear methods. Expanding on this, Peralta et al.[65] used real-time spin noncollinear methods to extract magnetic exchange couplings in several magnetic systems.

Given this success, real-time methods have been extended to the relativistic regime, where spin–orbit coupling operators require noncollinear solutions. Calculations of absorption spectra from a relativistic four-component method was first reported by Repisky et al.[66] in 2015, followed by the extension to exact two-component (X2C) Hamiltonians by Goings et al.[68] in order to study spin-forbidden optical transitions (Figure 2). Real-time X2C methods were extended shortly thereafter to the calculation of nonlinear optical properties by Repisky and coworkers.[69] The extension of real-time methods to the relativistic regime proves critical to the accurate treatment electronic dynamics for heavy elements. The spin–orbit coupling, which connects different spin states, weakly allows otherwise spin-forbidden processes, leading to qualitatively different electronic absorption spectra compared to non-relativistic and even scalar relativistic methods. Only in relativistic two- and four-component real-time methods can one observe otherwise spin-forbidden peaks, such as the singlet to triplet transition in atomic mercury, shown in Figure 2. Furthermore, as spin–orbit phenomena becomes more pronounced for inner-shell electrons, utilizing relativistic Hamiltonians is required to capture the multiplet structure of $L_{2,3}$ absorption resonances in X-ray absorption near-edge structure
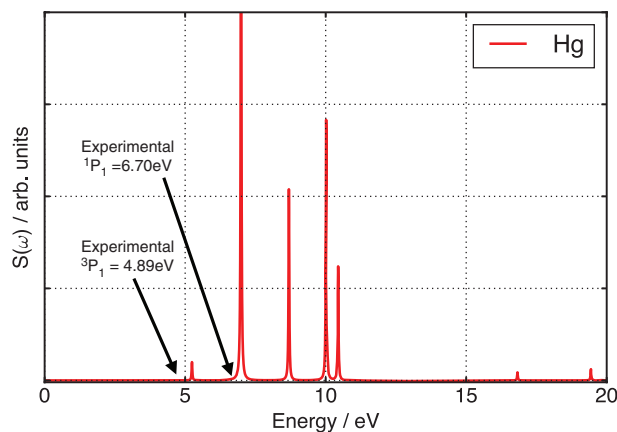

FIGURE 2 | Absorption spectra for atomic mercury obtained with real-time electron dynamics. The dynamics utilized an X2C Hamiltonian, which contains an ab initio treatment of spin–orbit coupling. This allows for the observation of the otherwise spin-forbidden $^3P_1$ transition. (Adapted from Ref 68 with the permission of AIP Publishing.)

(XANES). Motivated by this, Kadek et al. reported a real-time extension of the four-component Dirac–Kohn–Sham equations to the simulation of XANES spectra.[67]

Nonlinear response

A great advantage of real-time approaches is their ability to describe highly nonlinear phenomena. Response formalisms are certainly the most cost effective approaches to describe the lowest order responses of a system, but higher order responses can only be determined by first solving for all lower order responses. This can become quite expensive and higher order response equations can also be difficult to converge (although, up to five-photon absorption has been reported using response theory[145,146]). Individual orders or response can also be extracted from real-time simulations as shown by Ding et al.[39] Using information from just a few short simulations, one can determine polarizabilities, hyperpolarizabilities, and second hyperpolarizabilities in very close agreement with those calculated with response theory. This approach is generally applicable to all real-time methods and has been used in the past with RT-TDDFT, RT-X2C, and TD-CI.[39,69,80] Similar techniques have also been used by other groups, but these were not applicable to such high-order response.[42,147] Since explicitly time-dependent approaches are able to describe the response of a quantum system to arbitrary order, they have also become the methods of choice for describing the highly nonlinear process of high harmonic generation (HHG).

HHG occurs when a medium is illuminated with a laser at a particular frequency and then emits pulses at integer multiple frequencies of the initial pulse. It is largely used to generate high-energy attosecond pulses that can then be used to carry out ultrafast experiments.[148,149] The process of HHG is often interpreted through a simple three-step model where the electron escapes the molecule via tunnel ionization, accelerates away until the sign of the field changes, and then accelerates back towards the molecule.[150,151] The validity of this model is approximated by the Keldysh parameter[152]

$$\gamma = \frac{I_P^{1/2}}{2U_P} \qquad (43)$$

where I_P is the ionization potential and the ponderomotive energy is $U_P = I/4\omega^2$ where I is the field intensity and ω the field frequency. It defines both the multiphoton ($\gamma > 1$) and the tunneling regimes ($\gamma < 1$). Simulations that describe HHG aim to keep the Keldysh parameter $\gamma \approx 1$ to remain close to the tunneling regime. The three-step model also provides an estimate for when harmonic generation should stop, often called the cutoff energy $E_{cutoff} = I_P + 3.17U_P$.

The HHG power spectrum can be extracted from the time-evolving dipole moment

$$P(\omega) = \left| \frac{1}{t_f - t_i} \int_{t_i}^{t_f} dt \mu(t) e^{-i\omega t} \right|^2 \qquad (44)$$

after being perturbed by a monochromatic external field. This expression uses the length gauge form of the dipole and many have suggested using the acceleration gauge to describe the power spectrum although they should be very similar for reasonably sized basis sets.[153,154] Commonly $\cos^2$ or $\sin^2$ pulse envelope functions are used to perturb the system[76,155] and the envelope can even be optimized to enhance or damp specific harmonics.[156] HHG spectra can also be sensitive to the basis sets used and to the treatment of continuum states.[155]

Real-time methods in complex and nonequilibrium environments

Because of the explicit time-dependence, real-time methods have been fertile ground for nonequilibrium phenomena in complex environments. One early use of real-time methods was in the study of molecular conductance. Although conductance and studies of currents through molecules is amenable to steady-state investigations (e.g., the static Landauer–Büttiker[157,158] approach), there are many situations where the system is not in a steady-state. This may be when the current is initially applied, driving the system into a steady-state, or in situations where current drives various mechanical effects within a molecule. Furthermore, even in a steady-state picture there may be dynamical instabilities and fluctuations in electron flow. There have been several studies investigating the nonequilibrium effects on molecular conductance with real-time methods,[12–20] by either explicitly incorporating electronic sources and sinks connected by a molecular junction or applying an electrical bias across a molecule. The systems were simulated in real-time, allowing insight into the nonequilibrium behavior of the molecules in a complex environment.

The nonequilibrium response of solvent–solute interactions has been an active area of research in dynamics. Clearly, incorporating a realistic description of the solvents is challenging on account of the high number of degrees of freedom of an explicit solvent. One way is to take a QM/MM approach and include the molecular environment explicitly (albeit at reduced cost).[21,22] Another way around this is to embed the molecule in a polarizable continuous medium (PCM), where the solvent degrees of freedom are replaced by an effective classical dielectric. The dielectric medium and the molecule are brought into self-consistency, with both the molecule and the medium polarizing each other. This has been brought into the real-time methods by Li and coworkers.[23–25] One of the challenges, however, has been that the response of the solvent has been instantaneous. Realistically, however, the solvent takes finite time to reorganize and repolarize, and this has measurable effects on molecular response. To correct for the nonequilibrium response of solvent and solute, a time-dependent PCM method was introduced,[26,27] which incorporates an equation of motion for the dielectric polarization, which allows for descriptions of electronic dephasing and dipole lifetimes. This same idea was subsequently extended to TD-CI.[28] Very recently, RT-TDDFT was combined with block-orthogonalized Manby–Miller embedding theory[29,159] as a way of cheaply accounting for a solvated molecular response.

In the past few years, there has been work to extend similar ideas to embedding molecules in a thermal bath, in order to study the nonradiative relaxation and dephasing of molecular systems. The time-dependent open self-consistent field (OSCF2) method introduced by Nguyen et al.[31,33] is one recent example. This method adds to the molecular equations of motion a Markovian dissipative correction,

which has the practical effect of describing nonradiative lifetimes within RT-TDDFT. It furthermore allows for nonconstant relaxation rates, and, at longtimes, OSCF2 comes to equilibrium with the correct Fermi–Dirac statistics, a condition that some common methods for nonadiabatic dynamics (e.g., Ehrenfest and surface-hopping) do not satisfy.[31]

Complex absorbing potentials

Most *ab initio* techniques that describe absorption spectra are designed to handle bound state transitions, so different strategies are needed for transitions near and above ionization. These transitions are characterized by resonance states, which are metastable and autoionize after a short time, and continuum states. Resonance states can be thought of as discrete states strongly coupled to the continuum and are associated with complex eigenvalues of the Hamiltonian, known as Siegert energies[160]

$$E_{res} = E_R - \frac{i\Gamma}{2} \qquad (45)$$

where E_R is the center of the resonance and Γ is the width. Obviously, these complex energies are inaccessible by Hermitian Hamiltonians, however, a non-Hermitian Hamiltonian can be formed for which the Seigert energies are eigenvalues. There are several ways to accomplish this end, but the most common approach in real-time simulations is to add a complex absorbing potential (CAP) to the Hamiltonian

$$H'(t) = H(t) - i\eta W \qquad (46)$$

where W is the absorbing potential and η defines the strength of the CAP.

A CAP serves as an absorber to prevent reflections caused by using either a finite basis set or simulation box.[161] Essentially it gives electrons somewhere to go when trying to escape the molecular system. It must be placed far enough away from the system so that it does not interact strongly with the ground state or low lying excited states, but close enough to perturb the resonance states. This means that it must be outside the Coulomb well, but still have sufficient overlap with the maximum extent of the electrons. Schlegel and coworkers have used PCM machinery to define this boundary in the past.[162] CAPs are very useful when propagating the wave function on a finite grid in order to avoid reflections off the edge of the simulation box. The η parameter is usually tuned to be strong enough to prevent this reflection, but weak enough to prevent

reflection off of the CAP.[163] These potentials have been put to good use by Schlegel and coworkers with TD-CIS using atom centered basis functions in order to describe time-resolved photoionization and its angular dependence.[79,162,164]

Lopata and Govind used similar ideas when developing their non-Hermitian RT-TDDFT approach. A non-Hermitian Fock or Kohn–Sham matrix is constructed with finite lifetimes for each of the orbitals allowing them to describe transitions to bound, resonance, and continuum states.[8,50] An example of their work comparing modeled extreme UV absorption of acetylene is presented in Figure 3, which shows that this technique performs well even in regions of the spectrum near many ionization potentials. Klinkusch et al.[165] take a different approach and directly added finite lifetimes to the state energies when using TD-CIS to describe ionization rates. White et al.[155] also used the same approach to describe HHG with TD-CIS showing a dramatic reduction in the noise of the spectra.

Real-time molecular quantum electrodynamics

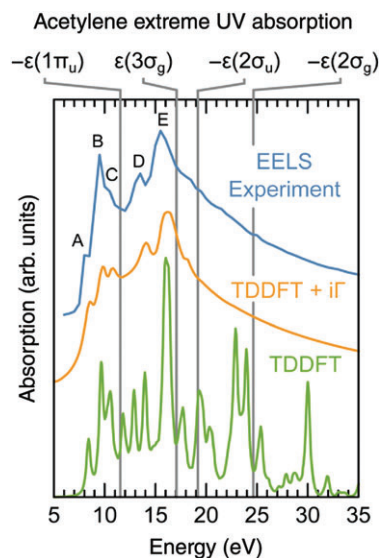Nearly all real-time methods describe the interaction between matter and light semi-classically. In this

FIGURE 3 | Absorption spectra of acetylene modeled with RT-TDDFT (green) and non-Hermitian RT-TDDFT with an imaginary absorbing potential (orange) compared with an EELS experimental spectrum (blue). The gray lines denote DFT Koopmans' ionization potentials. The absorbing potential adds a finite lifetime to resonance states and shows dramatic improvement when compared against the experimental spectrum. (Reprinted with permission from Ref 8. Copyright 2013 American Chemical Society.)

sense, the electromagnetic field affects the molecule, but the molecule has no effect on the electromagnetic field. Recently, there have been attempts at treating light and matter on equal footing in RT-TDDFT. This area of investigation comes from the growing interest in combining a quantum description of matter with a quantum description of the electromagnetic field. This leads to the well-known field of molecular QED.[166] QED sets the foundation for understanding the quantum nature of photon–matter interactions and gives the most complete theoretical description of absorption and (spontaneous) emission. Furthermore, cavity QED experiments, which trap a small number of photons in close proximity to atoms and molecules have highlighted the need to understand the interactions between matter and light when the quantum nature of light becomes important. While quantum optics has studied two-level systems in the presence of many-photon fields (Jaynes–Cummings model),[167] the extension to realistic multistate systems remains difficult due to the near-intractability of the underlying equations.

In essence, molecular QED describes the coupled nature of the electronic Hamiltonian with quantized electromagnetic field modes that look like quantum harmonic oscillators. The molecular system can absorb energy from populated photon states as well as release energy out through emission to the electromagnetic field. Moreover, the interaction between photons and electrons can lead to polaritons, which are quasiparticles generated by the strong coupling of excitons and a photon field. This leads to new spectroscopic features beyond any semi-classical treatment. In recent studies by Flick et al.,[94,168] researchers demonstrated how their extensions of QED to TDDFT (called QEDFT) showed previously unseen phenomena in the quantum description of the light–matter interaction. While a detailed description of their QEDFT methods is beyond the scope of this review (see Refs 89–93 for details) there are important phenomena arising from the quantum light–matter interaction that cannot be captured in the traditional semi-classical techniques that most real-time methods utilize.

One interesting phenomena that is unique to the quantized treatment of the photon-molecular system is that an initially excited state can periodically emit and then reabsorb a photon. This is impossible in semi-classical descriptions of radiation–matter interaction, because the electromagnetic field is always external to the system: in QED, the excited molecule coupled to the quantized electromagnetic field, emits a photon, which may reflect back in cavity QED experiments, only to be reabsorbed by the molecular subsystem. Moreover, Flick et al. found that if the coupling with the photon resonance is strong enough, the photon mode will actually modify the bare electronic excited states, leading to split peaks in the absorption spectrum. This phenomena is known as a vacuum Rabi oscillation. Because the real-time time-dependent electronic structure is extended to the photon–molecule system as a whole, this is possible within QEDFT. For fields with high photon number states, this could be extended to a treatment of multiphoton absorption (and emission) and nonlinear phenomena without recourse to orders of response theory.

CONCLUSIONS

Here we have summed up much of the recent progress in real-time time-dependent electronic structure theory. Since the late 1990s, there has been an explosion of work into real-time methods. Real-time methods have been used to simulate many types of spectroscopic signatures in molecular systems and with advances in algorithms and signal processing techniques, seem poised to be competitive with other techniques such as frequency-domain response theory. Yet the fundamental advantage of real-time methods lies in both its non-perturbative nature and its intuitive elegance. To the first point: no matter what type of system is being studied with real-time methods, all external interactions are treated nonperturbatively. Electromagnetic fields have finite value, electronic and environmental responses back-react into each other, electron currents flow dynamically—no steady-state approximations here! And this is how chemistry is in its full complexity. We are free to add and remove interactions, be they fields or thermal baths or solvents or electron sources and sinks, and the molecule responds, as it wishes, evolving according to its dynamical laws. This leads us to our second point: the intuitive elegance of these methods. The laboratory chemist does not measure an absorption spectrum by finding the poles and residues of her test tube of chemicals. Rather, the chemist applies an appropriate laser pulse under carefully selected conditions and observes the molecular response. So too with real-time methods. In each simulation, the molecule and its perturbing interactions are carefully chosen to observe a molecular response, and from this response we learn a bit more about that molecule. Theory imitates experiment.

Over the past several years, we have witnessed an increase in the types of applications of real-time methods, and most of them have relied on the

increasing sophistication of the external perturbations. CAPs have allowed us to study ionization processes, including a dissipative bath or a time-dependent solvent response has allowed us to study excited state lifetimes, including relativistic interactions has enabled spin-dependent responses, and strong fields have enabled studies of high-harmonic generation and nonlinear optical effects. Of course, each of these new interactions must make some sort of approximations, and the way forward seems likely to improve on these approximations. We would like to suggest three pressing questions relevant to the future of real-time electron dynamics. First: '*How can we include a proper treatment of electromagnetic fields beyond the electric dipole approximation?*' Many processes, particularly in the high-energy (X-ray) regimes require terms beyond the electric dipole, including electric quadrupole and magnetic dipole terms. These terms are necessary, but challenging to include, not for least of which is the gauge-origin issue.[169–171] Along this line, more work needs to be done to properly include magnetic fields into the description, to show chemistry driven by magnetic fields (e.g., magnetic circular dichroism requires a static magnetic field). The way forward using explicit London orbitals seems promising,[172–176] but a time-dependent extension remains to be seen. Second, '*What phenomena can we observe beyond the semi-classical paradigm of matter–light interactions?*' The QEDFT of Rubio and coworkers seems promising, but is still in its infancy. Quantum optics has long known the importance of using a quantized electromagnetic field, but the extension to molecular systems is intriguing. After all, molecules interact with photons, not classical fields. What might chemistry look like in the cases where molecules interact individually with photons? What would a molecular cavity QED experiment tell us? Finally, '*How can we go beyond DFT and HF to properly account for electron correlation in real time?*' Recent advances in real-time coupled cluster have made this question more achievable, but more work needs to be done to develop efficient methods for correlated real-time dynamics. One intriguing possibility is to use time-dependent reduced density matrices as a way of propagating correlated systems in time. Beyond a more accurate treatment of excited state and time-dependent phenomena, correlated wave-function-based methods would allow for true studies of optimal control,[177–179] wherein electromagnetic field pulses could be shaped and crafted to drive chemical reactions. Because DFT and HF rely on a single Slater determinant, such optimal control studies are challenging,[180] if not impossible. The problem is further compounded in RT-TDDFT, since most available functionals are adiabatic and designed for the ground state, leading to many problems.[181–187] Real-time electron dynamics has come a long way since the first applications to realistic chemical systems in the late 1990s, and its applications seem mostly limited only by the creativity of its practitioners and developers. However, the pace towards more realistic systems and better descriptions of complex phenomena show no signs of slowing down.

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