Real-Time Time-Dependent Electronic Structure Theory

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BIOGRAPHY

Xiaosong Li earned a B.S. Chemistry from the University of Science and Technology of China in 1999 and a Ph.D. in Theoretical Chemistry from Wayne State University in 2003. Following a post-doctoral training at Yale University, he joined the University of Washington as Assistant Professor in the fall of 2005. He was promoted to Associate Professor in 2011 and to Full Professor in 2015. Currently, he is the Harry and Catherine Jaynne Boand Endowed Professor and Associate Chair of Chemistry at the University of Washington. His research focuses on developing and applying time-dependent relativistic and non-relativistic electronic structure theories for studying excited state chemical processes that underpin energy conversion, photocatalysis, and ultrafast spectroscopies. In addition to his work at University of Washington, he is an Associate Editor of Chemical Physics Reviews, American Institute of Physics.

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Kenneth Lopata earned a B.S. in Chemical Physics from the University of Toronto in 2004 and a Ph.D. in Chemistry from the University of California, Los Angeles in 2010. Between 2010 and 2013, he held the Wiley Postdoctoral Fellowship at Pacific Northwest National Laboratory. He subsequently joined Louisiana State University as an Assistant Professor in 2013, and was promoted to Associate Professor in 2019. His research interests focus on developing and applying time-dependent quantum chemistry methods to simulate the attosecond motion of electrons in molecules and materials during and immediately following interaction with intense and/or high energy laser pulses.

Abstract

Real-time electronic structure methods provide an unprecedented view of electron dynamics and ultrafast spectroscopy on the atto and femtosecond timescale, with vast potential to yield new insights into the electronic behavior of molecules and materials. In this Review, we discuss the fundamental theory underlying various real-time electronic structure methods, as well as advantages and disadvantages of each. We give an overview of the numerical techniques that are widely used for real-time propagation of the quantum electron dynamics, with an emphasis on Gaussian basis set methods. We also showcase many of the chemical applications and scientific advances made by using real-time electronic structure calculations and provide an outlook of possible new directions.

1 Introduction

Real-time electronic structure theory explicitly considers the time-dependence of a quantum electronic system by evolving the time-dependent Schrödinger or Dirac equation, Eq. (1), in the time domain,

$$i\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = \hat{H}(\mathbf{r},t)\Psi(\mathbf{r},t). \tag{1}$$

In Eq. (1) and throughout this review, atomic units are used. The non-equilibrium condition of the Hamiltonian under external perturbation gives rise to the time-evolution of the wave function or the electron density that underlies all response properties of a quantum electronic system. A complementary approach, not reviewed here, is frequency-domain response theory, which has been widely applied to chemical systems with remarkable success. Instead, this review focuses on the time-dependent electronic structure wave function or density, explicitly propagated in the time domain.

Historically, the early work for explicitly time-dependent solutions of the time-dependent

Schrödinger equation began in the late 70's and early 80's in the field of nuclear physics with a mean-field time-dependent Hartree-Fock (TDHF) approximation for studies of nuclear collisions and their scattering profiles.[1–5] In 1990, Cederbaum and coworkers laid the ground work for propagating correlated electronic wave functions in real time with the development of the multi-configurational time-dependent Hartree (MCTDH) method.[6] In 1994, Micha and Runge used a density-matrix based real-time time-dependent Hartree-Fock (RT-TDHF) approach with a traveling atomic orbital basis for describing electron rearrangement during atomic collisions.[7] However, despite these developments, real-time methods did not become a practical computational tool for many years because the explicit time-propagation of correlated electronic wave functions remained computationally expensive and the Hartree-Fock approach lacks important electron correlation effects.

In 1996, Bertsch and Yabana, for the first time, developed and applied the real-time time-dependent density functional theory (RT-TDDFT) approach within the local density approximation (LDA) for studies of dynamic response properties.[8] Their efforts in explicitly time-dependent electronic structure theory,[9–11] combined with the advent of usable real-space density functional theory (DFT) codes,[12–14] have led to great interest in real-time methods in the condensed matter physics community. However, the application of RT-TDDFT in the quantum chemistry and spectroscopy communities remained limited due to the lack of implementations of RT-TDDFT within the generalized gradient approximation (GGA) and hybrid GGA approximations, the modern day workhorses for computational chemistry and materials science. In 2005, Li and Schlegel introduced an efficient implementation of RT-TDHF[15] in a Gaussian-type atomic orbital basis, followed by an RT-TDDFT extension[16] by Li and Isborn in 2007 that could use generalized hybrid density functionals which include exact exchange. The development of real-time electronic structure theory in an atomic orbital basis, which allows for low-cost, accurate simulations of molecular spectroscopies and electronic dynamics using GGA and generalized hybrid functionals, has led to many Gaussian basis set based real-time implementations in widely used codes in the quantum

chemistry community capable of handling both small and large molecular and finite cluster systems.[17–23] With the development of scalable plane-wave and real-space grid based implementations,[24–27] simulations of large-scale condensed phase systems have also become possible.

With advancements in computing power and numerical algorithms, there has been renewed interest in explicit time-propagation of correlated methods such as multi-configurational self-consistent-field (MCSCF),[28–32] configuration interaction (CI),[33–39] algebraic diagrammatic construction,[40–46] and coupled cluster (CC)[22,35,37,47–51,51–55] theories. Although wave function based real-time techniques scale poorly compared to RT-TDDFT, they afford systematically improvable accuracy and allow for accurate simulations of electronic dynamics in strong fields. Alternatively, correlated electron dynamics can be modeled through the time evolution of the one-electron reduced density matrix (RDM)[56–60] or the two-electron RDM,[61,62] as opposed to the wave function, but such methods are plagued by N-representability[63] problems resulting from the truncation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY)[64–67] hierarchy of equations of motion for the RDMs.[61,62]

Motivated by the need for an explicit and accurate description of electron spin interaction with internal (*e.g.*, spin-spin and spin-orbit) and external (*e.g.*, magnetic field) perturbations, there has been a growing interest in extending real-time methods beyond the framework of the time-dependent Schrödinger equation. In 2014, Li and coworkers introduced a non-relativistic real-time time-dependent two-component method to simulate electron spin dynamics.[68] This work demonstrated that the *ab initio* simulation of electron spin dynamics requires at least two components in the description of electronic degrees of freedom. In 2015, Repisky and Ruud presented the first fully relativistic four-component RT-TDDFT (4c-RT-TDDFT),[69] followed by a formally equivalent relativistic two-component implementation (2c-RT-TDDFT) by Li in 2016.[70] The development of these real-time time-dependent Dirac methods has enabled the computational investigation of magnetic and spin-orbit effects in molecular spectroscopy and electronic dynamics.

The non-relativistic Hamiltonian for an N-electron system interacting with a time-dependent electromagnetic field is defined as

$$\hat{H}(\mathbf{r},t) = \sum_{i}^{N}\left(\frac{1}{2}\boldsymbol{\pi}^2 - U(\mathbf{r}_i,t)\right) + \sum_{i<j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|} + V_{ext}, \tag{2}$$

where the first term includes the electron kinetic energy and the coupling to the field, the second term is the electron-electron repulsion term V_{ee}, and V_{ext} includes the electron-nuclear attraction term and other external potentials, such as the system-bath interaction. The external electromagnetic perturbation is usually treated classically and defined by a vector potential $\mathbf{A}(\mathbf{r},t)$ and a scalar potential $U(\mathbf{r},t)$. $\boldsymbol{\pi} = \mathbf{p} + \mathbf{A}$ is the generalized momentum that includes the vector potential $\mathbf{A}$ along with linear momenta $\mathbf{p}$. This term gives rise to the electron kinetic energy and electron-field coupling. Note that in some cases, the electron-field interaction is included in the V_{ext} term but here we include this coupling by incorporating the vector and scalar potentials in Eq. (2). The majority of this review focuses on approximate solutions to the time-dependent Schrödinger equation and their scientific applications. Development of practical real-time methods within the time-dependent Dirac framework is an emerging direction and some aspects will be discussed in Sec. 2.5.

Equation (2) is the general form of the non-relativistic Hamiltonian that drives electronic dynamics via the time-dependent Schrödinger equation. Real-time methods, like other *ab initio* methods, must numerically solve the underlying Schrödinger or Dirac equation (Eq. (1)) through mean-field approximations, such as Hartree-Fock (HF) and DFT, or wave function based techniques, such as CC and CI. For treating large systems, low-cost semiempirical approaches, continuum models, or molecular mechanics can be used to simulate responses from the complex environment. The fundamental theory and mathematical *ansatz* of these techniques will be reviewed in Secs. 2.1 to 2.6. In addition, real-time methods must also rely on robust numerical techniques and representations (Sec. 3) to explicitly integrate the quantum system in time and resolve quantum observables from time-signals without introducing

nonphysical behavior.

Most scientific applications of real-time methods concern electronic responses to external perturbations, such as an electromagnetic field [$\mathbf{A}(\mathbf{r},t)$ and $U(\mathbf{r},t)$], electron-nuclear coupling (V_{Ne}), and system-bath coupling (V_b). These perturbations give rise to the spectroscopic signatures, population transfer, and energetic decay of an electronic system. In the absence of these driving forces, time-evolution of an electronic wave function will exhibit either coherent oscillations that travel through phase space in the case of a pure coherent wave function, or remain stationary in the case of an eigenstate. Real-time electronic structure theory is thus a powerful tool for simulating diverse chemical phenomena, many of which will be reviewed in Sec. 4.

Applications of real-time methods span the field of spectroscopy, including valence-electron UV/Vis and photoelectron,[9,10,15,18,34,69–88] circular dichroism,[89–94] core-electron X-ray absorption,[49,95–98] nonlinear optical response,[14,99,100] photoionization,[71,101–115] and magnetization dynamics.[68,116,117] Real-time electronic structure methods have also found utility in studies of molecular electronics,[118–127] optimal control,[117,128–131] as well as coherence and charge-transfer dynamics.[16,132–151] To probe chemical processes in complex environments, real-time electronic dynamics have been coupled to polarizable[32,152] and non-polarizable molecular mechanical layers,[74,153] implicit solvation models,[138,139,154–157] quantum subsystems,[158] and thermal baths in an open quantum system formalism.[20,150,159–165] Recently, the coupling of a molecule to a quantized electromagnetic field[166–174] — real-time quantum electrodynamics (QED) — has led to first-principles studies of photon absorption and emission and simulations of cavity QED experiments. The focus of this review is on real-time electronic structure; thus we do not focus on nuclear motion. However, because different electronic structure methods lend themselves to different ways of coupling with nuclear motion, it is worth briefly mentioning some of these methods here. See extensive reviews such as[175–180] and references therein for more in-depth discussions and an overview of mixed quantum-classical dynamics methods. Exact electron-nuclear dynamics are obtainable via solution of

the full time-dependent Schrödinger equation for the entire (electronic plus nuclear) system: a computationally prohibitive prospect for all but the smallest of molecules with only a few active electrons.[181] Various approximate methods have been introduced with the aim of achieving reliable results at lower costs.[7,132,182–211] Two of the most widely used methods are trajectory surface hopping and the Ehrenfest approach.[184,189] These mixed quantum-classical formalisms use the classical equation-of-motion for nuclear degrees of freedom and quantum mechanical evolution of the time-dependent electronic wave function, such as RT-TDHF, RT-TDDFT, TD-CC, TD-CI, *etc.*, but differ in how the electronic potential energy surface is computed. Trajectory surface hopping methods, introduced specifically to account for the branching of trajectories due to electron-nuclear coupling, often use fitted potential surfaces or compute electronic forces and couplings on-the-fly.[184,189,212–225] Surface hopping therefore does not generally make use of real-time electronic structure. Analogous methods can also be built from nuclear motion on the ground state electronic surface, which can provide time-evolving ground state occupied and virtual orbitals to be used for time-domain surface hopping methods, see for example Refs. 226,227; these techniques ignore feedback from the excited state population to the nuclear motion as well as ignoring all electronic coherences between states that are captured by real-time electronic structure methods.

In contrast, the Ehrenfest approach naturally couples to real-time electronic structure methods, propagating the nuclei as classical particles subject to a force from a weighted average of all the electronic states of the system.[16,128,129,135,175,188,201,210,228–237] The time-evolving expansion coefficients of the electronic wave function, which are governed by the electronic time-dependent Schrödinger equation, determine the weights in the average of the potential energy surfaces. This method can avoid explicit computations of the excited states by representing the wave function as a superposition state, while still accounting for electronic non-adiabaticity, making the Ehrenfest dynamics an excellent approach for simulating dense manifolds of electronic states. Indeed, for methods based on real-time propagation of the electron density, such RT-TDHF and RT-TDDFT, excited states and their respective popu-

lations are ill-defined; evolving the classical nuclei on this electronic superposition state yields Ehrenfest dynamics. The drawback of the Ehrenfest approach is the restriction to motion on a single average potential energy surface, which can lead to nonphysical results, such as over-coherence, particularly in the asymptotic limit.[209,238–243] Recently, Fedorov and Levine proposed a systematically improvable multiple cloning approach to mitigate issues arising from long-time propagation of Ehrenfest dynamics on unphysical mean-field surfaces.[237]

In this review, we highlight the theory of various real-time electronic structure methods, as well as advantages and disadvantages of each. We give an overview of the numerical techniques that should be considered for real-time electron propagation, with a focus on Gaussian basis set approaches, and we showcase many of the chemical applications for real-time electronic structure calculations.

2 Theory of Real-Time Time-dependent Electronic Structure Methods

We use the following notations throughout the rest of this review:

- $K, L, ...$ are Slater determinants.
- $i, j, k, l, ...$ are occupied molecular orbitals.
- $a, b, c, d, ...$ are virtual molecular orbitals.
- $p, q, r, s, ...$ are general molecular orbitals.
- $\mu, \nu, ...$ are atomic orbitals.

All equations use atomic units, with $e^2 = \hbar = m_e = 1$. Primed notations (*e.g.*, $\mathbf{F}', \mathbf{P}'$) are used for matrices in the orthonormal basis and unprimed notations for matrices (*e.g.*, $\mathbf{F}, \mathbf{P}$) in the atomic orbital (AO) basis.

2.1 Real-Time Time-Dependent Hartree-Fock and Density Functional Theory

Many excellent articles, reviews, and books exist focusing on details of TDDFT within both the linear response matrix formulation and within the real-time electronic propagation formulation.[146,244–252] We refer the reader to these works to gain a more detailed perspective of the theoretical underpinnings of TDDFT, including details of the Runge-Gross[253] and the van Leeuwen[254] proofs of mappings from the density to the potential that show that all time-dependent properties can be extracted from the time-evolving electron density. Here, we especially wish to highlight similarities and differences between RT-TD Hartree-Fock (RT-TDHF) and RT-TDDFT. We therefore initially present these two methods on an equal footing within a molecular orbital or Kohn-Sham (KS) picture, which is required by Hartree-Fock and by generalized KS hybrid DFT methods due to the inclusion of exact exchange, before focusing on some of the relevant issues specific to RT-TDDFT.

For both TDDFT and TDHF within an orbital basis, a set of time-dependent one-particle equations is given by

$$i\frac{\partial}{\partial t}\phi_i(\mathbf{r},t) = \hat{H}(\mathbf{r},t)\phi_i(\mathbf{r},t), \tag{3}$$

where i runs over all N electrons and the time-dependent electron density is

$$n(\mathbf{r},t) = \sum_{i=1}^{N} |\phi_i(\mathbf{r},t)|^2. \tag{4}$$

Although numerous theoretical differences exist between TDDFT and TDHF as discussed in the citations listed above, the main, practical difference is the treatment of the electron-electron repulsion term V_{ee} in the Hamiltonian $\hat{H}(\mathbf{r},t)$ in Eq. (2). For both TDHF and TDDFT, V_{ee} depends on the time-dependent density or the time-dependent orbitals, and therefore becomes a time-dependent operator.

For Hartree-Fock, V_{ee} contains Coulomb and exchange operators that describe average

electron-electron interactions within the single particle picture

$$V_{ee}^{HF}(\mathbf{r},t)\phi_i(\mathbf{r},t) = \left[\sum_j^N \int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}',t)\phi_j(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}\right]\phi_i(\mathbf{r},t) - \left[\sum_j^N \int d\mathbf{r}' \frac{\phi_j^*(\mathbf{r}',t)\phi_j(\mathbf{r},t)}{|\mathbf{r}-\mathbf{r}'|}\right]\phi_i(\mathbf{r}',t), \tag{5}$$

where the first term provides an average Coulombic electron-electron interaction and the second term describes the non-local exchange contribution to the energy that results from the use of a Slater determinant for describing an anti-symmetric wave function. Both terms depend only on the instantaneous orbitals at time t. The missing electron-electron interaction energy in Hartree-Fock theory is called the correlation energy, the lack of which arises from the mean-field single particle approximation.

For density functional theory, the electron-electron interaction term V_{ee} contains the same average Coulombic electron-electron interaction (often called the Hartree term in the physics community), which can also be written in terms of the electron density $n(\mathbf{r},t)$, and an exchange-correlation term V_{xc}

$$V_{ee}^{DFT}(\mathbf{r},t)\phi_i(\mathbf{r},t) = \left[\int d\mathbf{r}' \frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|} + V_{xc}[n;\Psi_0,\Phi_0]\right]\phi_i(\mathbf{r},t), \tag{6}$$

where the unknown exchange-correlation potential V_{xc} is formally a function of: the electron density n at all points in space and at all previous points in time, Ψ_0 the initial many-body wave function, and Φ_0 the initial state to be used for the non-interacting Kohn-Sham wave function. Unlike TDHF theory, TDDFT up to this point is formally exact. Although the Coulomb/Hartree energy contains contributions from each electron in orbital ϕ_i interacting with itself as part of the total density n, this erroneous self-interaction energy should be exactly canceled in the exchange contribution of V_{xc}, as it is for the exact non-local exchange in Hartree-Fock theory.

The Liouville equation generalizes the time-dependent Schrödinger equation to

$$i\frac{\partial\hat{\rho}(t)}{\partial t} = [\hat{H}(\mathbf{r},t),\hat{\rho}(t)], \tag{7}$$

where $\hat{\rho}(t)$ is the density operator and $\hat{H}(\mathbf{r}, t)$ is the time-dependent many-body Hamiltonian. This expression is only valid for Hermitian Hamiltonians, *i.e.*, without complex absorbing potentials. The time-dependent molecular orbitals ϕ_i are often created from a linear combination of basis functions $\{\chi_\mu\}$ as $\phi_i = \sum_\mu c_{\mu,i}(t)\chi_\mu$, where $c_{\mu,i}(t)$ are the time-dependent coefficients. The elements of the Hartree-Fock or DFT density matrix $\mathbf{P}$ are then given in this basis by

$$P_{\mu\nu}(t) = \sum_p f_p c^*_{\mu,p}(t) c_{\nu,p}(t). \tag{8}$$

where f_p is the occupation of orbital p. Transforming the density matrix $\mathbf{P}$ to the orthonormal basis and now writing it as $\mathbf{P'}$ in this basis, we can then express the TDHF or TDDFT equation as

$$i\frac{\partial \mathbf{P'}(t)}{\partial t} = \left[\mathbf{H'}(t), \mathbf{P'}(t)\right], \tag{9}$$

where $\mathbf{H'}(t)$ is the Hamiltonian matrix (integrated over $\mathbf{r}$), here the Fock matrix for TDHF or the Kohn-Sham matrix for TDDFT, in the orthonormal basis.

This equation is a starting point for both solving for the density response in the frequency domain via a matrix formulation, usually by keeping only the terms that are first order in the perturbation to obtain the linear response,[255–258] and for propagating the electron density in the time domain by numerical integration.[259] Real-time propagation reveals time-resolved electron distributions responding to a perturbation, such as the electron density of an acetylene molecule under the influence of an applied laser pulse as shown in Fig. 1.[260]

However, a key challenge with RT-TDHF and RT-TDDFT is that the Hamiltonian becomes time-dependent, not just from the time-dependent perturbation, but from the dependence of the Hartree-Fock and DFT Hamiltonian on the time-dependent density in the Coulomb/Hartree and exchange-correlation potentials. This time-dependence of V_{ee} contrasts with correlated electronic dynamics methods wherein the exact form of V_{ee} is used and the only source of time dependence in the Hamiltonian is the external perturbation. The time-dependence of the Hartree-Fock / DFT Hamiltonian creates a nonlinear equation,

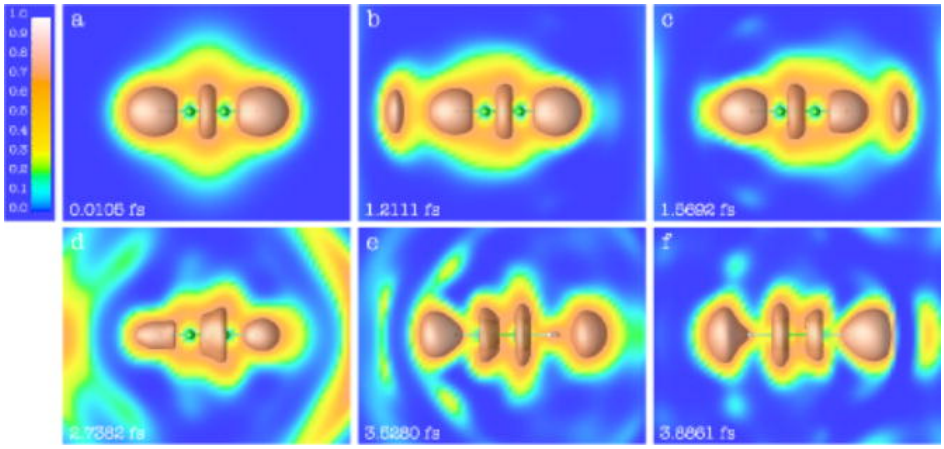

Figure 1: Snapshots of the time-dependent electron localization function of acetylene during application of a laser pulse. The electronic transition is from a bonding π to an antibonding π^* state. Adapted with permission from Ref. 260. Copyright (2005) American Institute of Physics.

which exhibits a host of inaccuracies for the RT-TDHF method and for the RT-TDDFT method with the common approximations to V_{xc}. These inaccuracies include unphysical peak-shifting,[77,261–266] incorrect Rabi oscillations,[84,267,268] and incorrect charge-transfer dynamics.[140,252,269] Because TDDFT is formally exact, these inaccuracies derive from the practical implementation of TDDFT, which requires approximations in choosing the form of the initial Kohn-Sham state Φ_0 and in choosing the form of the exchange-correlation potential V_{xc}. In practice, the initial Kohn-Sham state Φ_0 is usually chosen to be a single Slater determinant constructed from the single particle orbitals ϕ_i, as in Hartree-Fock theory. A recently developed formulation where the number of Kohn-Sham orbitals and their occupations are updated on the fly shows promise for alleviating some of the inaccuracies of RT-TDDFT.[268] The most common approximation to V_{xc} is to ignore all previous time-dependence on the electron density and to use the instantaneous electron density with a V_{xc} parametrized or derived for the ground state: $V_{xc}[n;\Psi_0,\Phi_0](\mathbf{r},t) = V_{xc}[n(t)](\mathbf{r})$. This adiabatic approximation, which ignores all memory dependence of the electron density, is equivalent to a frequency-independent kernel in linear response.

2.1.1 The adiabatic approximation in TDDFT

Formally, RT-TDDFT electron density propagation is exact, assuming the use of the exact time-dependent exchange-correlation potential. In contrast, RT-TDHF is inherently approximate because electron correlation effects are formally missing from the Hamiltonian and therefore from the electron propagation. The phase information encoded in the orbitals leads to some incorporation of memory via the exact exchange energy contribution in TDHF or in orbital-dependent TDDFT, but these memory effects[270,271] do not fix the dramatic errors in the RT-TDHF and RT-TDDFT electron dynamics. The exact V_{xc}, which would yield the exact electron density propagation, formally depends on the density at all points in time, as well as the initial wave function and initial Kohn-Sham state.[272,273] However, this memory dependence of the potential at time t on the density at all previous points in time $t' < t$ is not well-understood. As a result of this lack of knowledge, almost all TDDFT calculations ignore the history dependence of the electron density completely, with some notable exceptions discussed below. The dependence of V_{xc} on the initial wave function and Kohn-Sham state is usually ignored as well. Therefore, in almost all applications, RT-TDDFT is used within the adiabatic application, in which V_{xc}, usually a ground state functional, only uses input from the instantaneous electron density (see Fig. 2).

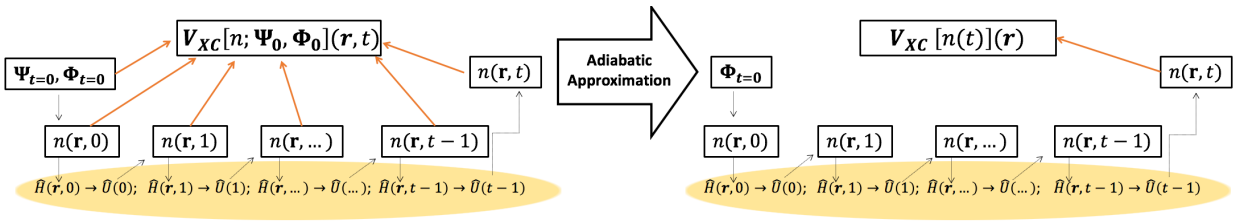

Figure 2: The commonly used adiabatic approximation in TDDFT uses only the instantaneous electron density $n(\mathbf{r},t)$ as an input to the exchange-correlation potential, ignoring the dependence on the electron density at all previous points in time.

Despite its widespread use for modeling charge transfer in complex systems, RT-TDDFT as it is used in practice within the adiabatic approximation suffers from a number of deficiencies for small model systems. The RT-TDDFT method within the adiabatic approximation

is not able to capture Rabi oscillations, where if an electric field of frequency resonant with an allowed transition is applied to the system, single electron transitions occur between the states.[84,267] For RT-TDDFT, a field that is initially resonant with an energy gap will no longer be resonant as soon as electron density transfers out of the ground state. As a result, the electron transfer into the excited state is not complete when the electric field is applied, limiting RT-TDDFT's applicability to model pump-probe spectroscopy and non-equilibrium dynamics. Intricately connected with this issue is the incorrect extent and rate of charge transfer within RT-TDDFT for the exactly solvable Hubbard dimer. For this system, in addition to obtaining the exact dynamics, the dynamics were also simulated within the adiabatically exact approximation, revealing that the error is in fact due to the adiabatic approximation rather than any errors in the exchange or correlation functional for the instantaneous electron density.[140,269] Note that using the adiabatically exact functional is a non-trivial task, but recent progress in numerically constructing the exact Kohn-Sham potential for a given density makes this possible for model systems with smooth potentials (see Fig. 3).[274–279] The lack of time-dependence within the adiabatic approximation, which corresponds to a lack of frequency-dependence in the frequency domain used with linear response theory, was shown by Maitra, Cave, and Burke in 2004 to be linked to the lack double excitations within TDDFT.[280] However, Li and Isborn in 2008 showed that although RT-TDDFT cannot capture the response of two-electron excitations, it can recover the electron density of closed-shell doubly-excited states.[77] Another related problem observed with approximate RT-TDDFT is the phenomena of peak-shifting within the computed absorption spectra.[77,261–266] Although the energy of the spectral peaks computed with RT-TDDFT agree with the energy of the resonances computed from linear response theory within the matrix formulation of TDDFT if a ground state electron density is used as a reference, as the electron density evolves away from the ground state the peaks in the absorption spectrum unphysically shift in energy. This spurious shift is due to the changing character of the evolving electron density. Both RT-TDDFT within the adiabatic approximation and RT-TDHF

suffer from the problems of incorrect Rabi oscillations and peak-shifting; these problems are due to the nonlinear nature of the potential, which depends on the time-dependent electron density. Thus, a challenge in going beyond the adiabatic approximation requires that any time-dependence built into V_{xc} repair this resonance condition.[265,266]

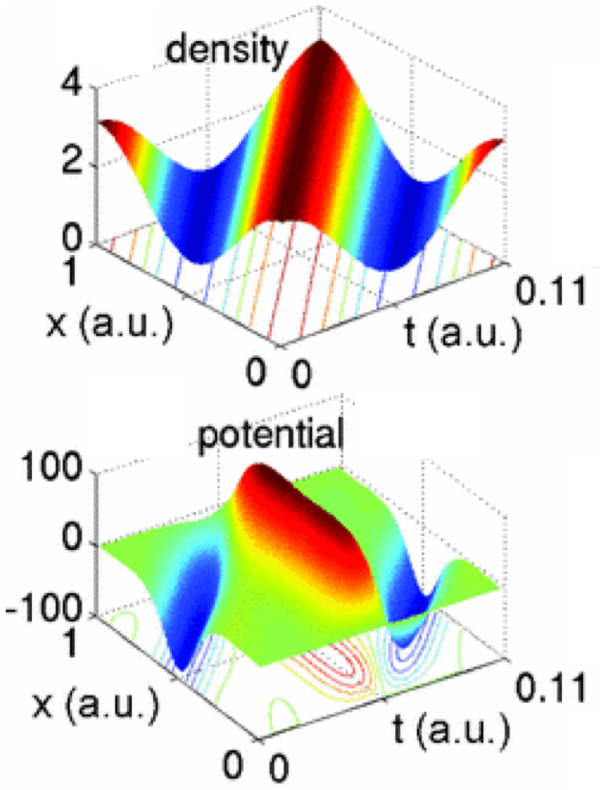

Figure 3: The density and corresponding correlation potential in atomic units created from density-potential mapping. Adapted with permission from Ref. 277. Copyright (2013) American Physical Society.

Previous studies have attempted to explore the time-dependence of the V_{xc}, with some progress in developing time-dependent potentials via the current TDDFT formalism.[281–289] Very recent work by Maitra and co-workers has introduced a new class of nonadiabatic approximations to V_{xc} that are functionals of the one-body reduced density-matrix and the exchange-correlation hole.[290,291] The dependence of the density evolution on the initial Kohn-Sham state going beyond a single Slater determinant has also been recently explored.[292] All efforts to go beyond the adiabatic approximation require careful attention to exact condi-

tions.[265,290,293–296]

In contrast to RT-TDDFT and RT-TDHF, for correlated wave function based time-dependent approaches there is no dependence of the Hamiltonian on the electron density, and therefore no unphysical peak-shifting. Wave function based methods instead propagate the time-dependent coefficients corresponding to different electronic states, rather than time-dependent orbitals. The adiabatic approximation of RT-TDDFT becomes less justified as the electron density is propagated away from the ground state, which is the case for many non-equilibrium and pump-probe simulations. Although correlated wave function based methods often have greater computational expense than RT-TDDFT for complex systems, they have the potential to perform better at modeling these far-from-ground state phenomena.

To evolve the system from an excited state, an alternative to propagating the system with a resonant laser pulse is to instead initialize the system in an excited state. This technique offers a way to partially bypass some of the problems with adiabatic TDHF/TDDFT for resonant processes and allows for computation of excited state dynamics and nonlinear properties. The accuracy of the technique, however, hinges on the preparation of an initial state that yields physically meaningful dynamics and avoids undesirable broadband excitation due to the rapid change in potential. Additionally, there are as-of-yet unaddressed formal problems such as the initial-state dependence for TDDFT.[273,297] The simplest approach for preparing an initial state close to an excited state is to directly manipulate the orbital populations without relaxation, either by promoting an electron to an unoccupied orbital,[136] or by removing it to emulate valence or core-level ionization.[298] An improvement on this approach is to instead propagate from a state computed from the linear-response eigenvectors.[86,299] Another approach is to converge the system in the presence of a static field, typically to create a charge separated state. Van Voorhis and coworkers showed that using constrained DFT (cDFT),[300] which minimizes the energy with the constraint that particular fragments of a system have a particular charge. This gives an initial state with improved intramolecular charge migration dynamics as compared to an orbital hole. This is

due to reduced self-interaction errors with cDFT.[301]

2.1.2 Accuracy of TDHF and TDDFT

Many reviews,[245,249,251,252,302] books,[247,248] and benchmarking studies[250,303–312] highlight the accuracy and pitfalls of TDDFT for common approximations for V_{xc} for various excited state properties. Although these reviews mostly focus on the more common linear response matrix formulation of TDDFT rather than real-time TDDFT, the accuracy for real-time and linear response formulations will be similar, assuming that the ground state electron density is used as a reference in both cases. Thus, the use of these functionals for TDDFT calculations can be expected to work well for the valence excited states of medium-sized organic molecules, although qualitatively incorrect transitions are predicted for thiophene and thienoacenes.[313]

TDDFT with standard approximate functionals has larger errors in modeling other kinds of excited states, including those with charge-transfer, Rydberg, or double excitation character. Approximate local exchange in DFT leads to a lack of Coulombic attraction between the excited electron and hole in TDDFT, so that charge-transfer transitions are generally much too low in energy.[245,314–316] These spuriously low-energy charge-transfer transitions are particularly problematic when computing the excitation energies of a molecule in explicit solvent.[317–320] The charge-transfer problem can be remedied using exact exchange,[316] with long-range corrected hybrid functionals and optimally tuned functionals providing much improved treatment of charge-transfer excitations.[304,321–326] Rydberg transitions are also often too low in energy using approximate TDDFT methods[302,327–331] because the V_{xc} does not exhibit the correct $-1/r$ limit as the distance r between an electron to the nucleus becomes large. Both TDHF and the usual adiabatic approximations for V_{xc} in TDDFT yield singly-excited states, therefore give a very poor description for states that have doubly-excited character. Such mixed states are often important for describing surface crossings, conical intersections, and extended conjugated systems.[280,302,332–337] For modeling core-electron excitations, there is a consistent improvement in the absolute values of the calculated excitation

energies with increasing Hartree-Fock exchange.[95,338–340] Particularly, short-range exchange has been shown to be an important component of hybrid functionals applied to core excitations. Both TDHF and TDDFT should be used with extreme caution in modeling open-shell systems such as transition metal complexes[341–343] or systems with multi-reference character where a single Slater determinant provides a poor starting reference.

2.2 Real-Time Time-Dependent Semi-Empirical Methods

Semiempirical methods have a long history.[344] With the growing interest in excited state properties and dynamics of large molecular systems, these methods have been revisited in recent years. The first examples of semiempirical methods (*i.e.*, the Hückel[345] and Pariser-Parr-Pople (PPP) methods), were limited to the description of π networks in organic systems. This treatment was later extended by Hoffman to both π and σ bonding.[346] Subsequently, Pople and Segal developed a series of semiempirical Hamiltonians based on HF theory, namely, the complete neglect of differential overlap (CNDO),[347,348] intermediate neglect of differential overlap (INDO),[349] and neglect of diatomic differential overlap (NDDO).[350] The INDO (INDO/S) Hamiltonian was further reparametrized by Zerner and co-workers in order to evaluate UV/Vis spectra for organic systems within the frameworks of configuration interaction with single excitations (CIS) and the random phase approximation (RPA),[351–355] respectively. Since then, this approach has been used for a broad range of systems including organic electronics, organic dyes, conjugated polymers, biological molecules and nanoparticles.[356–368] INDO/S parameters are now available for transition metals, lanthanides, and actinides.[369–372] More recent improvements to the INDO/S method, INDO/X, have also been reported by Voityuk.[373] Other approximate methods include the modified neglect of diatomic orbital (MNDO)[374,375] and its parametrized model 3 (PM3) or MNDO-PM3 methods.[376,377] The semipirical density functional tight binding (DFTB) method,[378–380] which is formally based on DFT, has also been extensively developed over the last two decades.

Despite this long history, real-time formulations of semi-empirical methods have only been

reported within the last two decades. The PPP Hamiltonian, which includes the important Coulomb interaction among π electrons, is particularly useful for studies of electronic properties of conjugated molecules. Mukamel and co-workers have successfully developed and employed real-time PPP Hamiltonian for studies of spectroscopic signals and electron dynamics of conjugated organic molecules.[381–385] Bartell *et. al.*[386] and Ghosh *et. al.*[387] have reported real-time time-dependent implementations of the PM3 and INDO/S methods using the Liouville superoperator approach and Chebyshev time propagation framework to study the time-dependent response to a weak pulse. They studied the UV/Vis spectra of a range of molecules, including large systems like the tyrosine chromophore in the ubiquitin protein (Fig. 4), the betanin dye molecule in the presence of methanol and water, and the Nile Red chromophore in a variety of solvents (acetone, ethanol, toluene and *n*-hexane). Both approaches yield spectra that are comparable in quality to those obtained from RT-TDDFT simulations or experiment. Large scale real-time DFTB simulations have also been used to model electron dynamics in complex systems such as solvated nanodroplets,[148] plasmonic nanoantennas,[388,389] and dye TiO_2 nanoparticle hybrids for charge injection,[390,391] such as those shown in Fig. 5.

2.3 Real-Time Time-Dependent Configuration-Interaction Methods

Time-evolved multiconfigurational wave functions are ideally suited for modeling time-resolved spectroscopies or excited-state properties in strong perturbations, in part, because they do not exhibit the deficiencies of RT-TDDFT that result from the use of approximate adiabatic exchange-correlation functionals of the density.

The conceptually simplest multiconfigurational wave function approach is time-dependent configuration interaction (TD-CI), wherein the wave function $\Psi(t)$ is expressed as a linear

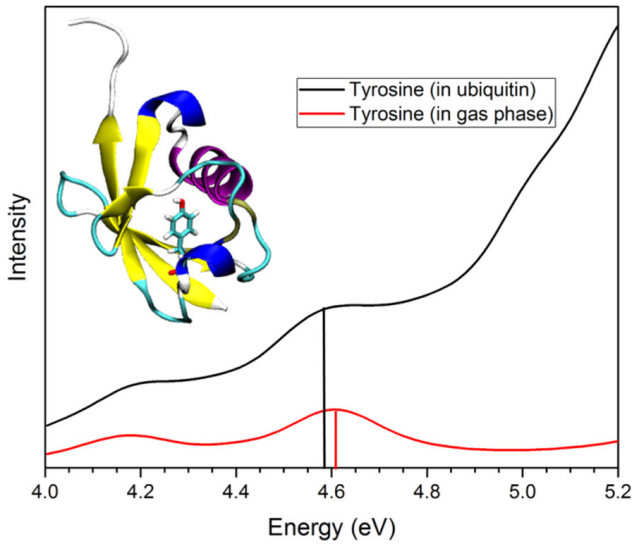

Figure 4: RT-INDO/S spectra of tyrosine in the gas phase and in the ubiquitin protein environment. The experimentally observed small red shift within the protein environment is qualitatively reproduced. Adapted with permission from Ref. 387. Copyright (2017) American Chemical Society.

combination of electron configurations $\{\Phi_K\}$:

$$\Psi(t) = \sum_K C_K(t)\Phi_K. \tag{10}$$

Here, $\{C_K(t)\}$ are time-dependent CI expansion coefficients, and $\{\Phi_K\}$ represent electronic configurations (Slater determinants or configuration state functions). If all configurations are included in the wave function expansion, TD-CI gives the exact description of the dynamics of a many-electron system,

$$i\dot{\mathbf{C}}(t) = \mathbf{H}(t)\mathbf{C}(t). \tag{11}$$

The total number of configurations in the determinant-based full CI framework is

$$N_{\text{det}} = \binom{N_{\text{orb}}}{n_{\text{e}}} \tag{12}$$

where N_{orb} and n_{e} are the total number of orbitals and electrons, respectively, in the system. Since the full TD-CI method is exponentially complex, the CI expansion is often trun-

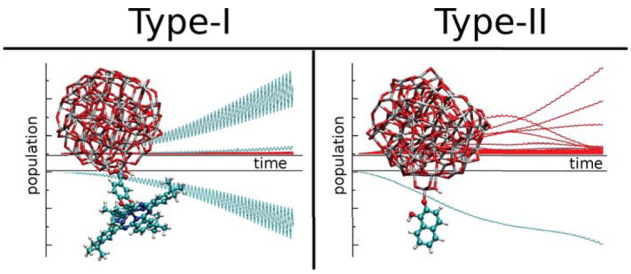

Figure 5: Population evolution of dyes involved in both direct (type-I) and indirect (type-II) photoinjection into TiO_2 were studied with real-time DFTB. Adapted with permission from Ref. 390. Copyright (2012) American Chemical Society.

cated in terms of either the excitation operator (*e.g.*, singles and doubles)[33,35–39,106,392,393] or the space used to construct the full CI basis (*e.g.*, the complete active space (CAS) approach).[28–30,32,107,110,394–396] As the size of the truncated space increases, the time-evolution of the approximate wave function approaches the asymptotic limit of the full TD-CI solution. As an example, the CAS Hamiltonian is given in the determinant basis as

$$\begin{aligned} H_{KL}(t) = \langle K| \sum_{tu} (h_{tu} + \sum_{i} (2(tu|ii) - (ti|iu)) \, |L\rangle \\ + \langle K| \frac{1}{2} \sum_{tuvw} (tu|vw)(\hat{E}_{tu}\hat{E}_{vw} - \delta_{uv}\hat{E}_{tw}) \, |L\rangle \end{aligned} \tag{13}$$

where t,u,v,w label the orbitals of the active space, and h_{pq} and $(pq|rs)$ represent one- and two-electron integrals, respectively. $\hat{E}_{pq}$ is a spin-adapted excitation operator

$$\hat{E}_{pq} = \hat{a}^{\dagger}_{p\alpha}\hat{a}_{q\alpha} + \hat{a}^{\dagger}_{p\beta}\hat{a}_{q\beta}, \tag{14}$$

defined in terms of the creation ($\hat{a}^{\dagger}$) and annihilation ($\hat{a}$) operators of second quantization, respectively.

The TD-CI wave function can be propagated in the basis of eigenstates of the CI Hamiltonian, in which case the time-evolution operator can be expressed as a unitary matrix. However, this approach requires that the Hamiltonian be fully diagonalized to obtain all CI states; the transition dipoles between all states must then also be computed. This approach

is computationally expensive and generally infeasible, with the exception of very small systems or small CAS problems. On the other hand, the time-consuming matrix-vector product in Eq. (11) can be computed within the determinant basis *on-the-fly*,[32,396,397] which reduces memory requirements and allows for the consideration of more complete CI expansions and the study of larger systems.

The CI wave function can be expanded in terms of excited determinants derived from restricted, unrestricted, or noncollinear mean-field reference functions. When a truncated CI expansion is used with a Slater determinant basis, the CI wave functions inherits any broken symmetries associated with the reference configuration. In a variational treatment, symmetry breaking can be advantageous in that it may lower the energy of the system. However, unphysical bright transitions to different spin states may arise from the broken symmetry wave function, and these features should be removed from calculated spectra and electric properties. Given a reference that is an eigenfunction of both $\hat{S}_z$ and $\hat{S}^2$, spin-adapted configuration state functions (CSFs), which are also eigenfunctions of these operators, are an appealing alternative to excited determinants when expanding the CI wave function. Within a CSF basis, the CI wave function will also be an eigenfunction of $\hat{S}_z$ and $\hat{S}^2$, and the effective CI space will be smaller because the Hamiltonian can be block-diagonalized according to spin state.[33,38,39]

TD-CI electron dynamics have been used to model photoionization,[28,106–108,110,112–115,393,398,399] linear spectroscopies,[32,35,39,392,394,400] and nonlinear optical responses.[29,30,37,38,107,392,393] Time-dependent configuration interaction singles (TD-CIS) is the most commonly used multiconfigurational approach. TD-CIS is particularly useful when the underlying chemical processes are mostly driven by single-electron dynamics, such those in linear optical response and photoionization. Unfortunately, TD-CIS tends to overestimate both static and dynamic hyperpolarizabilities due to a lack of electron correlation in the description of the ground state.[37,38,392,393]

In the nonlinear and nonperturbative regime, it is important that the wave function

include configurations which are multiply substituted, relative to the reference configuration. As such, the use of a complete-active-space CI (CASCI) formalism becomes advantageous. TD-CASCI has been used to investigate population dynamics and simulate spectroscopies.[32,396] This active-space approach has been generalized to the restricted active space (RAS) CI formalism which allows treatment of larger systems but possesses the drawback of a loss of size extensivity.[108] In TD-CASCI, the choice of initial orbitals is of key importance. This has recently been highlighted by Liu *et. al.*,[32] who investigated the effect of different initial orbitals in the TD-CASCI calculation of absorption spectra.[32] Similarly, in the numerical grid implementation of the time-dependent truncated CI approach, pseudo-orbitals based on HF orbitals have been demonstrated to be a decent orbital basis for the study of strong-field ionization, photoionization, and X-ray IR pump probe ionization.[108]

Recent years have also seen the development of TD-CASSCF where the wave function obeys the time-dependent variational principle by allowing variations in both the CI coefficients and the orbitals;[28,31,394,399,401] this approach contrasts with TD-CASCI wherein the orbitals remain fixed. This technique has also been extended to the RAS partitioning, allowing a detailed analysis of the role that multi-electron excitations play in the description of nonlinear properties, as well as the study of high harmonic generation spectra and ionization of carbon and beryllium atoms.[29,30]

2.4 Real-Time Time-Dependent Coupled-Cluster Methods

As discussed in Sec. 2.3, wave function-based time-domain approaches do not exhibit many of the well-known failures of RT-TDDFT, making them desirable candidates for modeling strong or long-time light-matter interactions. However, real-time methods built upon the configuration interaction expansion of the wave function suffer from their own problems. For example, the lack of correlation effects in TD-CIS often renders it unreliable (*e.g.*, for estimating dynamic and static hyperpolarizabilities[37,38,392,393]). A truncated CI scheme such as CI with single and double excitations (CISD) is neither size extensive nor is it particularly

accurate, and multiconfigurational CI is exponentially complex. On the other hand, coupled-cluster (CC)-based approaches are highly accurate, rigorously size extensive when truncated at any excitation order, and can be realized in polynomial time.

The ground-state (CC) coupled-cluster wave function is given by

$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle \tag{15}$$

where $|\Phi_0\rangle$ represents a single-determinant reference function, and $\hat{T}$ is the cluster operator, defined in second-quantized notation as

$$\hat{T} = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4}\sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \dots . \tag{16}$$

If the cluster operator is not truncated, full CC theory is numerically equivalent to the full CI. Further, as mentioned above, CC theory has the useful property that it is rigorously size extensive should Eq. (16) be truncated to any excitation order (*i.e.*, at the level of single and double excitations, as in CCSD[402]). The CC ground-state energy and cluster amplitudes are determined using a projection approach that is nonvariational and which slightly complicates the evaluation of properties because the Hellman-Feynmann theorem cannot be applied. The complete parametrization of the ground state thus requires a generalized Hellman-Feynmann theorem and a stationary Lagrangian function of the form

$$L = \langle\tilde{\Psi}_{\mathrm{CC}}|\hat{H}|\Psi_{\mathrm{CC}}\rangle, \tag{17}$$

where

$$\langle\tilde{\Psi}_{\mathrm{CC}}| = \langle\Phi_0|e^{-\hat{T}}(1+\hat{\Lambda}), \tag{18}$$

and $\hat{\Lambda}$ represents a de-excitation operator, defined as

$$\hat{\Lambda} = \sum_{ia} \lambda_a^i \hat{a}_i^\dagger \hat{a}_a + \frac{1}{4} \sum_{ijab} \lambda_{ab}^{ij} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_b \hat{a}_a + \dots . \tag{19}$$

The non-Hermiticity of this formalism and the fact that both right- and left-hand CC wave functions are required to define ground-state properties play important roles in the extension of CC theory to the time domain.

Given a time-dependent Hamiltonian operator, $\hat{H}(t)$, the simplest way to achieve a time-dependent CC (TD-CC) theory is to build time-dependence into the right-hand CC wave function [$\hat{T} \rightarrow \hat{T}(t)$] while ignoring the non-Hermiticity of the theory and assuming that the underlying molecular orbitals are independent of time. Under these assumptions, which define the TD-CC formalism of Huber and Klamroth,[47] the time-dependent Schrödinger equation can be left-multiplied by $e^{-\hat{T}(t)}$ to obtain

$$i\hbar \; e^{-\hat{T}(t)} \frac{\partial}{\partial t} e^{\hat{T}(t)} |\Phi_0\rangle = e^{-\hat{T}(t)} \hat{H}(t) e^{\hat{T}(t)} |\Phi_0\rangle, \tag{20}$$

and programmable expressions for the time derivatives of the cluster amplitudes can then be obtained upon considering the Baker-Campbell-Hausdorff expansions of both the similarity-transformed Hamiltonian and time derivative operators that arise in Eq. (20).[403] Few groups follow this precise scheme, though, for two reasons. First, a correct description of time-dependent properties (*e.g.*, the energy, dipole moment, *etc.*) requires knowledge of the time-evolution of both the right- *and* left-hand CC wave functions. Indeed, the CC wave functions should satisfy a time-dependent bivariational principle,[404] and the complete specification of the time evolution of the system requires the integration of both the time-dependent Schrödinger equation and its complex conjugate. Second, Huber and Klamroth[47] observed that, in practical computations at the time-dependent CCSD (TD-CCSD) level of theory, the lack of time-dependence of the orbitals apparently leads to numerical instabilities that emerge when considering either large basis sets or intense external electric fields. Pedersen

and Kvaal[405] later confirmed intense-field-induced instabilities within a more sophisticated TD-CCSD formalism that evolved both the t- and λ-amplitudes.

Regarding the time-evolution of the molecular orbitals, in the 1970s, Hoodbhoy and Negele[403,406] and Schönhammer and Gunnarsson[407] separately proposed that the molecular orbitals should evolve in time, with the former authors suggesting that the CC amplitudes could be evolved within the orbital basis defined by the equations of motion of TDHF theory. In 2012, Kvaal[404] refined these ideas with his orbital adaptive TD-CC (OATDCC) heirarchy, which employs time-varying biorthogonal orbitals and interpolates between the MCTDHF and TDHF approaches when the cluster operator is chosen to include all excitation levels or none, respectively. A similar treatment, based upon time-varying orthonormal orbitals, can be found in the time-dependent orbital-optimized CC (TD-OCC) method of Sato *et al.*,[50] although it should be noted that, for systems with more than two electrons, orbital-optimized CC theory does not converge to the full CI limit.[408]

Some aspects of the structure of both the OATDCC with double excitations (OATDCCD) and TD-OCC with double excitations (TD-OCCD) approximations resemble those of Huber and Klamroth's TD-CCSD, with two significant exceptions. First, OATDCC and TD-OCC ignore single-particle transitions in the cluster operator, as they are rendered redundant through the time dependence of the orbitals. Second, and more significantly, the TD-CC scheme of Huber and Klamroth considers only the time evolution of the t-amplitudes (that define the right-hand CC wave function), whereas OATDCC and TD-OCC evolve both the t- and λ-amplitudes (as does the TD-CCSD approach of Pedersen and Kvaal[405]). Huber and Klamroth attempted to circumvent the need to consider the time evolution of λ-amplitudes by defining time-dependent quantities in terms of an approximate CISD wave function, constructed from TD-CCSD amplitudes. However, observables computed in this way incorrectly assume complex values upon interaction of the system with an oscillating electric field. On the other hand, Pedersen and Kvaal[405] demonstrated that a time-dependent formalism that respects the non-Hermiticity of CC theory will retain physically meaningful (*i.e.*, real) ob-

servables; small imaginary contributions to quantities such as the energy are purely numerical artifacts that can be removed through the use of a suitable integrator.

The nonlinear nature of the cluster operator leads to complicated equations for the time-evolution of the cluster amplitudes. The complexity of these equations and any related potential numerical issues can be avoided by keeping the cluster amplitudes fixed at their time-independent, ground-state values and considering time-evolution of the system only at the equation-of-motion CC[409–411] (EOM-CC) level of theory.[22,35,37,49,52,53] Within the conventional EOM-CC framework, the I^{th} electronic state is represented by

$$\hat{R}_I|\Psi_{\rm CC}\rangle = (r_0 + \sum_{ia} r_i^a \hat{a}_a^\dagger \hat{a}_i + \frac{1}{4}\sum_{ijab} r_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i + \dots)e^{\hat{T}}|\Phi_0\rangle, \tag{21}$$

where the expansion coefficients r_0, r_i^a, *etc.*, comprise the (right-hand) eigenvectors of the normal-ordered similarity-transformed Hamiltonian,

$$\bar{H}_N = e^{-\hat{T}}\hat{H}e^{\hat{T}} - E_{\rm CC}. \tag{22}$$

Here, $E_{\rm CC}$ represents the energy associated with the ground-state CC wave function, which is recovered in the EOM framework with $\hat{R}_0 = 1$. The non-Hermitian nature of the similarity-transformed Hamiltonian implies that these right-hand eigenfunctions comprise one half of a biorthogonal set of functions; the complementary left-hand eigenfunctions are

$$\langle\tilde{\Psi}_{\rm CC}| = \langle\Phi_0|e^{-\hat{T}}(l_0 + \sum_{ia} l_a^i \hat{a}_i^\dagger \hat{a}_a + \frac{1}{4}\sum_{ijab} l_{ij}^{ab} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_b \hat{a}_a + \dots). \tag{23}$$

In this representation, a general time-dependent wave function can be represented by right- and left-hand states

$$|\Psi(t)\rangle = \hat{R}(t)e^{\hat{T}}|\Phi_0\rangle, \tag{24}$$

and

$$\langle\tilde{\Psi}(t)| = \langle\Phi_0|e^{-\hat{T}}\hat{L}(t), \tag{25}$$

whose time evolution are governed by the time-dependent Schrödinger equation and its complex conjugate, respectively.

We are only aware of two examples of laser-driven electron dynamics described by time-dependent EOM-CC (TD-EOM-CC). In 2011 Sonk *et al.*[35] used TD-EOM-CC with single and double excitations (TD-EOM-CCSD) to explore the response of butadiene to short, intense laser pulses, and in 2012 Luppi and Head-Gordon[37] applied TD-EOM-CCSD to model high harmonic generation in H_2 and N_2. In both cases, the time-dependent wave function was expanded in the basis of field-free eigenstates of the similarity-transformed Hamiltonian. In this basis, the transition dipole matrix that comprises the field interaction is not Hermitian, which could potentially lead to dynamics that do not conserve the norm of the wave function. The similarity-transformed Hamiltonian is also not strictly Hermitian, even though it is diagonal in this basis. In both Refs. 35 and 37 the non-Hermitian components of the matrices are disregarded. The largest difference between the two formalisms described in these papers is that Sonk *et al.*, having Hermitized the similarity-transformed dipole matrix, employed a propagation scheme suitable for a Hermitian theory (that is, the time-dependent state is characterized by only a single wave function), whereas Luppi and Head-Gordon retained distinct left- and right-hand time-dependent wave functions.

Nascimento and DePrince[22,49] have also developed a TD-EOM-CC formalism with a slightly more limited scope than those discussed above. In their work, the linear absorption lineshape function given by Fermi's Golden Rule is obtained from the Fourier transform of a dipole autocorrelation function. This treatment is similar to that employed decades earlier in the context of fluorescence and Raman spectroscopy[412–414] and in the vibrational coupled-cluster approach proposed by Prasad in 1988.[415]

It can be shown[22,49] that each Cartesian component of a linear absorption lineshape function can be expressed as the Fourier transform of a dipole autocorrelation function

defined as

$$I_\xi(\omega) = \int_{-\infty}^{\infty} dt\ e^{-i\omega t} \langle \tilde{M}_\xi(t) | M_\xi(0) \rangle. \tag{26}$$

Here, $\langle \tilde{M}_\xi(0)|$ and $|M_\xi(0)\rangle$ are left- and right-hand dipole functions defined at time $t = 0$ by

$$\langle \tilde{M}_\xi(0)| = \langle \Phi_0 | (1 + \hat{\Lambda}) \bar{\mu}_\xi \tag{27}$$

and

$$|M_\xi(0)\rangle = \bar{\mu}_\xi |\Phi_0\rangle, \tag{28}$$

respectively, and $\bar{\mu}_\xi$ represents the ξ^{th} component ($\xi \in x, y, z$) of the similarity-transformed dipole operator ($\bar{\mu}_\xi = e^{-\hat{T}} \hat{\mu}_\xi e^{\hat{T}}$). A dipole strength function, $S(\omega)$, which is formally equivalent to the oscillator strengths which arise within conventional EOM-CC theory, can then be obtained from the real part of this lineshape as

$$S(\omega) = \frac{2}{3} \omega \sum_\xi \mathrm{Re}\{I_\xi(\omega)\}. \tag{29}$$

Nascimento and DePrince applied this formalism to the evaluation of UV/Vis absorption spectra[22] at the TD-EOM approximate second order coupled-cluster (CC2)[416] level of theory and X-ray absorption fine structure[49] at the TD-EOM-CCSD level of theory. As with other real-time approaches, one of the benefits of TD-EOM-CC is that broad-band absorption spectra can be generated from a single time-domain simulation (for each Cartesian component of the absorption lineshape function). For example, Fig. 6 illustrates a TD-EOM-CCSD absorption spectrum for carbon monoxide that spans 600 eV. More recently, Nascimento and DePrince have generalized this moment-based TD-EOM-CC formalism to other linear electronic spectroscopies, demonstrating, for example, the numerical equivalence of electronic circular dichroism spectra generated at the TD-EOM-CC and conventional EOM-CC levels of theory.[52] Further, DePrince, Li, and their coworkers[53] have also recently extended TD-EOM-CC theory to the description of relativistic effects within the

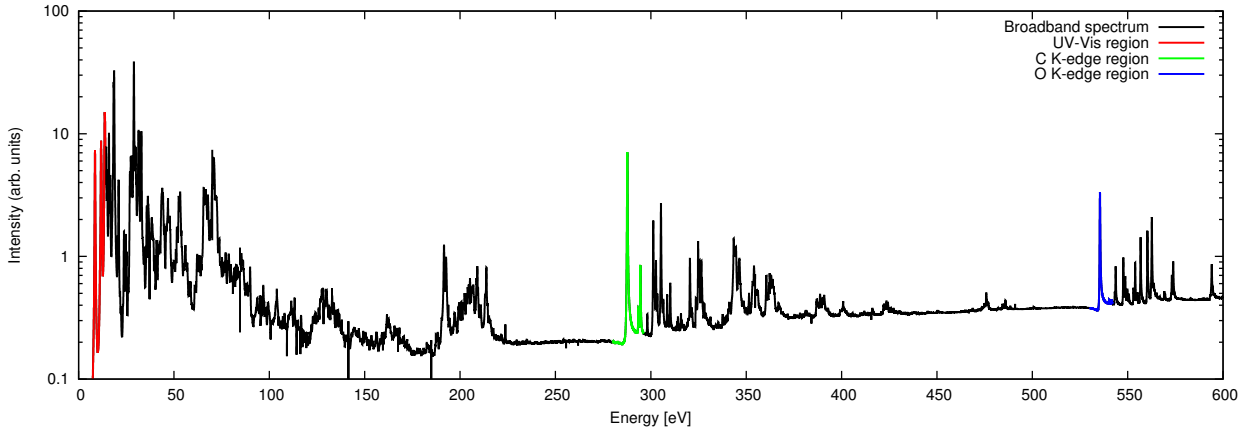

Figure 6: Broadband absorption spectrum for carbon monoxide computed at the TD-EOM-CCSD/aug-cc-pVTZ level of theory. Adapted with permission from Ref. 49. Copyright (2017) American Chemical Society.

exact two-component[98,417–431] framework.

Closely related to time-dependent CC theory is the time-dependent algebraic diagrammatic construction (ADC) approach,[40–46,432] which has been applied to a variety of problems, including ultrafast charge[40,45] and energy[43,44] migration, metastable states,[41,42] and X-ray absorption spectroscopy.[46] The ADC formalism is Hermitian and its extension to the time domain is thus slightly less complicated than that of CC theory.

2.5 Real-Time Time-Dependent Two-Component and Relativistic Methods

Conventional electronic structure methods are incapable of simulating time-dependent spin precession. The reason for this shortcoming is the common choice to align electronic spins (anti-)parallel with respect to each other within the electron configuration. In single-reference techniques, such as unrestricted Hartree-Fock and spin-density density functional theories, this choice leads to spin orbitals that are eigenfunctions of the spin operator $\hat{S}_z$. As a result, the number of spin-up and spin-down electrons will be conserved throughout any dynamical process.

In order to obtain a proper description of spin precession, one must consider the full vector form of the time-dependent magnetization $\mathbf{m}(\mathbf{r})$. The dynamics of $\mathbf{m}(\mathbf{r})$, which corresponds to the spin quantization axis, requires a non-collinear spin electronic structure framework, such as that provided by two-component or generalized Hartree-Fock/Kohn-Sham methods.[68,433–450] Smooth transitions between various spin configurations are enabled through the spinor basis,

$$\psi_k(\mathbf{x},t) = \begin{pmatrix} \phi_k^{\alpha}(\mathbf{r},t) \\ \phi_k^{\beta}(\mathbf{r},t) \end{pmatrix}, \tag{30}$$

where the spatial functions $\{\phi_k^{\alpha}(\mathbf{r},t)\}$, $\{\phi_k^{\beta}(\mathbf{r},t)\}$ are expanded in terms of a common set of basis functions $\{\chi_\mu(\mathbf{r})\}$

$$\phi_k^{\alpha}(\mathbf{r},t) = \sum_{\mu} c_{\mu k}^{\alpha}(t)\chi_\mu(\mathbf{r}), \tag{31}$$

$$\phi_k^{\beta}(\mathbf{r},t) = \sum_{\mu} c_{\mu k}^{\beta}(t)\chi_\mu(\mathbf{r}). \tag{32}$$

The first example of *ab initio* non-collinear real-time electronic dynamics was reported in 2014.[68] In that work, Ding, *et al.* derived and utilized a density-matrix based two-component Liouville-von-Neumann equation in the orthonormal basis:[68,70]

$$i\frac{\partial}{\partial t}\begin{pmatrix} \mathbf{P}'^{\alpha\alpha}(t) & \mathbf{P}'^{\alpha\beta}(t) \\ \mathbf{P}'^{\beta\alpha}(t) & \mathbf{P}'^{\beta\beta}(t) \end{pmatrix} = \left[\begin{pmatrix} \mathbf{F}'^{\alpha\alpha}(t) & \mathbf{F}'^{\alpha\beta}(t) \\ \mathbf{F}'^{\beta\alpha}(t) & \mathbf{F}'^{\beta\beta}(t) \end{pmatrix}, \begin{pmatrix} \mathbf{P}'^{\alpha\alpha}(t) & \mathbf{P}'^{\alpha\beta}(t) \\ \mathbf{P}'^{\beta\alpha}(t) & \mathbf{P}'^{\beta\beta}(t) \end{pmatrix}\right], \tag{33}$$

where $\mathbf{P}'^{\alpha\alpha}(t)$ and $\mathbf{F}'^{\alpha\beta}(t)$ are the density and Fock/Kohn-Sham matrices in an orthonormal

basis, which are transformed from AO-basis quantities in with a spin-blocked structure,

$$P^{\sigma\tau}_{\mu\nu}(t) = \sum_{i}^{N} c^{\sigma}_{\mu i}(t) \cdot c^{\tau *}_{\nu i}(t), \quad \sigma, \tau \in \{\alpha, \beta\} \tag{34}$$

$$\mathbf{F}^{\sigma\tau}(t) = \mathbf{h}^{\sigma\tau}(t) + \delta_{\sigma\tau}\left[\mathbf{J}^{\alpha\alpha}(t) + \mathbf{J}^{\beta\beta}(t)\right] - (1-\zeta)\mathbf{V}^{\sigma\tau}_{xc} + \zeta\mathbf{K}^{\sigma\tau}(t), \tag{35}$$

The magnetization densities $\mathbf{P}'^{\alpha\beta}$ and $\mathbf{P}'^{\beta\alpha}$ give rise to the non-collinear spin projection on the x and y rotational axes. The off-diagonal Fock/Kohn-Sham matrices, $\mathbf{F}'^{\alpha\beta}$ and $\mathbf{F}'^{\beta\alpha}$, arise from the spin coupling with external (*e.g.*, magnetic field) and internal (*e.g.* spin-orbit coupling) perturbations. For hybrid DFT, the HF exchange integral $\mathbf{K}$ takes on a fractional value scaled by a non-zero scaling factor ζ, whereas $\zeta = 0$ for pure DFT kernels.

The non-relativistic Hamiltonian ignores interactions explicitly associated with the spin degrees of freedom, such as the spin-spin interactions, spin-orbit couplings, and spin-magnetic field interactions. Although it seems the extension of the non-relativistic time-dependent many-electron methods to the relativistic case is straightforward, incorporation of special relativity introduces new conceptual difficulties. First, the theory of special relativity assumes the equivalence of all inertial reference frames under Lorentz transformation of the space-time coordinates. A relativistic quantum mechanical description of a molecular system requires a definition of a Lorentz invariant molecular Hamiltonian, which is not readily established. As a result, separation of the space-time coordinates must be performed in a particular reference frame and will only be valid in this reference frame. For molecular systems, the most convenient reference frame is the Born-Oppenheimer frame where the nuclei are at rest, and the electromagnetic potential created by the nuclei is simply a scalar potential.

The time-dependent two-component framework [Eq. (33)] is well-suited for the inclusion of scalar relativistic or spin-coupling effects, subject to an appropriate transformation from the bi-spinor or four-component representation of the Dirac equation, such as the Douglas-Kroll-Hess,[451–453] the normalized elimination of the small components[454,455] or the

zeroth order regular approximation (ZORA)[456,457] and the the exact two-component (X2C) method.[98,417–431] Because relativistic methods are not the focus of this review, we refer readers to Refs. 458, 459, and 430 for a more thorough review of the subject matter. Applications of the relativistic real-time four-component method were first reported by Repisky, *et al.*[69] and more recently by De Santis, *et al.*[460] for computing absorption spectra. In 2016, a real-time relativistic two-component method was developed by Goings, *et al.*[70] to study spin-forbidden excitations; this approach was then extended to the description of nonlinear optical properties by Repisky, *et al.*[100]

2.6 Real-Time Methods in Complex and Non-Equilibrium Environments

Chemical properties, including nuclear conformation, spectroscopy, and chemical reactivity, can often be dramatically modified by interaction with the surrounding medium (*e.g.*, through solvation).[461–464] These environmental interactions could be steric[465,466] or specific electronic perturbations such as hydrogen bonding, dipole-dipole, or non-covalent interactions.[467–469] Unfortunately, treating the system and its surrounding environment with high levels of theory is a computationally intractable.

Instead, practical theoretical models focus on capturing the most important aspects of the system-environment interaction. One of the most computationally tractable approaches is the polarizable continuum model (PCM) that replaces the explicit atomistic environment with an implicit solvent model.[470–478] The real-time time-dependent formalism of the equilibrium PCM (TDPCM) has been developed into the RT-TDHF/RT-TDDFT framework.[138,139,154] In the initial approach, the environment was kept in equilibrium with respect to the polarization of the system by relaxing the solvent dielectric constant from the dynamic, high frequency (optical) value to the static, zero-frequency value according to an empirical relaxation model. Later, a non-equilibrium TDPCM approach was introduced to explicitly treat the evolution of the dielectric medium as it responds to the time-dependent

system polarization.[155,156]

Although continuum models can provide an accurate description for systems with weak interaction with the environment,[474,479–481] an atomistic description of the environment becomes necessary for strong specific system-environment interactions (*e.g.*, solute-solvent hydrogen bonding or protein active sites).[482] Hybrid time-dependent models treat the high-level time-dependent electronic dynamics quantum mechanically (QM), while the environmental response is described at a classical molecular mechanics (MM) level.[483–485] The most common example of these hybrid QM/MM models electrostatically embeds the QM system on effective point charges to represent the environment atoms. Morzan *et al.* employed an electrostatic embedding model in a real-time QM/MM method to capture the solvatochromic shift of formamide in water.[486] Marques *et al.* used an electrostatic embedding model to in- … green … before and after protonation by … these … od agreement with experiment, … rating … dels for simulating absorption … nents

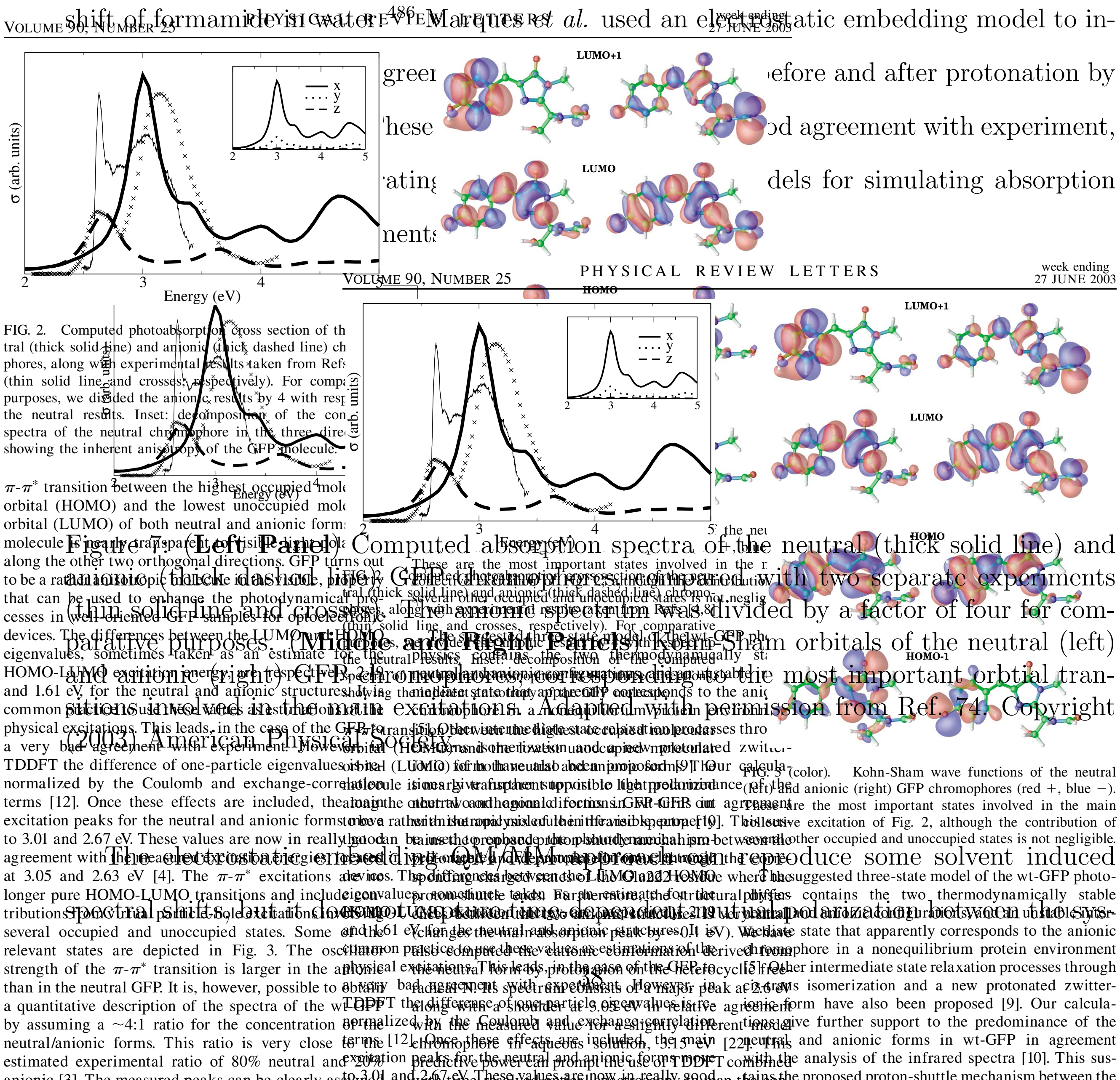

Figure 7: (Left Panel) Computed absorption spectra of the neutral (thick solid line) and anionic (thick dashed line) GFP chromophores compared with two separate experiments (thin solid line and crosses). The anionic spectrum was divided by a factor of four for comparative purposes. (Middle and Right Panels) Kohn-Sham orbitals of the neutral (left) and anionic (right) GFP chromophores corresponding to the most important orbtial transitions involved in the main excitations. Adapted with permission from Ref. 74. Copyright (2003) American Physical Society.

The electrostatic embedding QM/MM approach can reproduce some solvent induced spectral shifts, but it does not capture time-dependent mutual polarization between the sys-

tem and its environment. Recently, many approaches for including the system-environment mutual polarization have been explored, including "fluctuating charges",[487–490] "effective fragment potentials",[491,492] "induced dipoles",[493–497] and Drude oscillator-based models.[498] Li and Mennucci have extended the polarizable molecular mechanics (MMPol) based on the induced dipole formalism[493,494] to the real-time regime coupled with RT-TDHF/RT-TDDFT[152,499] and TD-CASSCF.[32] In these approaches, the electronic degrees of freedom of the environment, modeled by the induced dipoles with frequency independent polarizabilities in the MMPol regime, respond instantaneously to the electric field at each polarizable site. This approximation is reasonable and useful for cases where the electric field generated by the QM region is oscillating much more slowly than the response in the MM region.[499,500]

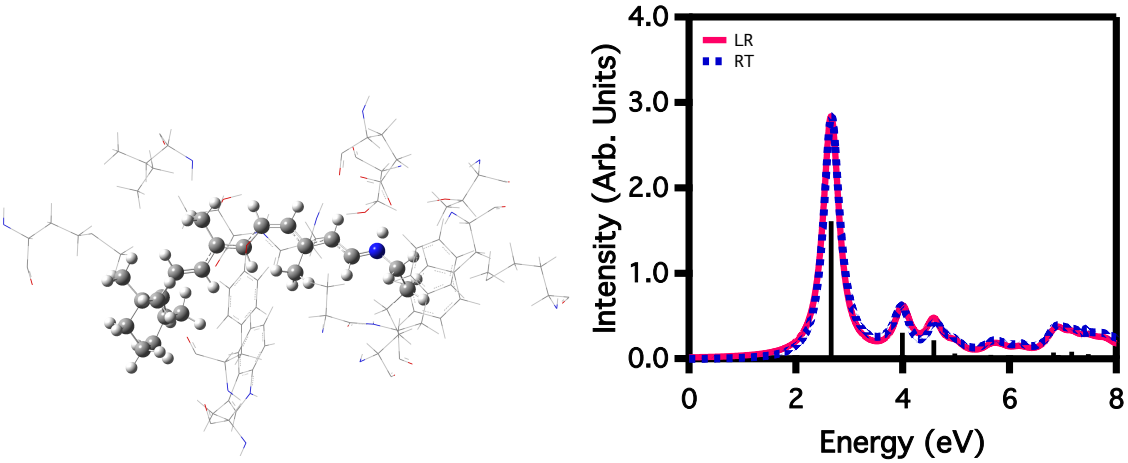

Figure 8: (**Left**) 11-*cis* retinal protonated Schiff base (RPSB) in a shell of residues from bovine rhodopsin. The chromophore is covalently bonded to the Lys296 residue. The free valency created on C_δ by the division of the QM (shown in a ball and stick representation) and MM (shown in a line representation) regions was capped with a hydrogen link atom. See Ref. 494 for details in the partitioning scheme. (**Left**) LR- and RT-TDDFT/MMPol computed absorption spectrum of RPSB in bovine rhodopsin. Adapted with permission from Ref. 152. Copyright (2017) American Chemical Society.

Studies coupling the polarizable embedding approach with real time electron dynamics have been successful at predicting spectroscopic properties, such as solvatochromic shifts, as well as providing unique insight into the responsive dynamics of the electronic degrees of free-

dom in a classical environment. Wu *et al.* captured the solvatochromic effects of water on the absorption spectrum of coumarin, a common solvatochromic dye; this study also investigated the physical extent of the mutual polarization between dye and solvent after perturbation, demonstrating the diminishing effects of polarizable solvent on the dynamics of the quantum subsystem as a function of distance.[501] Donati *et al.* explored spectroscopic properties of a similar chromophore, coumarin-153, in methanol and in a covalently bound environment that cannot be modeled with continuum embedding approaches.[152] The calculated absorption spectrum of retinal protonated Schiff base (RPSB) in rhodopsin (Fig. 8) demonstrated the mutual polarization of electronic degrees of freedom in environments tightly coupled to the quantum system.[152]

3 Numerical Techniques

3.1 Basis Set Representations

Over the years real-time time-dependent electronic structure approaches have been developed in a number of widely used electronic structure programs, with wave function or density matrix representations ranging from Gaussian-type functions,[15,17–23,33,502] numerical atomic orbitals,[14,503–505] real-space grids,[27,506–508] planewaves,[24,122,127,509–514] and mixed Gaussian-type functions and planewaves.[26] Other promising representations include Lagrange functions,[515–517] finite elements[518,519] and maximally localized Wannier functions.[520]

Of the various real-time electronic structure approaches, RT-TDDFT has been explored with all the above mentioned basis sets, while post-Hartree-Fock theories have only been implemented with Gaussian orbitals, taking full advantage of their analytical properties.[521] This has allowed the development of ground-, excited-state and higher-order response properties based on electronic structure theories of increasing complexity over many decades. It is also the mostly widely used basis set representation in quantum chemistry. Each of these representations have their strengths and weaknesses and the specific choice depends on the

system and phenomena being investigated, accuracy and algorithm requirements.

3.2 Time Propagation Methods

A key component in real-time schemes involves the time propagation of the wave function or the density matrix. The correspondence between quantum Hamiltonians and unitary time propagators (Stone's theorem[522]) imposes strict requirements on time-propagation algorithms. As a result, general purpose integrators like the Runge-Kutta method[523] are not necessarily appropriate for evolving the TDSE as they can become unstable with increasing system size, and stable propagation often necessitates the use of small time steps. On the other hand, algorithms based on the Magnus expansion,[15,259,524–527] which are unitary by construction, and other symplectic integrators[405,528–539] can be useful in this context. Beyond this review, we refer the reader to the reviews of Kosloff[540] and Castro and workers[259,541] for a more general overview of time propagation schemes.

The goal of any time-propagation method is to find a numerical solution of the time-dependent Schrödinger or Dirac equation [Eq. (1)] or associated approximations. The Magnus expansion achieves this via an exponential form of the propagator $U(t, t_0)$ that relates wave functions or density matrices at different times as follows,

$$\Psi(t) = U(t, t_0)\Psi(t_0) \tag{36}$$

$$U(t, t_0) = \exp\left(\Omega(t, t_0)\right); \quad U(t_0, t_0) = I \tag{37}$$

Given this propagator, Eq. (1) can be cast as,

$$\frac{\partial}{\partial t}U(t, t_0)\Psi(t_0) = \tilde{H}(t)U(t, t_0)\Psi(t_0) \tag{38}$$

where $\tilde{H}(t) \equiv \frac{-i}{\hbar} H(t)$. In the Magnus expansion, $\Omega(t, t_0)$ is written as a power-series,

$$\begin{aligned}\Omega(t, t_0) = & \int_{t_0}^{t} \tilde{H}_1 dt_1 \\ & + \frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \left[\tilde{H}_1, \tilde{H}_2\right] \\ & + \frac{1}{6} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \left([\tilde{H}_1, [\tilde{H}_2, \tilde{H}_3]] + [\tilde{H}_3, [\tilde{H}_2, \tilde{H}_1]]\right) + \cdots\end{aligned} \tag{39}$$

where $\tilde{H}_k = \tilde{H}(t_k)$. One can think of each order in this series as a correction accounting for the proper time-ordering of the Hamiltonian. A higher order expansion allows for larger time steps, but this benefit must be weighed against the subsequent requirement that more Hamiltonian evaluations be carried out at every time step. One complication with the Magnus propagation approach arises from requiring the knowledge of the Hamiltonian at a future time, which, in the case of single-particle theories like RT-TDHF and RT-TDDFT, is unknown.[18] As a result, different predictor schemes have to be used, which also have to conserve time-reversibility.

The simplest propagator based on the Magnus expansion just uses the first term in Eq. (39),

$$\Omega(t, t_0) \approx \int_{t_0}^{t} \tilde{H}_1 dt_1 \tag{40}$$

Equation (40) can be numerically integrated with a forward-Euler-like time integrator but more accurate approaches are based on second-order methods.

A popular second-order method approximates the first term in Eq. (39) by the midpoint rule, leading to an $\mathcal{O}(\Delta t^2)$ time integrator[132,542]

$$\psi(t_{k+1}) = \exp\left(\Delta t \tilde{H}(t_{k+1/2})\right) \psi(t_k) \tag{41}$$

where Δt is the time step and subscript k is the time index. Modifying the time index to eliminate the need to evaluate the Hamiltonian at fractional time steps, by changing the time step to $2\Delta t$, leads to the modified midpoint unitary transformation (MMUT) method[15,95,526]

$$\psi(t_{k+1}) = \exp\left(2\Delta t \tilde{H}(t_k)\right)\psi(t_{k-1}) \tag{42}$$

The MMUT method is a leapfrog-type unitary integrator that assumes $\tilde{H}$ is linear over the time interval and that higher-order terms go to zero when this approximation is applied to Eq. (39). Other integrators based on the Magnus expansion have also been developed.[259,527] These integrators are all symplectic and consequently practically energy conserving. The Runge-Kutta class of methods, on the other hand, are non-symplectic and are thus subject to energy drifts over the course of a long-time simulation. Real-time methods using Magnus integrators require the evaluation of a matrix exponential, which is non-trivial and often the most time consuming step. In matrix form, Equation (42) can be rewritten as

$$\mathbf{P}'(t_{k+1}) = \mathbf{U}(t_k) \cdot \mathbf{P}'(t_{k-1}) \cdot \mathbf{U}^\dagger(t_k) \tag{43}$$

$$\mathbf{U}(t_k) = \exp\left[-i2\Delta t \mathbf{H}(t_k)\right] \tag{44}$$

The time-evolution matrix $\mathbf{U}(t_k)$ can be constructed using various methods such as direct diagonalization or power-series- or Lanczos-based approximations.

For small Hamiltonian matrices (*i.e.*, those for which direct diagonalization at every time step does not create a bottleneck), the time-evolution matrix can be constructed using the eigenvectors $\mathbf{C}(t_k)$ and eigenvalues $\boldsymbol{\epsilon}(t_k)$ of the matrix representation of the Hamiltonian at time t_k

$$\mathbf{C}^\dagger(t_k) \cdot \mathbf{H}'(t_k) \cdot \mathbf{C}(t_k) = \boldsymbol{\epsilon}(t_k) \tag{45}$$

$$\mathbf{U}(t_k) = \mathbf{C}(t_k) \cdot \exp\left[-i2\Delta t \boldsymbol{\epsilon}(t_k)\right] \cdot \mathbf{C}^\dagger(t_k) \tag{46}$$

The Baker-Campbell-Hausdorff (BCH)[543] and other polynomial expansions offer an attractive alternative to matrix diagonalization as they only involve general matrix multiplication operations, which are more straight-forward to parallelize.[18] Defining $\mathbf{W} = -i2\Delta t\mathbf{H}(t_k)$ and writing Eq. (42) in matrix form,

$$\mathbf{P}'(t_{k+1}) = e^{\mathbf{W}_k}\mathbf{P}'(t_{k-1})\,(t)\,e^{-\mathbf{W}_k}, \tag{47}$$

we can use the BCH expansion to evolve the density matrix as,

$$\mathbf{P}'(t_{k+1}) = \mathbf{P}'(t_{k-1}) + \frac{1}{1!}\left[\mathbf{W}_k, \mathbf{P}'(t_{k-1})\right] + \frac{1}{2!}\left[\mathbf{W}_k, [\mathbf{W}_k, \mathbf{P}'(t_{k-1})]\right] + \frac{1}{3!}\left[\mathbf{W}_k, [\mathbf{W}_k, [\mathbf{W}_k, \mathbf{P}'(t_{k-1})]]\right] + \ldots \tag{48}$$

The BCH expansion has been shown to have superior convergence properties as compared to a simple power series expansion.[18]

The Chebyshev expansion approach[259,544–546] has also been explored as an alternative to diagonalization in the construction of the time-evolution operator given by Eq. (44).[544,545,547–551] Since the Chebyshev expansion requires matrix eigenvalues within the spectral range of $[-1, 1]$, an approximate estimate of the upper and lower bounds of the eigenspectrum is used to achieve this mapping of the Hamiltonian matrix.[387,551]

Propagation schemes for correlated wave functions (*i.e.*, at the CI, CC, or ADC levels of theory) are oftentimes based on simple procedures, such as the fourth-order Runge-Kutta (RK4) integrator[22,47,49,50] (or RK4 augmented by a variational splitting[552] scheme[404]). However, the utility of more sophisticated integrators has also been explored in this context. For example, for linear and Hermitian expansions of the wave function, the real and imaginary parts of the wave function form a pair of conjugate variables that obey classical equations of motion, a fact that has inspired the development of high-order explicit symplectic integrators for general wave packet dynamics;[536,538,539] explicit symplectic integrators of this form have been applied to electron dynamics at the truncated CI level of theory.[36] Pedersen and Kvaal

have noted that the t- and λ amplitudes of CC theory form a pair of conjugate variables that obey complex classical equations of motion and have developed an implicit symplectic integrator tailored to that problem.[405] In addition, many applications[40,43–46] of time-dependent ADC theory employ the short iterative Lanczos (SIL) scheme.[553] In SIL, a tridiagonal subspace approximation to the Hamiltonian is constructed according to the Lanczos procedure, and the system is evolved according to dynamical equations associated with this approximate Hamiltonian. This approximation is only valid for short time intervals, after which the Lanczos procedure must be repeated to construct an updated approximation to the Hamiltonian. This SIL procedure has been extended to imaginary-time dynamics at the ADC level of theory,[432] where it has been demonstrated that imaginary time TD-ADC with SIL becomes competitive, in terms of computational effort, with frequency-domain ADC calculations.

3.3 Signal Processing

Real-time methods can be very efficient for computing spectra in molecules and materials with a high density of states as, in principle, an entire absorption spectrum can be computed from a single real-time simulation (see Sec. 4.1). In a nutshell, this requires computing the frequency-dependent response of the system via Fourier transforms (FT) of the dipole moment following interaction with a laser pulse with sufficient bandwidth to cover a spectral region of interest. In practice, a narrow-in-time pulse (or delta function) is typically used. Real-time methods, however, suffer from two main drawbacks: first, the spectra generated from the dipole moment do not contain any information about the molecular orbitals or excited states involved in each transition, which is typically how spectra are interpreted. Second, long simulation times are typically required to resolve the spectra via FTs, with denser spectra requiring longer simulations.

Many approaches exist for interpreting spectra generated via real-time methods. The simplest approach is to visualize each transition by exciting a particular mode with a narrow-band quasi-monochromatic field and plotting the deviation of the charge density (or other

observable) from the ground state.[18,95] This process, however, involves a separate simulation for each resonant peak, each of which requires a very long simulation times in order to selectively excite a particular mode. This makes it unsuitable for spectra with multiple nearby peaks. Alternatively, the FT of the deviation of the 3D time-dependent density from the ground state can be used to characterize each peak,[554] but this requires a FT at each point in space and involves either 4D data ($x, y, z, t \rightarrow x, y, z, \omega$) or reduction via integration over particular directions. Another method to extract orbital-resolved information involves projecting the wave function onto the ground-state molecular orbitals (MOs) in order to deconvolute the dipole moment into a sum of transitions between MO pairs.[69,555] In a density matrix TDHF/TDDFT framework, this procedure requires the projection of the density matrix and dipole operator onto the ground state MO basis:

$$\mathbf{P}^{\mathrm{MO}}(t) = \mathbf{C}^{\dagger}\mathbf{P}(t)\,\mathbf{C} \tag{49}$$

$$\mathbf{D}^{\mathrm{MO}} = \mathbf{C}^{\dagger}\mathbf{D}\mathbf{C}, \tag{50}$$

where $\mathbf{C}$ is the eigenvector matrix for the ground state Fock/Kohn-Sham matrix in the AO basis. Using these quantities, the time-dependent MO dipole contributions can be defined as

$$\mu_{ia,d}(t) = \mathbf{D}^{\mathrm{MO}}_{ia,d}\,\mathbf{P}^{\mathrm{MO}}_{ai,d}(t) + \mathbf{D}^{\mathrm{MO}}_{ai,d}\,\mathbf{P}^{\mathrm{MO}}_{ia,d}(t), \tag{51}$$

where $d = x, y, z$, and i, a are indices for the molecular orbitals, generally occupied and virtual, respectively. The total dipole given by

$$\mu_d(t) = \mu_{d,0} + \sum_{i=1}^{N_t}\sum_{a=i+1}^{N_t}\mu_{ia,d}(t), \tag{52}$$

where N_t is the number of steps in the simulation. The static contribution to the dipole is given by

$$\mu_{d,0} = \sum_{i=1}^{N_t}\mathbf{P}^{\mathrm{MO}}_{ii}\,\mathbf{D}^{\mathrm{MO}}_{ii,d}. \tag{53}$$

Note that here the matrices are assumed to be unitary (*i.e.*, no complex absorbing potential) and square (*i.e.*, no linear dependencies in the overlap matrix). For the more general case involving linear dependencies, see Ref. 555.

Since the FT is a linear operator, the total spectrum is simply the sum of the spectra for each of these transition dipoles, *i.e.*, in TDHF/TDDFT the spectrum is a sum of the contributions from all combinations of occupied→virtual MO pairs. Accordingly, the spectrum can be decomposed into orbital contributions, much like in linear response calculations (see Fig. 9). Note that $\mu_{ia}(\omega)$, which are not physical observables, can contain negative peaks

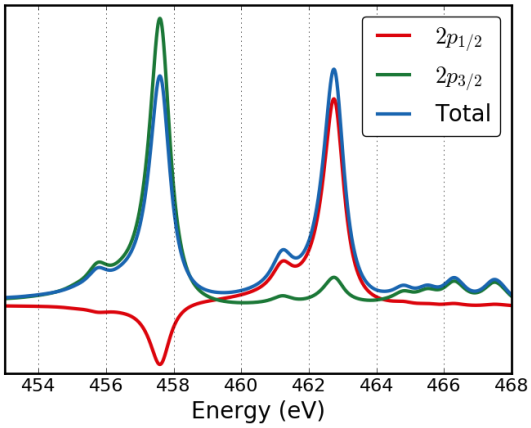

Figure 9: $L_{2,3}$ absorption edges for $TiCl_4$ modeled with B3LYP and the aug-cc-pVTZ basis set. The time evolving dipole was split into different spinor pairs and only contributions from the 2p orbitals are included. Adapted with permission from Ref. 98. Copyright (2018) American Chemical Society.

but the total dipole spectrum is guaranteed to be positive. The magnitudes of these features can be used to construct numerical weights of each MO pair to the peak by integrating over each peak (or via peak-fitting). These weights give a qualitative interpretation similar to linear response coefficients, which makes RT methods an essentially complete replacement to linear-response methods, albeit with more complicated and time-consuming data analysis. There are two important caveats, however. First, only optically active excitations can be measured, where as LR methods can capture selection or spin forbidden transitions. Secondly, this MO decomposition techniques are not valid for the case of strong-fields, where

Stark shifting of the orbitals makes the projection onto the ground state in Eq. (51) invalid.

The main drawback of real-time approaches over frequency-domain (eigenspectrum-based) methods is the long simulation times are often required to adequately converge a spectrum via a Fourier transform, *i.e.*, the Fourier "uncertainty principle". This issue can be especially problematic for high energy spectra with high spectral densities, such as those relevant to X-ray absorption. The simplest trick to improve spectral resolution is to preprocess the signal by damping and padding with zeros:

$$\tilde{\mu}(\omega) = \int_0^\infty dt\, m(t) e^{i\omega t} \tag{54}$$

$$m(t) = \begin{cases} \left[\mu(t) - \langle\mu\rangle\right] e^{-t/\tau}, & t \leq t_{\max} \\ 0, & t > t_{\max} \end{cases} \tag{55}$$

where $\langle\mu\rangle$ is either the dipole moment at $t = 0$ or the average, and τ is a damping parameter that corresponds to a phenomenolgical lifetime (linewidth) in the spectrum. This lifetime must be chosen to be small enough such that the discontinuity in Eq. (55) does not introduce ringing artifacts in the spectrum, which in practice can blur nearby peaks in a dense spectrum.

Fortunately, there are numerous alternatives to Fourier analysis that can be used to accelerate spectral convergence of time signals without resorting to broadending. Such harmonic inversion methods[556] include Prony's method, filter diagonalization,[557–559] Padé approximants,[560–562] and linear predictors.[563,564] These methods have applications in virtually all types of time-domain simulations ranging from classical electrodynamics,[561,562] to molecular dynamics,[564] to quantum dynamics.[555,557,559,565] There are advantages and disadvantages to each. As an example, filter diagonalization, fits the time signal to a sum of damped oscillations. This can rapidly converge spectra containing only a few dominant modes, but may have convergence issues for highly dense spectra. Padé approximants (discussed below) assume nothing about the line shape, but require a matrix inversion and can introduce

artifacts into the spectrum if the time signal is too short. These techniques are especially effective when used in conjunction with a dipole decomposition scheme, where each $\mu_{ia}(\omega)$ is computed separately using an accelerated transform, and the total spectrum is computed from the sum of these contributions. This strategy exploits the fact that each transition dipole is spectrally sparser than the total, which facilitates convergence of the accelerated transforms.

A good general purpose transform is the Padé approximant to the FT, which in a diagonal form consists of writing the discrete FT as a ratio of power series expansions:

$$\mu(z) = \sum_{k=0}^{M} c_k (z_k)^k = \frac{\sum_{k=0}^{M} a_k z^k}{\sum_{k=0}^{M} b_k z^k}, \tag{56}$$

where $M = N_t/2$, and $z_k = e^{-i\omega\Delta t}$, and the coefficients $\{c_k\} = \mu(t_k)$ are the discrete values of the input time signal. Thus, we have a linear system for the coefficients

$$\sum_{k=0}^{M} c_k z^k \sum_{m=0}^{M} b_m z^m = \sum_{k=0}^{M} a_k z^k \tag{57}$$

with $a_0 = c_0$ and $b_0 = 1$ chosen by convention. The unknown coefficients $\{a_k\}$ and $\{b_k\}$ are determined by solving the matrix equation:

$$\mathbf{G}\mathbf{b} = \mathbf{d} \tag{58}$$

where $\mathbf{G}$ is a $N_t \times N_t$ matrix with elements $G_{km} = c_{N_t - m + k}$, $\mathbf{d}$ is a column vector of length N_t with elements given by $d_k = -c_{N_t + k}$, and $\mathbf{b}$ is a vector of length N_t. The elements of $\mathbf{b}$ can be found via inversion of the $\mathbf{G}$ matrix, which has Toeplitz symmetry:

$$\mathbf{b} = \mathbf{G}^{-1}\mathbf{d} \tag{59}$$

The coefficients $\{a_k\}$ are then given by:

$$a_k = \sum_{m=0}^{k} b_m c_{k-m}, \quad k = 1, \ldots N_t \tag{60}$$

Once these coefficients have been determined, the FT can be computed using Eq. (56). Critically, since these coefficients are independent of frequency, the spectrum can be generated for an arbitrary spectral density. This is analogous to extrapolating the input signal to an arbitrarily long time. Although this procedure requires the solution of a linear equation [Eq. (57)] for each $\mu_{ia}(t)$, the cost of this procedure is modest, and, in practice, one can often compute a fully converged spectrum with 1/5 or less of a simulation time compared to a traditional FT (see Fig. 10). This approach is especially well-suited to X-ray absorption, since one needs only consider transitions from a limited set of occupied orbitals, much like orbital windowed linear response.[566]

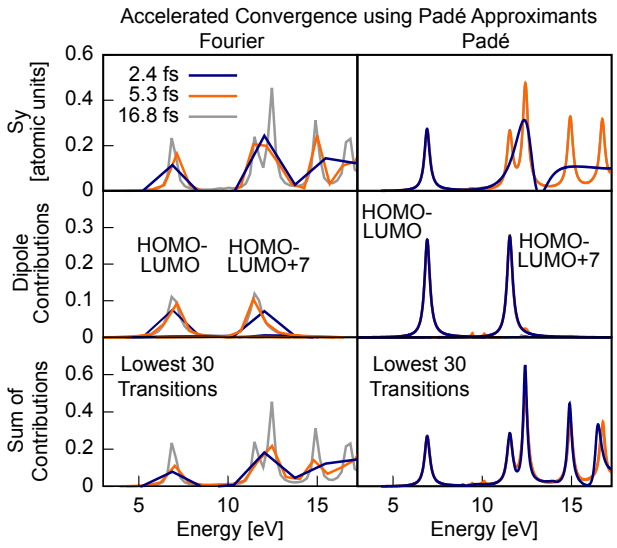

Figure 10: Convergence of the valence absorption spectrum for water using a conventional Fourier transform (FT; left) and Padé accelerated transition dipole scheme (PT; right) for various simulation times. PT of the total dipole converges roughly 3 times faster than the FT, and PT of the dipole contributions 7 times faster. Adapted with permission from Ref. 555. Copyright (2016) American Chemical Society.

4 Application of Real-Time Time-dependent Electronic Structure Methods

4.1 UV/Vis Spectroscopy

One of the biggest advantages of real-time electronic structure theory over solving for the lowest energy eigenstates is the ability to simulate the linear (UV-Vis) absorption spectrum of a system with a dense manifold of states. Using real-time electronic propagation, the entire energy spectrum is obtained after Fourier transform of the dipole moment (Sec. 3.3), providing the response of all electronic states that the system accesses via the applied perturbation. Real-time methods may be preferable over matrix eigenstate methods, and are particularly advantageous for metallic systems and clusters, where collective oscillations of the electrons are important for capturing plasmonic excitations.[144,145,151,567] However, for real-time propagation of the electron density with TDHF or TDDFT, the time-evolution of the electron density may be more cost efficient than solving for hundreds of excited states via a linear response matrix formulation that requires generating a matrix-vector product for all occupied-virtual orbital combinations, see Fig. 11.[85] The crossover point in computational cost will depend on the implementation, the requested number of states, the desired resolution of the spectrum, and time-step for numerical propagation.

The UV-Vis linear absorption spectrum can be obtained from a real-time simulation by Fourier transforming the field-free time-dependent dipole moment after perturbation by a weak, off-resonant perturbation (often an electric field applied as a delta function). To obtain oscillator strength values that are proportional to the linear response values, the dipole strength function $S(\omega)$ should be used

$$S(\omega) = \frac{1}{3}\mathrm{Tr}[\sigma(\omega)], \tag{61}$$

where $\sigma(\omega)$ is the absorption cross section tensor with diagonal elements that can be com-

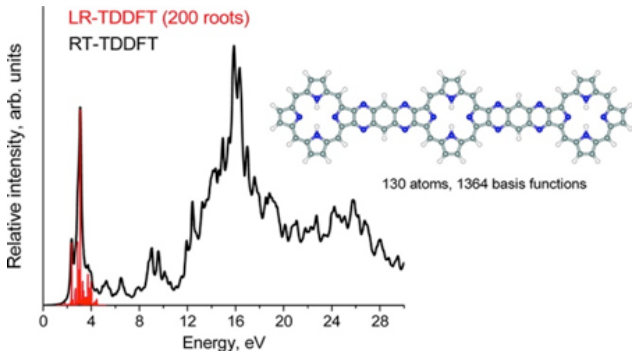

Figure 11: Absorption spectrum of $C_{72}H_{38}N_{20}$ (inset) calculated using the B3LYP functional in combination with the 6-31G(d) basis set. The linear response TDDFT spectrum contains 200 roots compared to the RT-TDDFT absorption spectrum from Fourier transform of the dipole moment. Adapted with permission from Ref. 85. Copyright (2015) American Chemical Society.

puted from the polarizability by

$$\sigma_{ii}(\omega) = \frac{4\pi\omega}{c}\mathrm{Im}[\alpha_{ii}(\omega)], \tag{62}$$

and

$$\alpha_{ii}(\omega) = \frac{\mu_i(\omega)}{E_i(\omega)}. \tag{63}$$

Here $\mu_i(\omega)$ and $E_i(\omega)$ are the Fourier transforms of the dipole moment and electric field for $i = x, y, z$, respectively.

Early applications of the real-time TDDFT method by Yabana and Bertsch computed the optical spectra for the benzene molecule[10] and for metallic lithium clusters.[8] A few years later, Ullrich and co-workers simulated the spectra and collision properties of sodium clusters,[230] with QM/MM UV-Vis spectral simulations of biological chromophores performed by Rubio and co-workers following closely after these early studies.[74,75] Real-time methods are now widely used for simulations of UV-Vis spectra for a variety of complex systems.[15,18,34,69,70,76–80,82,84–88,568,569]

4.2 X-ray Absorption Spectroscopy

Recent advances in synchrotron technology have greatly improved the temporal and energy resolution of X-ray photons, making X-ray absorption spectroscopy (XAS) an indispensable experimental technique in materials and chemical sciences. Excitation of core electrons to unoccupied bound orbitals or to the continuum allows XAS to probe element specific chemical processes that provide insights into the local electronic and binding environment.[570,571]

XAS K-, L-, and M-edge spectra are generated from photoexcitations of electrons in $n = 1$, $n = 2$, and $n = 3$ orbitals, respectively, where n is the principal quantum number. Because core electrons move close to the speed of light, relativistic effects play an important role in XAS. Scalar relativistic effects lead to contraction of core orbitals, which blue-shifts the entire XAS spectrum relative to a spectrum calculated with a non-relativistic Hamiltonian.[95,338,339,566,572–574] Spin-orbit coupling splits the degenerate $2p$ orbitals into $2p_{1/2}$ and $2p_{3/2}$ manifolds, giving rise to unique features in L-edge XAS spectra and a more complicated spectra at the M-edge. Therefore, electronic structure methods that include relativistic effects are needed to accurately describe XAS spectra, especially at the L- and M-edges. A uniform energy shift to spectra derived from non-relativistic calculations is often sufficient for describing the K-edge.

Many *ab initio* methods have been developed to model core excitations, and the majority of these approaches operate within the frequency domain. K-edge spectra have been obtained with linear response TDDFT (LR-TDDFT),[95,338,566,574–577] algebraic-diagramatic construction,[578–580] linear-response density cumulant theory,[581] coupled-cluster theory using both the complex polarization propagator[582,583] and the EOM-CC formalisms,[574] and restricted active space (RAS) multiconfigurational methods.[584,585] L-edge XAS spectra can be computed using RAS with perturbative spin-orbit coupling[586,587] and the more recently developed relativistic two-component LR-TDDFT.[340]

In the time-domain, non-relativistic RT-TDDFT[96] and time-dependent EOM-CC[49] have been applied to compute molecular K-edge XAS. Recently, time-dependent variational four-

and two-component relativistic TDDFT methods were developed to model the XAS L-edge spectra.[97,98] Two-component variational relativistic real-time methods are an attractive alternative to their four-component analogues due to the balance of the computational cost and theoretical accuracy offered by the former. For example, in work by Kasper *et al.* the $L_{2,3}$ spectra of $SiCl_4$, obtained using the real-time X2C method, were in excellent agreement with experimentally obtained spectra (Fig. 12) and similar in quality to those calculated at the four-component level.[98]

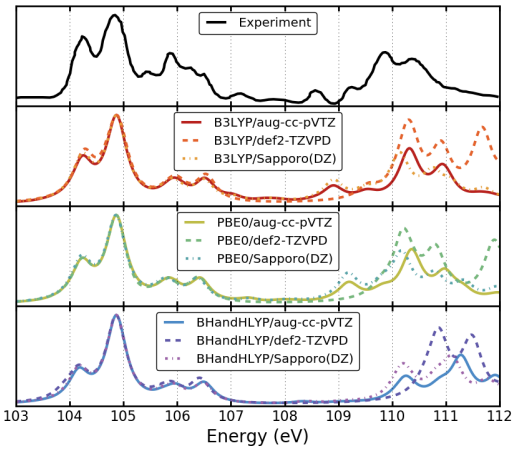

Figure 12: Two-component relativistic RT-TDDFT modeled $L_{2,3}$ absorption edges for $SiCl_4$, compared to experimental spectrum.[588] Adapted with permission from Ref. 98. Copyright (2018) American Chemical Society.

Finally, simulations of X-ray absorption can be challenging for systems with a high density of states, as finite basis set effects can introduce unphysical "intruder peaks" into XAS spectra. These features arise from transitions from valence orbitals to very high lying virtual orbitals, which should have zero lifetime since they reside within the continuum. Such peaks are unlikely to occur for smaller molecules, but are unavoidable for larger systems. This issue is avoided if using a large simulation box with a grid or planewave basis, provided an appropriate boundary condition is used (*e.g.*, complex absorbing potential). For more details regarding open TDDFT systems, see review by Rubio and coworkers.[589] For atom-centered basis set methods, however, it is usually more efficient to instead give the virtual states a

phenomenological lifetime[109] to filter the intruder peaks from the spectrum. This technique has been successfully applied to resolve the K-edge XAS spectrum of α-quartz (Fig. 13).[96]

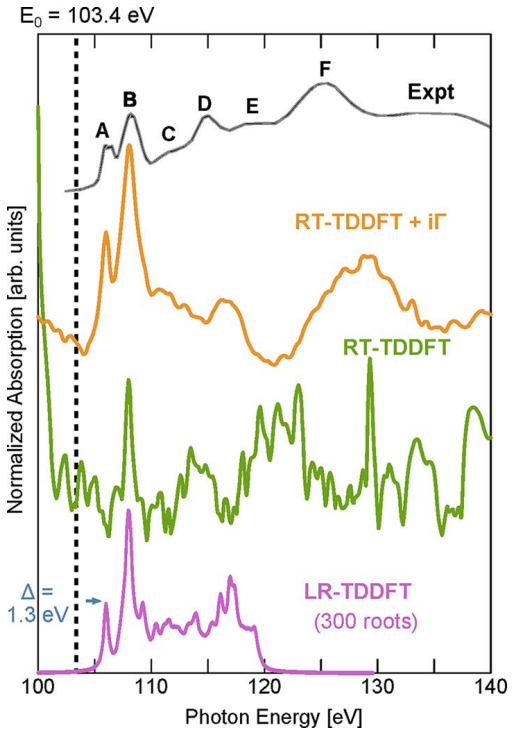

Figure 13: Computed real-time TDDFT K-edge XAS of α-quartz with (orange) and without (green) a complex absorbing potential, along with corresponding linear response TDDFT (purple) and experimental data. Adapted with permission from Ref. 96. Copyright (2015) American Chemical Society.

4.3 Excited State Absorption and Emission

There are numerous methods for probing excited state dynamics, such as transient absorption spectroscopy where modulations in the absorption as a function of time delay between a pump and a probe laser pulse encode the dynamics in the system.[590] Although conceptually simple, one of the main challenges with time-resolved experiments is the ability to characterize overlapping transient spectral features within an energy range. This problem grows with increases in system size and complexity of the electronic structure. From the standpoint of theory, the ability to simulate the excited-state dynamics and extract the corresponding

excited-state absorption (ESA) spectrum is of great value, allowing one to interpret and predict experiments. The success of such a procedure obviously hinges on the accuracy of the theoretical approach.

Currently, the primary approach to compute ESA is via response theory.[591,592] Within linear response (LR) theory, the poles of the response function yield the excitation energies of the system, and transition moments between excited states can be obtained from the second-order residues of the quadratic response function. Together, these quantities can be used to evaluate the ESA of a molecular system. The first-order residues of the quadratic response function can also be used to obtain the two-photon absorption. In spite of these advantages, quadratic response theory is a numerically prohibitive approach for the computation of ESA in large molecular systems with high densities of states as the excited states have to be treated individually, which can become computationally infeasible when seeking the full spectrum of the system. An alternative approach is to reformulate the problem by calculating the linear response from an excited state reference. Formally, this approach is equivalent to the quadratic response with respect to the ground state. However, this relationship only holds within an exact treatment (namely, full CI[591]) and not for approximate theories.

RT-TDDFT has been shown to be an efficient and appealing method for computing spectra of systems with high densities of states.[83,85] It has also been intuitively used in the context of pump-probe experiments by De Giovannini and co-workers,[82] where an electric field is first applied to pump the system to a target excited state and a second electric field is used to probe the response of that excited state. The outstanding question with this approach, however, is whether the probe pulse is actually interacting with the intended target excited state, since resonant excitations are problematic and challenging to achieve with RT-TDDFT.[82,84,246,261–263,267,593,594]

Fischer and co-workers[86] have proposed an alternate approach that circumvents the RT-TDDFT-specific challenges associated with resonant excitations but that still relies upon RT-TDDFT to probe the response of the target excited state. One first performs a LR-TDDFT

gradient[595,596] calculation to compute the density matrix of the excited state of interest. This serves as the initial superposition state for a subsequent RT-TDDFT calculation, which then effectively yields the response of the excited state of interest. In order to preserve the exact structure of this approach, an exact exchange-correlation kernel, which is a functional of the initial state and complete history of the density, would be needed.[597] However, in practice, approximate exchange-correlation functionals within the adiabatic approximation have to be used. Maitra and co-workers have formally analyzed the errors in the propagation of initial states that derive from these two key approximations.[297]

Despite the use of exchange-correlation approximations that are, in general, designed for the ground state, this strategy of seeding RT-TDDFT simulations with LR-TDDFT densities has been shown to reproduce the ESA features in a number of molecular systems, including zinc phthalocyanine[87] and tetrapyridyl porphyrins.[299] Li and co-workers have also combined RT-TDDFT with Ehrenfest dynamics simulations in order to investigate excited-state lifetimes.[134,135] Parkhill and co-workers[93] also developed a combined RT-TDDFT/nonadiabatic-relaxation model[20] to simulate the transient absorption spectra of pyrazole and a GFP-chromphore derivative. Lopata and co-workers alternatively used a constrained DFT initial state to compute transient X-ray absorption for pumped molecules, which showed a decreased in absorption and a blue shift in the frequency with increasing electron density around the absorbing atom.[598] Recently, Ghosh and co-workers[599] have also reported simulations of ESA with the semiempirical RT-INDO/S approach (see Sec. 2.2) that compares well with RT-TDDFT.

4.4 Charge Transfer, Plasmon Excitations, and Exciton Dynamics

Charge transfer, which we here consider as a process wherein electrons transfer between states or between regions of space, has central importance in biochemistry, in photosynthesis, in the generation and storage of electricity, as well as in electro-optic activity (*i.e.*, photovoltaic cells, fuel cells, organic chromophores for use in optical fibers and light-emission diodes etc.).

Real-time electronic structure methods can explicitly model time-resolved, nonperturbative charge-transfer and exciton dynamics in donor-acceptor or dye molecules applicable to the development of solar cells,[18,81,136,142,148,390,391,600,601] molecular conductance,[121] energy transfer between chromophores,[568] and plasmon behavior in noble metal nanowires and nanoparticles.[144,145,388] Here we first focus on simulations of charge transfer with fixed nuclei, then highlight some applications where the nuclear motion is key to driving the charge-transfer dynamics.

Within the RT-TDDFT method, inaccuracies in charge transfer can be traced both to the approximate exchange-correlation functional and the adiabatic approximation. Errors due to the approximate exchange-correlation functional affect excitation energies and charge transfer rates. Local and semi-local density functionals yield a very poor description of charge-transfer excitations, but improved excitation energies are often predicted with long-range correction to the exchange functional.[325,602,603] However, errors in charge transfer due to the adiabatic approximation are much more challenging to remedy. When a resonant field is applied to the ground state to induce charge transfer to the resonant excited state for a model double-well potential for two electrons, RT-TDDFT within the adiabatic approximation qualitatively fails,[140] see Fig. 14. However, another study suggests that the charge transfer from an excited state to the ground state might be more accurately captured by the adiabatic approximation.[265] For a detailed explanation of the impact of the adiabatic approximation on the charge-transfer dynamics of model systems, see work by Maitra as discussed in references 140, 265, and 252.

Despite the poor behavior of RT-TDDFT within the adiabatic approximation simulating the charge transfer of model systems, it is widely used for simulating the charge transfer of more complex systems such as organic materials and metal nanoparticles. In 2011, Chapman *et. al.* simulated RT-TDDFT ultrafast charge-transfer dynamics in a photoexcited fullerene complex.[136] A charge-transfer event was observed following the photoexcitation of C_{60}:DMA (DMA=N,N-diethylamine) where the initial electron-hole pair is localized in

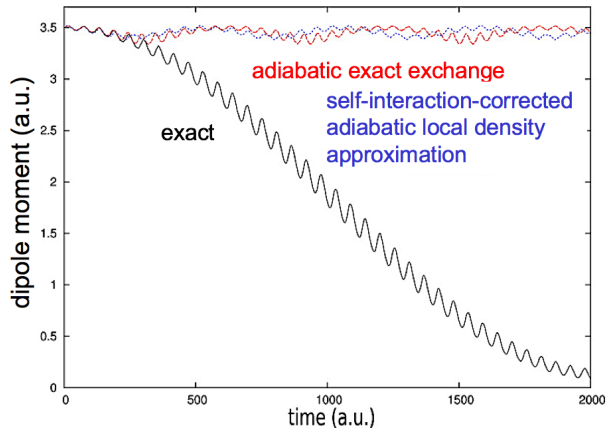

Figure 14: Absolute values of dipole moments for the charge transfer from the ground state between closed-shell fragments for exact propagation (solid black line), RT-TDDFT with adiabatic exact exchange (dashed red line), and RT-TDDFT with the self-interaction-corrected adiabatic local density approximation (dotted blue line). The calculations were performed in the presence of a resonant field for a model double well potential with two electrons in one dimension. Adapted with permission from Ref. 140. Copyright (2013) American Chemical Society.

fullerene (Fig. 15). This charge transfer can potentially give rise to a long-lived photogenerated electron-hole pair. A subsequent study, using RT-TDDFT with a time-dependent polarizable model,[138] has shown that solvated ligand-to-fullerene charge transfer is enhanced relative to vacuum due to solvent reorganization of excited electronic states and solvent-solute coupling.[139] A follow up real-time time-dependent DFTB study was performed by Oviedo and Wong on the same system using explicit toluene and water solvent molecules but different system conditions.[148]

Using real-time time-dependent DFTB, Sanchez and co-workers have studied the nonequilibrium charge injection mechanism from both catchetol and cresol dye molecules to a TiO_2 nanoparticle (Fig. 16).[390,391] The simulations of a Type II photo-injection mechanism showed direct promotion of an electron from the dye to the first unoccupied level of the conduction band of the nanoparticle during the application of the resonant field. The evolution of the molecular orbital populations showed an exchange from the highest occupied molecular orbital of the dye to a manifold of high-energy orbitals from the conduction band of the

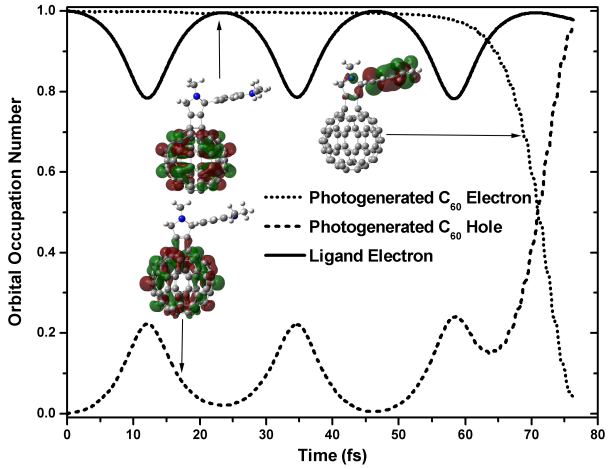

Figure 15: Time evolution of photogenerated electron (dotted line) and hole (dashed line) localized on C_{60}, and an electron localized on the DMA ligand (solid line) following a fullerene-localized excitation. Adapted with permission from Ref. 136. Copyright (2011) American Chemical Society.

nanoparticle.

RT-TDDFT electronic dynamics has also been applied to study excitonic and plasmonic dynamics in metal nanowires and metal nanoparticles. Ding *et. al.* illustrated the electronic dynamic characteristics of a molecular plasmon in silver nanowires from the perspective of a coherent multi-electron oscillation.[144] This work was later extended to the investigation of the exciton transfer rate and diffusion length driven by the pure dephasing mechanism in a silver nanowire array (Fig. 17).[145] The team of Ilawe, Oviedo, and Wong demonstrated that highly long-range electronic couplings in a multiparticle plasmonic nanoantenna system were responsible for electronic excitation transfer(Fig. 18),[388] finding that the common nearest-neighbor Förster resonance energy transfer model is inadequate for accurately characterizing electronic excitation transfer. Real-time TDCI calculations have also been used to model rapid dephasing of plasmon-like excitations in model systems[36] that could be interpreted as electron thermalization.[604]

Using RT-TDDFT with Ehrenfest dynamics, Meng and Kaxiras investigated electron and hole dynamics upon photo-excitation in dye-sensitized solar cells made from three model

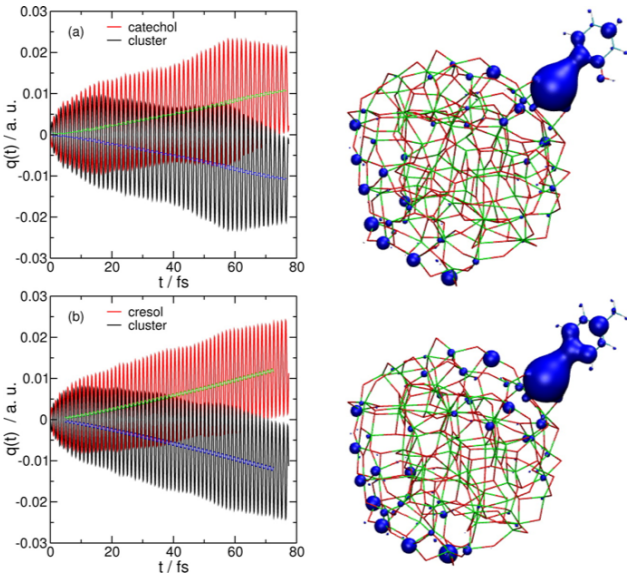

Figure 16: Changes in Mulliken charges with respect to their ground state values as a function of time for a dye chromophore and TiO_2 nanoparticle together with the plots of the spatial distribution of electrons involved in the optical excitation during the application of resonant electric field. Adapted with permission from Ref. 391. Copyright (2012) American Chemical Society.)

dyes interfaced with a TiO_2 semiconductor surface.[600] The amount of charge transfer was determined by the integral of excited electron (hole) density projected onto the TiO_2 orbitals. They found that after excitation, the electron gradually delocalizes and is injected into the semiconductor TiO_2 region, on a time scale of 125-175 fs, whereas the hole does not penetrate through the interface region. The hole injection time is much longer than the time for electron injection, and hole injection only starts after the excited electron has been completely injected into the TiO_2(Fig. 19).[600] Ehrenfest dynamics on the RT-TDDFT surface has been used to simulate the charge transfer in a light-harvesting molecular triad with good comparison with experimental time scales,[141] as well as charge delocalization and transfer in an organic polymer-fullerene photovoltaic system,[143] with both studies showing that vibronic motion is key to driving the charge transfer dynamics. When exciton-phonon coupling is considered in RT-TDDFT Ehrenfest dynamics, molecular vibrations have been shown to induce molecular plasmon decay and transfer.[149,567] Petrone and co-workers have applied

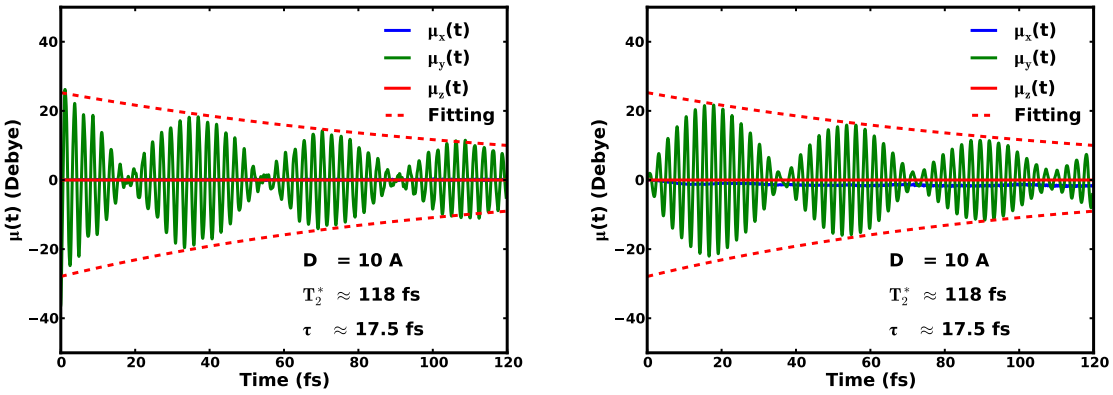

Figure 17: Time evolving dipole moments (Cartesian components) in the first (left) and second (right) silver nanowire at an interchain separation distance of 10.0 Å. Adapted with permission from Ref. 145. Copyright (2015) American Chemical Society.

RT-TDDFT to study the dynamics of photoexcited charge carriers in ladder-type donor-acceptor block copolymers.[142] Shortly after the formation of the exciton, the electron and hole densities dissociate to yield a pseudo charge-separated state. Based on the observed orbital pathways involved in the short-time dynamics, p and n type conductivity have been identified in different block copolymers. When the charge carrier dynamics is coupled to molecular vibrations, the dynamical evolution of the polaron pair can be observed. Donati and co-workers have applied RT-TDDFT Ehrenfest dynamics and wavelet analysis to investigate the formation of polaron pairs in a thiophene oligomer.[605] The formation of a polaron pair is modulated by the out-of-plane motion of the polymer backbone dynamics with an observed lifetimes of ∼10 fs.

4.5 Nonlinear Properties and Multi-Dimensional Spectroscopy

One of the great advantages of real-time approaches is their ability to model the nonlinear response of a system to electromagnetic radiation. These techniques allow one to consider pulse shapes and field strengths representative of those applied in experimental settings. Simulations thus go beyond the perturbative regime, capturing all orders of response simultaneously. As a result, real-time time-dependent approaches have emerged as the a key

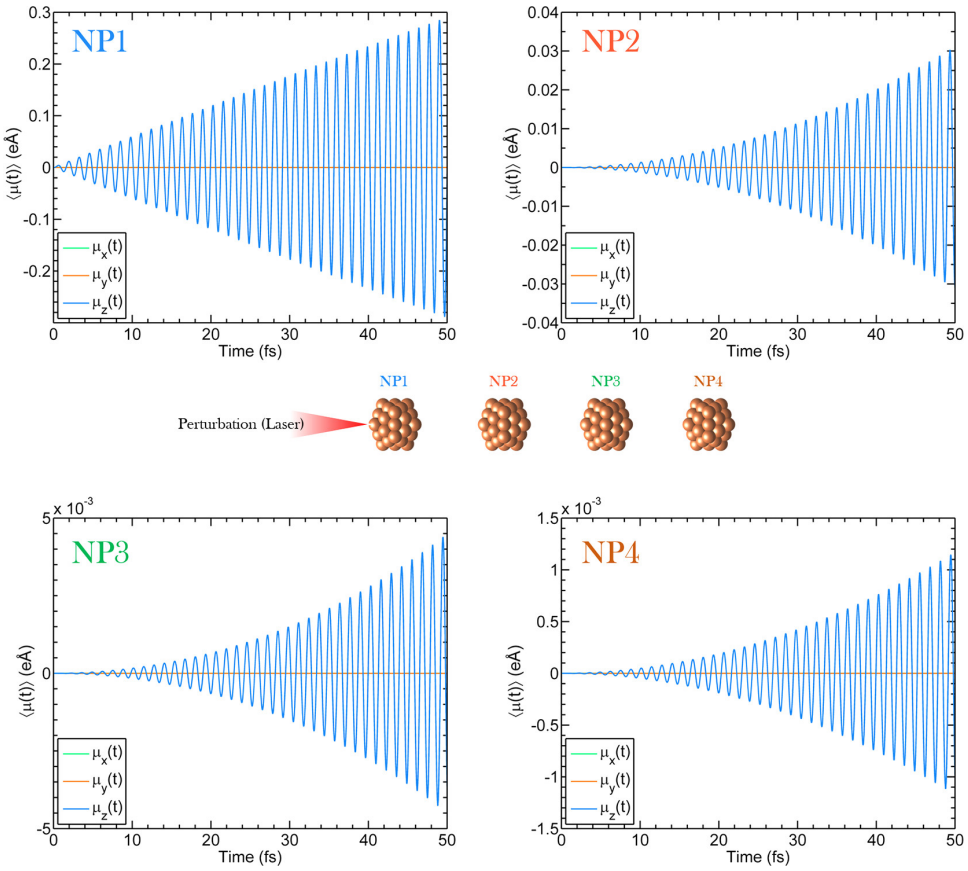

Figure 18: Time-dependent dipole moments induced in the four nanoparticles of a plasmonic nanoantenna system upon optical excitation of nanoparticle 1 (NP1) with a sinusoidal electric field perturbation. The induced dipole moments in the nanoparticles are indicative of the electronic excitation transfer in the multiparticle plasmonic nanosystem. Adapted with permission from Ref. 388. Copyright (2017) American Chemical Society.

method for describing highly nonlinear processes and properties.

High harmonic generation (HHG), arising from the interaction between molecular (hyper)polarizabilities and an external field, occurs at integer multiple frequencies of the driving frequency of the laser that illuminates the medium.[606,607] As such, HHG can supply high-energy attosecond pulses for ultrafast spectroscopy experiments.[606–609] From the computational point of view, the HHG power spectrum can, in principle, be extracted from the time-evolution of the dipole moment,[610] after the system is perturbed by a monochromatic external field. One challenge in extracting such nonlinear response properties from real-time electronic structure simulations is that all orders of response are combined in one time sig-

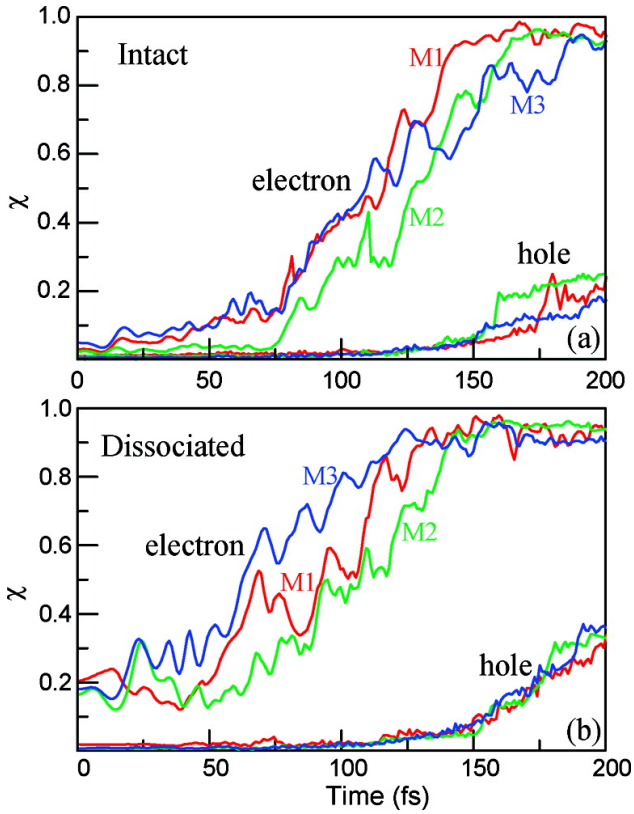

Figure 19: Comparison of electron and hole dynamics of three model dyes of increasing size, in intact and dissociated forms, representing the injection probability from the dye to the TiO_2 nanocrystal surface. Adapted with permission from Ref. 600. Copyright (2010) American Chemical Society.

nal, which is apparent from the expansion of the dipole moment interacting with an external monochromatic field, $\mathbf{E}(t) = \mathbf{A}\cos(\omega t)$,

$$\mu_i(t) = \mu_i^0 + \sum_j \mu_{ij}^{(1)}(t)A_j + \sum_{jk} \mu_{ijk}^{(2)}(t)A_jA_k + \sum_{jkl} \mu_{ijkl}^{(3)}(t)A_jA_kA_l + \cdots \tag{64}$$

$$\mu_{ij}^{(1)}(t) = \alpha_{ij}(-\omega;\omega)\cos(\omega t) \tag{65}$$

$$\mu_{ijk}^{(2)}(t) = \frac{1}{4}\left[\beta_{ijk}(-2\omega;\omega,\omega)\cos(2\omega t) + \beta_{ijk}(0;\omega,-\omega)\right] \tag{66}$$

$$\mu_{ijkl}^{(3)}(t) = \frac{1}{24}\left[\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)\cos(3\omega t) + 3\bar{\gamma}_{ijkl}(-\omega;\omega,\omega,-\omega)\cos(\omega t)\right] \tag{67}$$

Here, ω and $\mathbf{A}$ are the frequency and the amplitude vector of the field, respectively, and $\alpha(-\omega;\omega)$, $\beta(-2\omega;\omega,\omega)$, and $\gamma(-3\omega;\omega,\omega,\omega)$ are the frequency-dependent (hyper)polarizabilities,

which give rise to the linear response and second- and third-harmonic generations. $\beta(0;\omega,-\omega)$ and $\gamma(-\omega;\omega,\omega,-\omega)$ also appear in the dipole expansion; these terms are related to optical rectification and degenerate four-wave mixing, respectively. Equation (64) suggests that one can use some signal processing techniques to extract frequency-dependent (hyper)polarizabilities from the time-evolving dipole moment.

When the field strength is small, one can obtain linear and nonlinear molecular response properties by ignoring the higher order contributions. Chen *et al.*[611] used the filter diagonalization approach to extract the first hyperpolarizability tensor. Rehr *et al.*[14] obtained second-order response properties by applying the finite-field method in conjunction with a quasimonochromatic approximation to RT-TDDFT, driven by a Gaussian-enveloped external field. Bandrauk *et al.* resolved the high-order harmonic spectra of atomic hydrogen by numerical solving the time-dependent Schrödinger equation, with a Hamiltonian augmented by a linearly polarized laser pulse.[612] TD-CI has also been applied to compute the (non)linear properties of small molecules, and it has been shown that TD-CI based techniques outperform RT-TDDFT in the prediction of HHG spectra if higher order excitation operators are included in the TD-CI expansion.[29,30,37,38,392,393]

The most general approach for computing frequency-dependent polarizabilities and hyperpolarizabilities via real-time simulations was developed by Ding *et al.*[99] Individual orders are separated into independent expressions which are free from higher order contributions up to the fourth order. Using time-evolving dipole moments from just a few short simulations, one can determine polarizabilities, and first and second hyperpolarizabilities in good agreement with those calculated using response theory. For example, Fig. 20 shows the time-evolutions of the linear and nonlinear properties of the paramagnetic BeH molecule computed using TD-CI. The first- and second-order dipole responses show excellent agreement between the real-time signals and analytical expressions, and there are noticeable deviations, arising from the absence of higher-order corrections, of the real-time simulations from the truncated analytical expression for the third-order dipole response.

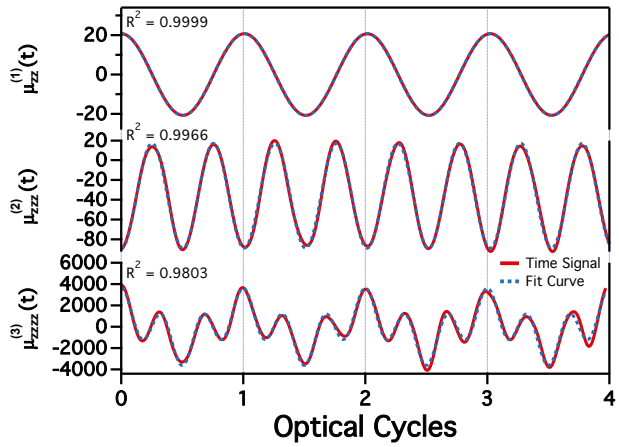

Figure 20: Time-evolutions of the first-, second-, and third-order responses of BeH modeled with the TD-CIS/6-31+G(d) level of theory. The fit curves and their R^2 values overlay the simulation data. Adapted with permission from Ref. 38. Copyright (2018) Elsevier.

The accuracy of calculated (hyper)polarizability tensors is sensitive to the approximate field-matter interaction and the quality of basis set.[393,613] The field-matter interaction is usually treated within the electric-dipole approximation in the length gauge form. Some have suggested the use of alternative gauges (*i.e*, the velocity or acceleration gauge) to improve the description of the power spectrum in finite basis sets.[614–616] Simple $\cos^2$ or $\sin^2$ pulse envelopes are often used to 'dress' the perturbing field,[37,393] but even the field envelope can be tailored to enhance or damp specific harmonics.[617] Additional diffuse functions have been shown to improve the quality of (hyper)polarizabilities extracted from the time-domain approach.[99] For TD-CI, recent work by Lestrange, *et. al.* suggests that accurate nonlinear properties may require CI expansions that span most of the full CI configuration space. Specifically, as much as 2/3 of the full CI space is needed to obtain nonlinear properties accurate to within 5% of the exact (full CI) values.[38]

Work by Konecny *et. al.*[100] has shown that nonlinear properties can be significantly affected by relativistic effects. In calculations on a $W(CO)_5py$ complex, it was found that the dominant component of the second harmonic generation tensor was shifted by about 35% compared to that obtained from a non-relativistic method. Importantly, this work also

demonstrated that these higher-order properties can still be captured using approximate relativistic methods such X2C, with almost no loss of accuracy compared to fully relativistic 4-component Dirac calculations.

Multidimensional nonlinear spectroscopy[618–621] has become an indispensable tool for probing molecular structure, structural/electronic dynamics, energy transfer, and chemical reactions and the nature of excited state correlations. Useful information on the couplings between molecular degrees of freedom (spin, vibrational, or electronic) can be obtained by disentangling a congested one-dimensional spectrum into n-dimensions by scanning the interpulse delays. Spreading the linear absorption spectrum in multidimensions allows one to monitor and unravel the dynamics of, *e. g.*, intermolecular energy transfer processes in molecular aggregates. Intense ultrashort pulses are needed to monitor subfemtosecond electronic processes. These signals are commonly simulated by the sum-over-states (SOS) technique, in which the signal is calculated from electronic eigenstates and the coupling to electric fields, which is treated perturbatively under the dipole approximation. Nonlinear signals are calculated from corresponding transition dipoles, transition energies, and dephasing rates. An alternative approach for computing multidimensional signals is to simulate the electronic dynamics by propagating the one-electron reduced density matrix, driven by multiple electric fields. In this way, one avoids having to explicitly calculate many electronic eigenstates. Nonlinear effects induced by intense external fields are automatically accounted for because the incoming fields are treated in a non-perturbative way. These effects can, in principle, be calculated with the wide range of real-time electronic structure methods discussed in this review.

In a novel application of real-time electronic structure methods, Mukamel and co-workers have recently used RT-TDDFT to implement a phase cycling[622] scheme to extract desired nonlinear signals from a finite set of RT-TDDFT simulations for multiple incoming fields with variable phases. The scheme was implemented for four-wave mixing signals. RT-TDDFT simulations were performed to compute XUV and X-ray nonlinear signals for the

CO molecule and were found to be in qualitative agreement with CASSCF sum-over-states (SOS) calculations.

In other recent nonlinear studies that have demonstrated the robustness of RT-TDDFT, Bruner and co-workers[298] reported a study of charge migration dynamics following nitrogen 1s ionization of nitrosobenzene comparable to that of post-Hartree-Fock wave function based methods, Cho and co-workers[623] simulated the electronic dynamics after a valence or core ionization in the glycine-phenylalanine dipeptide and calculated the resulting time-resolved X-ray diffraction signals, Bruner and co-workers[624] computed the resonant X-ray sum-frequency generation (SFG) signals of the oxygen and fluorine K-edges in acetyl fluoride and, more recently, Nascimento and co-workers have explored how subtle changes can be probed in nearly indistinguishable intramolecular chemical environments.[625]

In a nutshell, real-time propagation of the reduced single-particle density matrix, driven by external fields, allows for the simulation of multidimensional nonlinear signals in a non-perturbative manner, beyond perturbative response-based SOS methods. In addition, complex ultrafast nonlinear dynamics can also be simulated sufficiently accurately.

4.6 Spin and Magnetization Dynamics

Model Hamiltonians parametrized by experimental or empirical data have historically been the method of choice for modeling spin dynamics. These methods have succeeded in describing fundamental spin physics, but they are incapable of simulating the time-evolution of the spin-dependent wave function or density matrix. A fully time-dependent first-principles electronic structure description is needed to simulate spin dynamics driven by strong spin non-collinearity, spin-orbit coupling, or by interactions with intense external electromagnetic fields. In 2014, Ding *et. al.* reported the first fully *ab initio* real-time treatment of spin dynamics driven by an external magnetic field using a non-collinear two-component method.[68]

The one-electron Pauli Hamiltonian including magnetic field effects can be expressed as

$$h^{\text{Pauli}} = \hat{h}_0(\mathbf{r}) + \frac{1}{2}(\boldsymbol{\sigma} - i\mathbf{r} \times \boldsymbol{\nabla}) \cdot \mathbf{B} + \frac{1}{8}(\mathbf{B} \times \mathbf{r})^2, \tag{68}$$

where $\hat{h}_0(\mathbf{r})$ is the one-electron Hamiltonian in the absence of the external field. The second term accounts for spin and orbital Zeeman interactions, and the third term, which is quadratic in the strength of magnetic field, is the diamagnetic contribution. Figure 21 shows that, with this treatment, the magnetization of each spin precesses about the magnetic field at each lattice point.

Although the orbital Zeeman and the diamagnetic terms are relatively small and do not directly affect the spin dynamics, they play an important role in diamagnetism, especially in the presence of a strong magnetic field.[68,626–630] In the initial work by Ding, only the spin Zeeman term was considered in the spin-blocked core Hamiltonian in a real-time non-relativistic two-component framework,

$$\mathbf{h}' = \begin{pmatrix} \mathbf{h}'^{\alpha\alpha} & \mathbf{h}'^{\alpha\beta} \\ \mathbf{h}'^{\beta\alpha} & \mathbf{h}'^{\beta\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{h}'_0 + \frac{1}{2}B_z\mathbf{S} & \frac{1}{2}(B_x - iB_y)\mathbf{S} \\ \frac{1}{2}(B_x + iB_y)\mathbf{S} & \mathbf{h}'_0 - \frac{1}{2}B_z\mathbf{S} \end{pmatrix} \tag{69}$$

The orbital Zeeman and the diamagnetic contribution were later included by Sun *et. al.* in the two-component Hartree-Fock approach using the Pauli matrix representation.[631]

The non-relativistic spin-field coupling developed in Refs. 68 and 631 relaxes the standard spin constraints, allowing electrons to respond to external magnetic fields. However, the extension of real-time methods to the relativistic Dirac equation is critical for accurate treatment of spin and magnetization dynamics of transition metal and heavy element complexes. Spin-spin and spin-orbit couplings, which can connect different spin states, cause spin-forbidden processes to become weakly allowed, leading to features in electronic absorption spectra that are absent in non-relativistic treatments. For example, the ns^2 to ns^1np^1 transitions of group 12 atoms have been studied using relativistic RT-TDDFT at both the

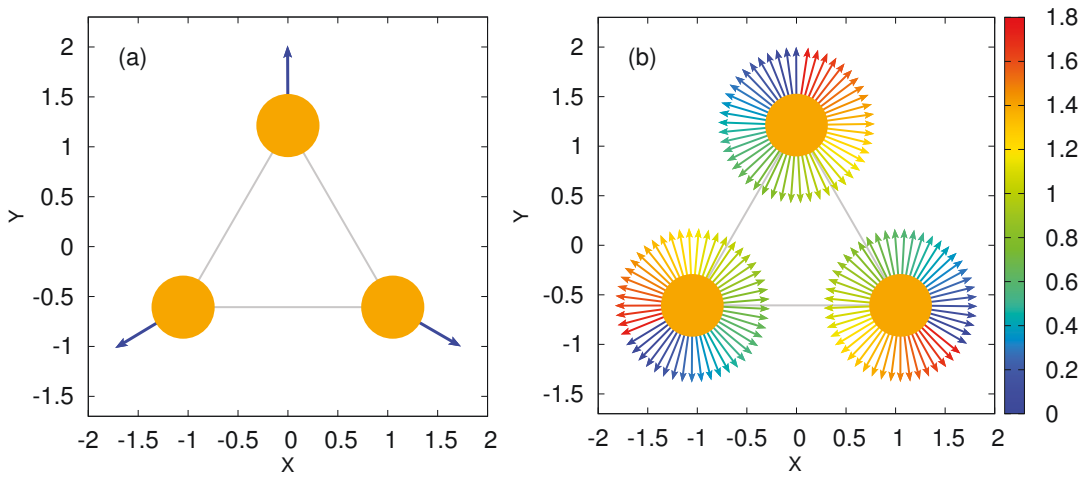

Figure 21: (a) the initial spin magnetization of an equilateral triangle formed by three Li atoms, Li_3, with an Li–Li bond length of 2.10 Å and (b) the time evolution of the spin magnetization in a uniform magnetic field that is applied perpendicular to the plane of the trimer ($B_z = 8.5 \times 10^{-5}$ a.u. [$\sim$20 Tesla]). The time-evolution is represented as the progression of coloration in units of picoseconds, and the magnetization vector is represented in units of Bohr magneton. Adapted with permission from Ref. 68. Copyright (2014) American Institute of Physics.

four-component and two-component levels of theory.[70,100] The $^3P_1$ state is weakly allowed by the presence of the spin-orbit coupling operator and a nonzero transition moment is observed. This effect becomes more important moving down the periodic table from Zn to Cd to Hg, as the magnitude of the relativistic corrections grows more prominent.

4.7 Electronic Circular Dichroism and Magnetic Circular Dichroism

Electronic circular dichroism (ECD) models the differential absorption of left- and right-handed circularly polarized light, proving a useful tool for determining the absolute configuration of chiral enantiomers.[632] RT-TDDFT has been developed for computing ECD spectra of molecules using grid-based[89,90] and atomic-orbital-based[92] simulation protocols. The ECD signal is determined by the isotropic rotatory strength for the transition between states $|\psi_n\rangle$

and $|\psi_j\rangle$, which is given by[632]

$$R_{jn} \equiv \mathrm{Tr}\left[\mathrm{Im}\left(\langle\psi_n|\boldsymbol{\mu}|\psi_j\rangle\langle\psi_j|\boldsymbol{m}|\psi_n\rangle\right)\right]. \tag{70}$$

where $\boldsymbol{\mu} = \mathbf{r}$ and $\boldsymbol{m} = \frac{-i}{2c}(\mathbf{r} \times \boldsymbol{\nabla})$ are the electric dipole and magnetic dipole operators, respectively (in the length gauge), and c is the speed of light.

The most common methods for computing the ECD spectrum are based on the response formalism,[633–642] or the complex polarization propagator technique.[643,644] In the time domain, if an electric dipole field is applied as a perturbation, the time-dependent magnetic dipole obtained from the electronic dynamics is required for simulating ECD. The Fourier transform of the time-dependent magnetic dipole gives the rotatory strength (Eq. (70))[89,92] as

$$R(\omega) = \sum_{j\neq n} \delta(\omega - \omega_{jn}) R_{jn} = \mathrm{Tr}\left[\frac{1}{\pi}\mathrm{Re}\frac{m_\alpha(\omega)}{\kappa_\beta}\right], \tag{71}$$

where κ is the magnitude of the electric field, and the labels α and β denote Cartesian coordinates. LR and RT-TDDFT methods have been shown to give essentially the same results in the weak field limit (*e.g.*, Fig. 22), though RT-TDDFT is able to compute the whole ECD band spectrum with only three simulations of the electron dynamics.

The moment-based TD-EOM-CC approach[22,49] described in Sec. 2.4 is applicable to any type of linear electronic spectroscopy, including ECD.[52] In this formalism, the ECD spectrum can be extracted from the Fourier transform of the electric-dipole–magnetic-dipole and magnetic-dipole–electric-dipole correlation functions (for specific expressions, the reader is referred to Ref. 52). One important distinction between the evaluation of linear absorption and ECD spectra at the TD-EOM-CC level of theory is that, in the latter case, the computational effort is doubled, as both the electric-dipole–magnetic-dipole and magnetic-dipole–electric-dipole correlation functions must be evaluated. This complication arises because the similarity-transformation of the Hamiltonian and other operators destroys their hermiticity. For spectroscopies like ECD that are defined by multiple operators (*i.e.*, the electric and

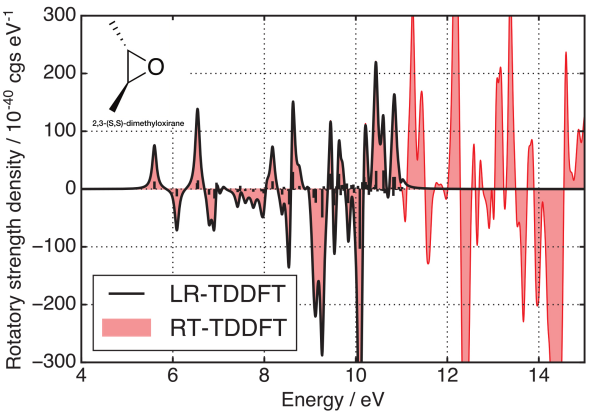

Figure 22: ECD spectra of 2,3-(*S*,*S*)-dimethyloxirane (DMO) computed at the PBEPBE/6-311+G** level of theory. Adapted with permission from Ref. 92. Copyright (2016) American Institute of Physics.

magnetic dipole operators), it is common[645] to restore symmetry properties of the transition amplitudes through an average. In this way, the rotatory strengths defined by Eq. (70) would become

$$R_{jn} \equiv \frac{1}{2}\Big(\mathrm{Tr}\left[\mathrm{Im}\left(\langle\psi_n|\boldsymbol{\mu}|\psi_j\rangle\langle\psi_j|\boldsymbol{m}|\psi_n\rangle\right)\right] + \mathrm{Tr}\left[\mathrm{Im}\left(\langle\psi_n|\boldsymbol{m}|\psi_j\rangle\langle\psi_j|\boldsymbol{\mu}|\psi_n\rangle\right)\right] \Big). \tag{72}$$

As in the case of linear absorption spectra, ECD spectra generated via TD-EOM-CC are numerically indistinguishable from those generated by conventional EOM-CC approaches, in the limit that all roots are computed in the conventional calculation. Further, because real-time simulations yield broadband spectra, one can easily quantify the degree to which TD-EOM-CC violates the Condon sum rule,[646] which states that the sum of all rotatory strengths from a given initial state should equal zero. In other words, the integrated area under a TD-EOM-CC-derived ECD spectrum should vanish. The analysis presented in Ref. 52 suggests that deviations from this rule are gauge dependent and are significantly more severe in the velocity-gauge than in the length-gauge.

In magnetic circular dichroism (MCD) experiments, an external static magnetic field is applied in addition to the circularly polarized probing light. The magnetic field breaks the

spin and orbital degeneracies through the couplings of spin and orbital angular momenta to the field. As a result, the optical selection rules are modified, giving rise to additional spectroscopic features that are otherwise inaccessible at zero field.[647] Although the simulation of an ECD spectrum only needs to treat electric field perturbations, both static magnetic and probing electric fields are necessary for simulating MCD. Various perturbative approaches to simulate magnetic field effects have been used with electronic structure methods for computing MCD spectra,[648–664] however they are not applicable to the real-time formalism, which requires a variational treatment of all external perturbations. This is particularly challenging for time-dependent electronic structure simulations using atomic orbitals; in the presence of electromagnetic fields, physical observables depend on the origin of the electromagnetic field.[615,665–671]

The MCD strength of excited state $|\psi_j\rangle$ can be defined as

$$R_j = -\frac{1}{3\mu_B|\mathbf{B}|}\sum_{\alpha\beta\gamma}\epsilon_{\alpha\beta\gamma}\mathrm{Im}[\langle\psi_0\left|\mu_\alpha\right|\psi_j\rangle^\gamma\,\langle\psi_j\left|\mu_\beta\right|\psi_0\rangle^\gamma], \tag{73}$$

where $\mathbf{B}$ is the external magnetic field, μ_B is Bohr magneton, and $\epsilon_{\alpha\beta\gamma}$ is Levi-Civita symbol ($\epsilon_{xyz} = \epsilon_{yzx} = \epsilon_{zxy} = 1$, $\epsilon_{yxz} = \epsilon_{xzy} = \epsilon_{zyx} = -1$, otherwise 0). The superscript γ explicitly denotes the direction of the applied magnetic field. The MCD strength function Eq. (73) requires the computation of the imaginary component of the quantity $\langle\psi_0\left|\mu_\alpha\right|\psi_j\rangle^\gamma\,\langle\psi_j\left|\mu_\beta\right|\psi_0\rangle^\gamma$ from time-dependent electronic structure methods. However, this quantity cannot be easily extracted from Fourier transformation of time-dependent observables. Bertsch *et. al*[91] expanded Eq. (73) in the power of electric field perturbation and obtained the following working expression for computing MCD spectra using real-time methods

$$R_j = \frac{1}{6\pi|\mathbf{B}|}\sum_{\alpha\beta\gamma}\varepsilon_{\alpha\beta\gamma}\mathrm{Re}\left(\frac{\mu_\alpha^\gamma}{\kappa^\beta} - \frac{\mu_\beta^\gamma}{\kappa^\alpha}\right). \tag{74}$$

Li and coworkers later derived the same expression based on a close connection between the real-time signal and the response function formalism, which leads to a more generalized

approach to compute any type of spectrum.[94]

Bertsch and coworkers included the orbital Zeeman term in the electronic Hamiltonian using a real-space local density approximation (LDA) to simulate effective $\mathscr{A}$ and $\mathscr{B}$ terms of MCD spectra.[91] More recently, Li and coworkers developed a RT-TDDFT approach to MCD that was generalized to hybrid GGA and included a variational treatment of the static magnetic perturbation.[94] That work demonstrated that, when simulating MCD, the most satisfactory solution to the gauge-origin problem arising from the use of an incomplete Gaussian-type basis[615,665–671] is to variationally include the effects of a uniform magnetic field with London orbitals.[631,640,664,672–678]

4.8 Electron Dynamics in Strong Fields

Interactions of molecules with intense laser pulses can result in a number of non-perturbative electronic phenomena involving ionization of electron(s).[679] These can be loosely categorized by the Keldysh adiabaticity parameter $\gamma = \frac{\omega\sqrt{2E_i}}{F}$, where E_i is the ionization potential of the molecule, and ω and F are the field frequencies and amplitudes, respectively. In the limit of high photon energy and low intensity (Keldysh $\gamma \gg 1$), multi-photon ionization dominates where multiple photons are absorbed. High intensity and low frequency fields ($\gamma \ll 1$) result in tunnel, barrier-suppression, and above-threshold ionization where the electron escape through or above the Coulomb potential confining the electron to the parent molecule. Molecular strong-field ionization can depend strongly on the geometry of the molecule (*e.g.*, charge resonance enhance ionization), as well as the light polarization with respect to the molecule. Since strong laser pulses produce electric fields comparable to those experienced by valence electrons in a molecule, simulating these phenomena requires a description of time-dependent electronic structure beyond the perturbation limit. In the strong-field regime, real-time techniques are particularly advantageous as they can explicitly simulate the non-perturbative electronic response to strong electric fields, such charge redistribution, multiphoton absorption, high-harmonic generation, strong-field ionization, photo-

electron spectroscopy, and shape and Feshbach resonances.[34,76,101,109,112,113,384,612,680–683]

Simulations of strong-field dynamics can be challenging for real-time methods, as these require a description of the wave function or density far from the molecule. Typically this is achieved with grid-based methods using a combination of a large simulation box along with some way of reducing spurious reflections from the edges of the box. These include: complex absorbing potentials (CAPs) to remove outgoing electron flux,[41,120,589,684–686] exterior complex scaling,[687–689] or masks that link an inner region (*e.g.*, TDDFT) to an outer region solved using known basis states (*e.g.*, free electron in field).[690,691] Although less commonly done, strong-field ionization can also be described using atomic-centered basis sets, which have the advantage of allowing wave function methods and hybrid TDDFT, but require either additional bases for the continuum (*e.g.*, B-splines[692,693]) or careful choice of CAPs. Since it is most relevant to real-time electronic structure methods discussed in this review, we now focus on the case of atom-centered basis sets with CAPs.

A typical CAP consists of an imaginary, position-dependent potential, which is added to the time-dependent Hamiltonian:

$$\hat{H}\left(\mathbf{r},t\right)=\hat{H}_0\left(\mathbf{r},t\right)-i\Gamma\left(\mathbf{r}\right), \tag{75}$$

Here, $\hat{H}_0\left(\mathbf{r},t\right)$ is the Hamiltonian without the CAP and $\Gamma\left(t\right)$ is a spatial potential that is zero around the molecule and smoothly increases at the boundary of the simulation. For the purposes of strong-field ionization (SFI), the results should not depend on the specific functional form of the CAP, nor its magnitude or location from the molecule, provided reflections are minimized. In most cases, smoothly increasing functions (*e.g.*, sigmoidal) are used.[112,589,682,685] Formally, this Hamiltonian is non-Hermitian which requires propagating the left $\langle\psi_L(t)|$ and right $|\psi_R(t)\rangle$ eigenvectors independently, with C-products used to compute the expectation values: $\langle A(t)\rangle = \left\langle \psi_L(t)\left|\hat{A}\right|\psi_R(t)\right\rangle$.[694] Generally, however, the standard equations of motion (Eq. (43)) and expectation values can be used, as well as the

(Hermitian) ground state computed via an SCF without the CAP. This approximation is valid when the CAP has negligible effect on the bound states.

Construction of a CAP in a grid or planewave basis is straightforward, as $\Gamma(\mathbf{r})$ is simply a local one-body potential. When using atom-centered basis sets, however, this requires projection onto the atomic orbitals,

$$\Gamma_{\mu\nu} = \langle\mu|\Gamma(\mathbf{r})|\nu\rangle = \int d\mathbf{r}\, \phi_\mu^*(\mathbf{r})\Gamma(\mathbf{r})\phi_\nu(\mathbf{r}) \tag{76}$$

These integrals can be performed either over the Cartesian or atom-centered grids. Using CAPs with atom-centered basis sets requires highly diffuse functions to describe the wave function far from the molecule.[112,113,681,682] The limited spatial extent of these bases also limits the range of the valid CAP positions, as a CAP too close to the molecule will affect the bound states, while too far results in an insufficient overlap of the basis with the CAP. If chosen correctly, simulations with a CAP will not affect the electron density near the molecule yet outgoing flux will be removed completely. Put another way, the eigenvalues for the bound states (occupied and virtual) should be unaffected by the CAP, whereas the unbound states acquire lifetimes. A CAP that is too "weak" or misplaced might not remove all outgoing charge, causing artificial reflections from the simulation box, whereas, conversely, a sharply shaped CAP might cause reflections from the potential itself. The protocol for choose the CAP location and strength is to determine a range of parameters where the results are insensitive. See Fig. 23 for an example.

Once a CAP has been chosen, experimental observables such at the SFI yield for a particular laser polarization and intensity can be computed from the change in the electronic norm. Weaker intensities can also be challenging for atom-centered basis sets, as they require CAPs far from the molecule to capture the tunnelling correctly. Additionally, basis set CAP calculations are "leaky" due to small amounts of norm being lost due to non-zero overlap with the ground state. This must be corrected for by subtracting this linear leakage

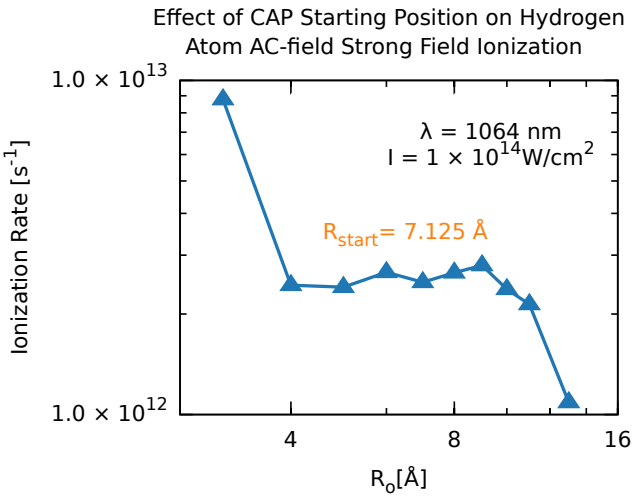

Figure 23: Strong-field ionization rates computed using an atomic orbital basis as a function of complex absorbing potential (CAP) starting distance R_0 for a hydrogen atom under 1064 nm light with intensity $1{\times}10^{14}$ W/cm^2. The rates are overestimated for smaller R_0 values due to the CAP affecting the ground state. The rates are underestimated at large R_0 due to insufficient overlap with the basis. The rates are insensitive between 4.0 and 9.0 Å, giving results in quantitative agreement with grid-based methods. Adapted with permission from Ref. 682. Copyright (2016) American Institute of Physics.

rate from the computed time-dependent norm.[682,683] Using TDCIS with CAPs, Schlegel and coworkers have successfully mapped out the angular dependence of the ionization rates for small molecules in strong fields (see Fig. 24).[112,113,681] These simulations shed light on the orbitals involved in strong-field ionization as well as the localization of the hole in the molecule.[683,695] When using TDDFT, the use of range-separated functionals has been shown to give significant improvements over traditional TDDFT, due to their correct long-range asymptotic potential and reduced self-interaction.[682]

5 Outlook

Real-time electronic structure methods provide an unprecedented view of electron dynamics on the atto and femtosecond timescales, with vast potential to yield new insights into the electronic behavior of molecules and materials. With recent development of accurate real-time post-SCF methods, advanced DFT functional forms,[696–698] and full quantum descriptions of

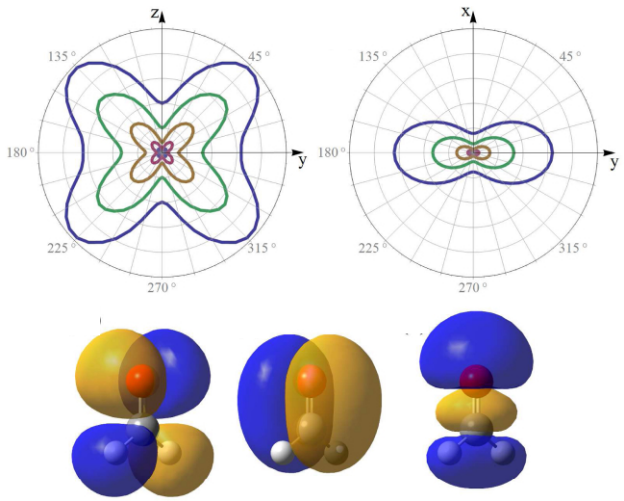

Figure 24: Angle dependence of the ionization yield for CH_2O calculated with the TDCIS-CAP approach: (Top Panel) polar plots, in plane with and perpendicular to the molecular axis, for field strengths of 0.04, 0.05, 0.06, 0.07, 0.08 E_h/ea_0, (Bottom Panel) Dyson orbitals for the $^2B_2$, $^2B_1$, $^2A_1$ states. Adapted with permission from Ref. 113. Copyright (2015) American Chemical Society.

the electrons and nuclei,[514,699,700] real-time simulations have become more accurate and have the capability of simulating ultrafast multidimensional spectroscopies and quantum dynamics in the presence of a strong electromagnetic field, in the relativistic regime, and in the quantum electrodynamics formalism.

The current prospect of universal quantum computing[701,702] provides an exciting new tool for the simulation of quantum dynamics because quantum computers obey the time-dependent Schrödinger equation by nature. Modeling time-dependent electronic dynamics in molecules and extracting information for the purpose of applications like spectroscopy, is relatively unexplored with regard to quantum algorithms. The next generation of real-time methods will encompass innovations in applied mathematics bolstered by high-performance software and/or quantum computing algorithms. The ever-improving computational efficiency of real-time methods will allow the simulation of the electron dynamics of larger scale and more complex systems, bringing chemical insight into dynamical processes with experimentally relevant spatial and time resolutions.

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